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Density functional theory simulation and interpretation of inelastic electron tunneling spectra of molecular junctions: from model to complex systems

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by Audrey Ségerie

Abstract: Using molecules to mimic the behavior and the functions of electronic components offers a broad potential towards the miniaturization of the electronic devices. The integration of such molecular components into nanoelectronic devices requires however a careful design to combine with their synthesis, preparation, and characterization. Understanding the physical phenomena at the nanoscale is another challenge to meet, where numerical simulations are very useful.

The Inelastic Electron Tunneling (IET) spectroscopy is one of these nanoscale-oriented techniques. It can probe the structure of single molecules sandwiched between metallic electrodes by detecting the inelastic interactions between the tunneling electrons and the vibrational modes of the molecule. This thesis deals with the simulation of IET spectra of these molecular junctions by relying on a Green's function approach combined with quantum chemistry calculations performed at the density functional theory level of approximation and with the analysis of the vibrational signatures in order to unravel their structural and electronic characteristics. In particular, this thesis considers systems of increasing complexity, starting from model dithiol-terminated compounds and going towards molecular switches, π -conjugated oligomers, and fullerene derivatives.

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Abbreviations list

AFM	Atomic Force Microscopy
ANO	Atomic Natural Orbital
AO	Atomic Orbital
C11	1-undecanethiol
CBS	Complete Basis Set
CGF	Contracted Gaussian Function
CGTO	Contracted Gaussian Type Orbital
DFT	Density Functional Theory
DZ	Double Zeta
DOS	Density Of States
ECP	Effective Core Potential
FWHM	Full Width at Half Maximum
GGA	Generalized Gradient Approximation
HF	Hartree-Fock
H-GGA	Hybrid Generalized Gradient Approximation
Hm-GGA	Hybrid meta Generalized Gradient Approximation
HOMO	Highest Occupied Molecular Orbital
IET(S)	Inelastic Electron Tunneling (Spectroscopy)
IR	Infrared Spectroscopy
L(S)DA	Local (Spin) Density Approximation
LDOS	Local Density Of States
LUMO	Lowest Unoccupied Molecular Orbital
MCBJ	Mechanically Controllable Break Junction
MO	Molecular Orbital
ODA	1,8 octanediamine
ODT	1,8 octanedithiol
OPE	OligoPhenyleneEthynylene
OPV	OligoPhenyleneVinylene
PGF	Primitive Gaussian Function
PGTO	Primitive Gaussian Type Orbital
QCME	Quantum Chemistry for Molecular Electronics
QZ	Quadruple Zeta
RECP	Relativistic Effective Core Potential
RSH-GGA	Range Separated Hybrid Generalized Gradient Approximation

SAM	Self-Assembled Monolayers
SFG	Sum-Frequency Generation
STM	Scanning Tunneling Microscopy
TZ	Triple Zeta
XC functional	Exchange-Correlation functional

Introduction

I. Introduction

I.A. General aspects

Aviram and Ratner in 1974^[1] suggested that a single molecule characterized by a donor-bridge-acceptor structure placed between two electrodes can act as an electronic component, stimulating the use of single molecule electronic devices. This so-called molecular electronics field has since attracted a great deal of attention^[2]. Using single molecules able to mimic the function of electronic components such as diodes^[3], transistors^[4], memories^[5] or switches^[6], presents a great potential in terms of miniaturization of the electronic circuits and offers the possibility to overcome the fundamental scaling limits of silicon-based electronics. Indeed, with molecular electronics the ultimate size limit is set by the atomic scale.

The molecular electronics field offers several advantages compared to Si-based microelectronics: i) the reduced size of the molecules (between 1 and 10 nm) interesting for high-density electronic devices with a high speed, ii) the exploitation of the potential intermolecular interactions to modify the electronic properties, making molecular devices sensitive to the chemical environment, iii) the chemical design and synthesis that enable to tune the electronic properties of such device, and iv) the structural flexibility of molecular systems to provide multiple distinct stable geometric configurations, presenting distinct optical and electronic properties that can not be expected from the rigid conventional silicon electronics.

The design of the simplest component of molecular electronics constituted by a single molecule sandwiched between two electrodes (molecular junction) remains challenging as they are hindered by several practical difficulties: i) the difficulty to ensure the presence of the molecule inside the junction, ii) the lack of reproducibility of their properties due to possible thermal and current-induced effects occurring during the experimental measurements^[7], iii) the control of the contact between the functional molecule and the metallic electrodes, as it greatly affects the transport properties^[8]. Indeed, the understanding and control of the electron transport process taking place through the frontier orbitals of the molecule being the closest to the Fermi level of the electrodes is crucial to optimize systems, which can be later involved in many applications such as molecular electronics^[9], biosensors^[10] and solar cells^[11]. Variations of the electron transport properties of a given system can be associated to its specific response towards external stimuli, such as changes of molecular configuration^[9f-j,m-n]. In this perspective, several studies have focused on the control of the contact configuration via a tuning of the end groups of the molecule anchoring to the electrodes^[12].

In order to get accurate descriptions of the molecular junctions at the atomic scale, different experimental techniques and theoretical methods have been developed^[11] to evaluate the relationships between the interactions at the interface, the tunneling charge carriers, the vibrational signatures, and the charge transport properties.

Several experimental techniques have been proposed to build nanojunctions, among which we can mention the scanning probe microscopy with the scanning tunneling microscopy (STM)^[13], the atomic force microscopy (AFM)^[14], the electrochemical deposition of nanogap electrodes^[15], the electromigration breakdown method^[16], and the mechanically controllable break junction (MCBJ)^[17]. This latter offers a strong control and tunability of the contact size, and enhances the reproducibility and mechanical stability of a single contact configuration, allowing to carry multiple measurements over several hours and thereby providing highly reliable conductance results.

I.B. Inelastic Electron Tunneling Spectroscopy (IETS)

One of the drawbacks of the STM technique is its lack of chemical sensitivity, due to the difficulty to interpret STM images determined by the convolution of the electronic structure of the tip and the surface. Ho^[18] has demonstrated that the Inelastic Electron Tunneling Spectroscopy (IETS) technique can help to analyze STM data and allows for the identification of individual adsorbed molecules within a limit of sensitivity typical of a vibrational spectroscopy. Studies based on the combination of the IET spectroscopy with the MCBJ technique have shown the possibility to get specific fingerprints relative to a controlled contact geometry^[19].

It was in fact in 1966 that Jaklevic and Lambe^[20] discovered that, when embedding a thin layer of molecules encapsulated in an oxide layer between two metallic electrodes, the oxide layer acts as a tunnel barrier for the electron transport from one electrode to the other and the tunneling electron can excite vibrational modes of the molecule. It has been the starting point of the so-called Inelastic Electron Tunneling Spectroscopy (IETS).

I.B.1. Tunnel effect: principle and applications

The term ‘electron tunneling’ refers to the motion of an electron passing through a classically impenetrable energy barrier, *i.e.* when the electron energy is lower than the barrier height ($E < V$). Indeed, according to classical mechanics a particle can not traverse a region requiring its potential energy to be greater than its total energy, since it would require a negative kinetic energy which is impossible by definition. However, as the experimental scale shrinks to molecular dimensions, classical concepts fail and quantum mechanics takes over. Due to the wave-like

aspect of particles quantum mechanics^[21] predicts that the transmission probability will be proportional to $e^{-Ad\sqrt{U-E}}$, where A is about $1.02 \text{ eV}^{-1/2} \text{ \AA}^{-1}$, as defined in Fig. (I.1).

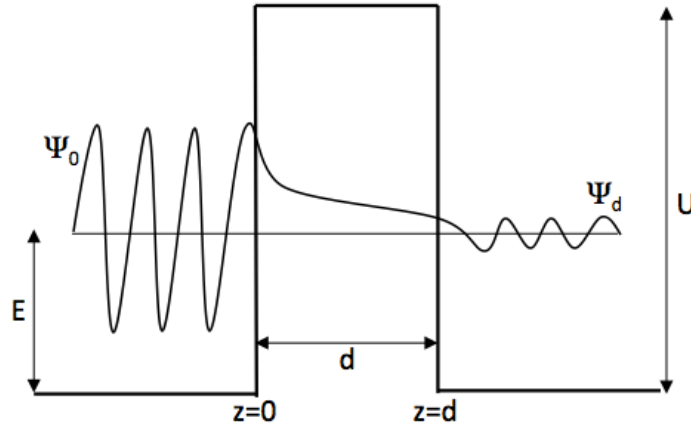


Fig. I.1. Schematic diagram of a wavefunction traversing a one-dimensional rectangular potential barrier, where U refers to the height of the potential barrier, E corresponds to the energy of the incident electron and d is associated to the thickness of the barrier. Ψ_0 and Ψ_d refer respectively to the wavefunction of the incident electron and of the one transmitted through the barrier.

Tunnel effect is involved in many scientific fields, such as nuclear physics, solid-state physics and atomic spectroscopy. The first example that we can mention in nuclear physics concerns the model introduced by George Gamow^[22], explaining the alpha decay of a radioactive nucleus as an example of tunnel effect. This phenomenon concerns relatively big unstable isotopes which need to eliminate nucleons in order to reach a stable nuclear configuration, via the radiation of an alpha particle (constituted of two protons and two neutrons). The elimination of this particle can be represented as a tunnel transfer since it evolves from a situation where it undergoes an attractive nuclear potential to a situation where it is repelled by electrostatic interactions with the other nuclear charges. Fig. (I.2) presents a simple one-dimensional model of the resulting energy barrier in the case of a nucleus characterized by a radius d .

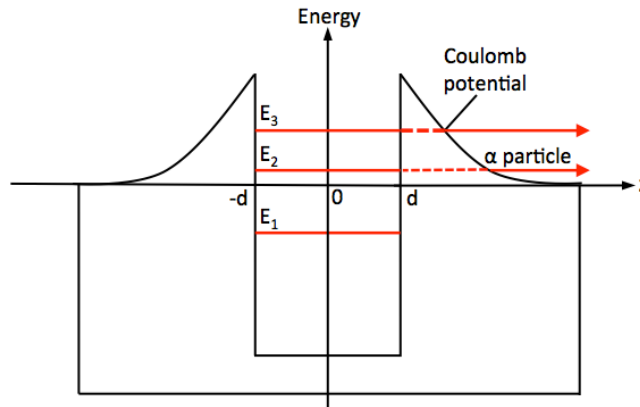


Fig. I.2. Illustration of the alpha decay of a radioactive nucleus explained by tunnel effect.

The region $-d < z < d$ corresponds to the inner part of the nucleus where the alpha particles are strongly bound because of nuclear forces, while in the regions outside the nucleus limits ($|z| \geq d$) an alpha particle would mainly undergo a repulsive Coulomb potential due to the interaction of its positive charge ($+2e$) with the charge of the reduced nucleus $+[Z-2]e$. We can see that a particle stable enough is not likely to escape the nucleus (e.g. particles on the energy level E_1), while particles on higher energy levels (e.g. E_2 or E_3) may penetrate the potential barrier by tunnel effect to enter the repulsive Coulomb region, causing the separation between the nucleus and one alpha particle.

We can apply a similar model to the case of the fusion of two nuclei. The major problem in this process consists in getting ions close enough for a fusion reaction to occur, since nuclear charges repel each other as they get closer. The nuclei can overcome the Coulomb barrier by tunnel effect, following the same principle as the Gamow model^[23].

We can also mention tunnel effect processes observed in solid-state physics, as they can occur in some semi-conductor devices, called tunnel diodes^[24] characterized by a non-classic conductance behaviour. Indeed, in a specific voltage region a tunnel diode may exhibit a negative differential conductance observed as a negative slope in the current-voltage curve, i.e. the current intensity decreases as the voltage increases. This phenomenon is associated to a negative resistance and originates from a tunnel effect in the direction of the current, and appears to be interesting for the development of oscillator and amplifier devices. These devices are mainly used in high-speed electronics applications because of the quasi-instantaneous character of the tunneling transfer, reducing strongly the distortions of the transmitted signal. Finally, we can mention the Josephson effect^[25] characterized by electron pairs tunneling through a thin insulating barrier between superconducting materials.

In the early 1980s, the invention of the scanning tunneling microscope (STM)^[13] by Binnig and Rohrer allowed to obtain spatially resolved images of single molecules adsorbed on conductive surfaces with an atomic resolution^[26] and thereby to overcome the spatial resolution of optical microscopes limited to $\sim 1 \mu\text{m}$. As shown in Fig. (I.3), a metallic tip having an atomically sharp apex is brought close to a metallic or semi-conducting surface with a tip-surface distance of typically 1 nm (corresponding to several atomic layers) and electron can tunnel through the barrier separating the tip and the surface. When a voltage is applied between the tip and the surface, a tunneling current can be detected, strongly depending on the tip-surface distance, the applied voltage and the local density of states. The exponential dependence of the current to the distance z yields the extremely high vertical resolution of STM: a change of 1 Å in z causes a

change of nearly one order of magnitude in current. The tip scans the xy plane of a sample surface thanks to a piezoelectric control system.

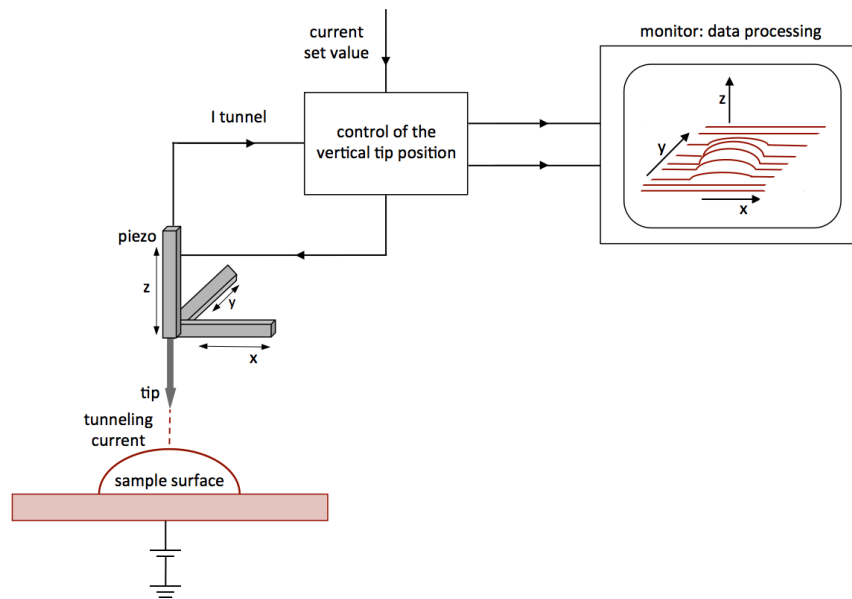


Fig. I.3. Schematic view of a Scanning Tunneling Microscope (STM).

In order to obtain STM images two different modes exist, the constant current mode (more frequently used) and the constant height mode, and are illustrated in Fig. (I.4). Practically, in the former, when the tip is brought close enough to the sample with respect to a convenient resolution, the intensity of the tunneling current is measured and this preset value is kept constant. The scanning consists in displacing the tip in the x-y plane while its z position is controlled via a feedback loop moving the tip along the z axis in order to keep the measured current equal to the preset value. This means that if the detected current is smaller than the preset value the tip is brought closer to the surface, but if the detected current is higher than the preset value the tip moves away from the sample. The variations along the vertical axis Δz are recorded and will be plotted for each scanning trajectory covering the xy plane, giving a topography of the scanned surface.

In the case of the constant height mode, no current preset value is defined as we let the feedback loop open and measure the variations of the tunnel current (associated to the variations of the LDOS). A STM measurement using this mode will allow a higher scanning speed with respect to the constant current mode, as we do not need to continuously adapt the position of the tip to follow the structure of the surface. Therefore the constant height mode is adapted to real-time studies of dynamic processes. However, this mode is only appropriate to the studies of flat surfaces as the tip could be deteriorated during the scan.

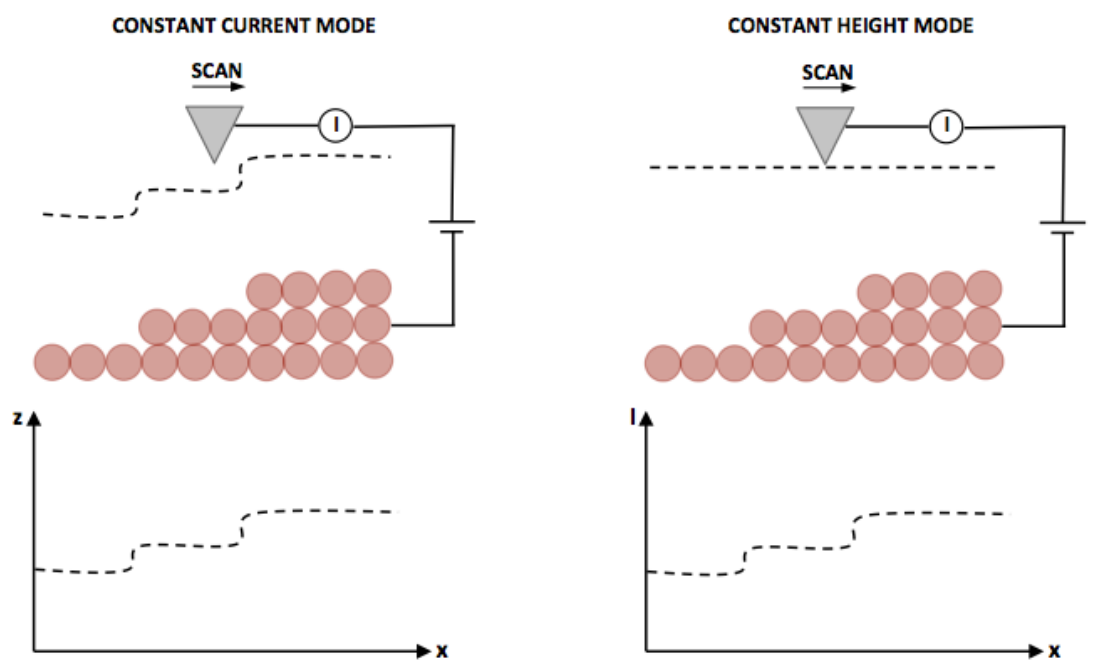


Fig. 1.4. Illustration of the constant current mode and constant height mode of a STM.

1.B.2. Principles of IETS

As we know, electron transport through molecular junctions is dominated by elastic processes due to the short traversal time of the electrons compared to the typical oscillation period of the molecular vibrations. When a negative bias is applied to the left metal electrode, the Fermi level is lifted. An electron from an occupied state on the left side tunnels into an empty state on the right side, and its energy is conserved: this is the elastic tunneling case [Fig. (1.5)]. During this process, the current increases linearly with an increase in the sample bias. When the applied voltage is large enough to satisfy the condition $eV \geq \hbar\omega$ (where e is the electron charge, V is the bias voltage, and ω refers to the frequency of a molecular vibrational mode) an electron going through the barrier from an occupied state (below the Fermi level of the metal) into an unoccupied state (above the Fermi level of the metal), is able to excite a vibrational mode, losing a quantum of energy $\hbar\omega$. This vibrational excitation opens an inelastic channel for current flow, that will add with the elastic contribution described hereabove. This inelastic tunneling process results from electron-phonon coupling and thus leads to a small increase of the total current which is characterized by a change in the slope of the I vs V curve, as a step in the dI/dV vs V curve and as a peak or dip in the d^2I/dV^2 vs V curve appearing at the $V = \frac{\hbar\omega}{e}$, *i.e.* at the frequency of the excited vibrational mode as illustrated in Fig. (1.5). In addition to the natural intrinsic linewidth of the IET peaks (related to the instrumentation), broadening effects can appear due to two different effects: (i) a thermal broadening effect due to the the Fermi level smearing *i.e.* the increase in temperature causes a broadening of the occupation of states near the Fermi level (E_F) and (ii) a

modulation voltage broadening. Concerning the first effect, Lambe and Jaklevic^[27] have observed that the increase of temperature leads to a broadening of the peak width and to a decrease of the peak height (even if the area under the curve appears to remain constant). The FWHM dependence to the temperature has been predicted to be $\frac{5.4 k_B T}{e}$ (see Fig. (I.6)), and this was also confirmed by Jennings and Merrill who studied the widths of the IET peaks of Al-Al oxide-Pb junctions as a function of temperature^[28]. If a given resolution is desired, there is therefore an upper temperature limit at which the experiment can be performed. As typical vibrational energies are in the 10s-100s of meV range, this implies that experimental investigation must be carried at cryogenic temperatures: *e.g.* for a vibronic energy of 100 meV (which corresponds to a vibrational wavenumber of 807 cm⁻¹) with a well-resolved linewidth (~ 5 meV) and knowing that $k_B = 0.086$ meV.K⁻¹, this implies that the working temperature has to be $T \sim \frac{5}{5.4 \times 0.086} \sim 10K$.

The broadening originating from voltage modulation is due to the dynamical technique used to get the second derivatives d^2I/dV^2 . A finite modulation of the voltage is applied, and the second harmonic of the current is detected. The effect of modulation voltage broadening has been at first studied by Klein et al^[29], who have found that the function F'' obtained experimentally is a convolution product of the exact second derivative $f'' = d^2I/dV^2$ with an instrumental function ϕ represented in Fig. (I.6), so that we have: $F'' = f'' * \phi$ where:

$$\phi(E) = \frac{8}{3\pi} \frac{1}{(eV_\omega)^4} (e^2 V_\omega^2 - E^2)^{\frac{3}{2}} \quad \text{for } |E| < eV_\omega$$

$$\phi(E) = 0 \quad \text{for } |E| > eV_\omega$$

and eV_ω refers to the modulation amplitude at frequency ω , since the applied voltage ranges from $-V_\omega$ to $+V_\omega$. Finally we can express the experimentally obtained peak linewidth W_{exp} as a function

of the three following contributions: $W_{exp} = \sqrt{W_{thermal}^2 + W_{modulation}^2 + W_{intrinsic}^2}$.

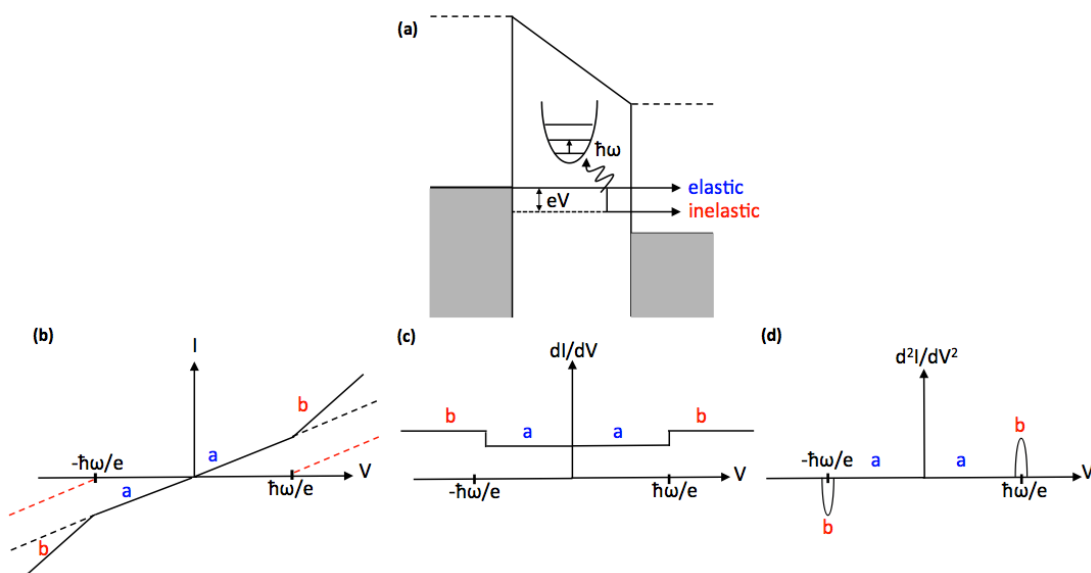


Fig. I.5. Representation of the energy diagram of an IET process (a), illustration of the I-V (b), conductance-V curves (c) and of an IET peak (d) that result from the opening of a vibrational mode conduction path occurring at $V = \hbar\omega/e$.

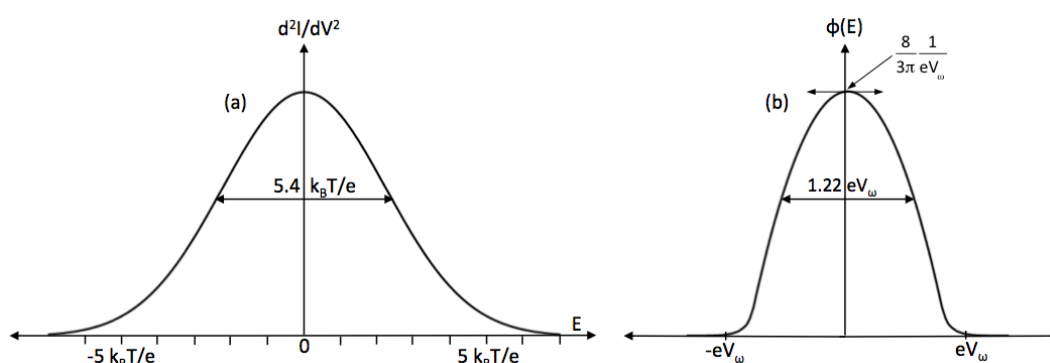


Fig. I.6. Representation of the lineshapes due to thermal broadening (a) and modulation voltage (b), redrawn from ref [29].

I.B.3. Specificities and advantages of IETS

IETS presents several specificities and advantages in comparison with other optical vibrational spectroscopies such as infrared (IR) and Raman, including notably a high sensitivity^[30].

Moreover, there are no rigorous selection rules defined in IETS, so that both IR- and Raman-active modes can appear in the spectra. Indeed, electrons tunneling through a scattering channel corresponding to a set of atomic orbitals are able to stimulate both IR- and Raman- active vibrational modes: the interactions occurring between the tunneling electron's longitudinal electric field and a (induced) molecular dipole moment are similar to those happening in infrared (Raman) excitations. In the case of the infrared absorption spectroscopy, the excitations of the vibrational states of a molecule are due to interactions between its net dipole moment and the transverse electric field of the infrared radiation. Similarly, in inelastic tunneling the net dipole

moment interacts with the longitudinal electric field associated to the tunneling electron, which will be able to give the necessary energy to excite some of the infrared-active vibrational modes. Regarding the Raman spectroscopy, vibrational excitations are induced by the interaction of the transverse electric field of the incident radiation with the induced dipole moment of a molecule due to its polarizability. Again, IET involves the interaction of an induced dipole moment with the longitudinal electric field of the tunneling electrons, what may excite some Raman-active vibrational modes.

The first experimental study dealing with the symmetry selection rules in IETS was performed by Kirtley and Hansma^[31] and concerns a molecular system based on anthracene in Al-Al₂O₃-Pb junctions. They have observed a very good agreement between the IET and optical (IR and Raman) spectroscopies, to within 1meV for most of the vibrational mode energies, comparable intensities of the Raman and infrared active modes in the IET spectrum, and smaller intensities concerning the optically inactive modes. It has also been shown that optically forbidden transitions (governed by the selection rules specific to the absorption and scattering of light) can appear as strong bands. The interesting complementarity of IETS with respect to IR and Raman vibrational spectroscopies can be illustrated with the studies of Hipps et al.^[32] performed on the ferrocyanide ion, showing the IET activity of two (T_{1g} and T_{2u}) modes appearing respectively at 354 cm⁻¹ and 474 cm⁻¹ not visible in infrared and Raman spectroscopies. We can add that the absence of strong combination and overtone bands makes the assignment of the observed IET bands easier^[30b].

As we have mentioned, the well-known selection rules of vibrational spectroscopies (infrared, Raman,...) can not be applied to IETS. Several studies of Troisi et al^[33] based on symmetry considerations has focused on the derivation of approximate (propensity) rules in order to predict the IET activity of a given vibrational mode, to understand why a given specific vibrational mode is specifically involved in the IET activity, and to help the assignment of experimental IETS measurements. As IET peaks are associated to vibrational modes that strongly modulate the electron transport (*i.e.* the overall coupling among orbitals connected to the electrodes at the Fermi energy), the establishment of propensity rules enables to characterize the pathway followed by the tunnelled electrons, which is constituted by the orbitals describing the electronic motions. In their studies, the calculation of the frequencies and intensities of the IET peaks have been performed by using a Landauer-Imry approach^[34] extended to the vibronic case where the retarded Green's function $G_{mn}(E)$ (m and n refer to the orbitals connected to the

electrodes) which is parametrically dependent on the set of normal modes $\{Q_\alpha\}$, is expanded in a Taylor series around the equilibrium position $\{Q_\alpha\} = 0$. By using Group theory to predict the symmetry of IET active modes (*i.e.* modes α providing non-null $\frac{\partial G_{mn}(E)}{\partial Q_\alpha}$ matrix elements) of planar conjugated systems investigated in molecular electronics^[35] connected to the electrodes through a S-Au bond with C_{2h} symmetry, they came to the following conclusions:

- If m and n (orbitals localized on the terminal sulfur atoms) are both σ -type (symmetric upon reflection in the molecular plane) or both π -type (antisymmetric upon reflection in the molecular plane), a_g and b_u modes give non-null $\frac{\partial G_{mn}(E)}{\partial Q_\alpha}$ matrix elements. However, if the m - n pair is symmetry related (m and n are interchanged by the C_2 axis parallel to the electrode planes), only the a_g modes strongly modulate the tunneling matrix elements and provide non-zero $\frac{\partial G_{mn}(E)}{\partial Q_\alpha}$ matrix elements. In the case of π -type orbitals, these modes involve in-plane motions such as C-C stretchings and C-C-C bending motions. We can mention that the IET intensity of the peaks associated to σ -type orbitals (channels) is expected to be very weak since σ -type transport through planar organics is much weaker than π -type transport. Finally, if the m and n orbitals have different symmetry (one of σ -type and the other of π -type), out-of-plane motions favour the intercommunication between the σ and π -type channels and thereby present important contributions in the IET response, corresponding to a_u and b_g modes for molecular systems having C_{2h} symmetry.

Note however that realistic molecular junctions can hardly be described in such a symmetric way since several parameters may have a significant impact on the control of the symmetry of the junction: i) the coordinative interactions between the molecule and the electrodes may cause fluctuations of the contact geometry^[36], ii) the presence of molecular interactions (in self-assembled monolayers), iii) the experimental technique used to contact the molecule with the electrodes such as break junctions^[17] characterized by uncontrollable details of the breaking process. For example the local shape of the electrodes and their configuration are unknown.

Troisi et al.^[33c] have investigated junctions presenting more complex molecular structures involving asymmetric molecules in an attempt to correlate the transport pathways followed by the electrons with the nature of the IET-active vibrational modes. The major conclusions of this study state that: i) the vibrational modes associated to the most favourable tunneling channel involving π -type orbitals are mainly dominated by (symmetric) combinations of C-C stretches following the transport pathway; ii) a coupling between the σ -type and π -type orbitals is made possible thanks

to out-of-plane motions, what allows for a better coupling of the σ -type orbitals to the gold electrodes.

In addition to the symmetry of the modes, other parameters can play an important role on the detectability of IET active modes. According to the work of Persson and Baratoff^[37], the shift of the resonance of a molecular orbital close to the Fermi level has an impact on the amplitude of the IET signal because the spatial distribution of this orbital influences the excitation probability of the vibrational modes. Measurements of IET responses of a single C₆₀ molecule adsorbed on different metallic surfaces^[38] has highlighted the effect of the orbital alignment on the detection of IET modes. Indeed, when the C₆₀ is observed on a Pb(111) surface, the IET spectrum is constituted by a large number of peaks, while only one mode is active when a Ag(110) surface is considered. In the former case, the C₆₀ LUMO resonance lies only at 0.2eV above the Fermi level (E_F), while in the latter case the position of the LUMO resonance is situated at 0.5eV above E_F ^[39] with a small overlap of the LUMO state with E_F . In the same way, the position of the tip above the molecule influences the detection of IET mode^[40] and is also explained by the fact that the coupling strength between the electron states and the molecular vibrations depends on the spatial extent of the molecular orbital.

Recent works by Bocquet and co-workers^[41] have proposed new propensity rules to rationalize the IET activity of certain vibrational modes. Considering a set of phenyl derivatives adsorbed on Cu(111) surfaces, they have shown that the ability of a given adsorbate to stabilize the inelastic electron can have a significant impact on the IET activity and depends on the electronegative nature and position of its substituents. Moreover, the orientation of this adsorbate with respect to the metallic surface has also a strong influence on the activity of the modes depending on the relative electronic density of the anchoring group making the contact with the metallic surface. Indeed, the effect of a negative π -polarization at the metal-molecule contact would prevent the incoming tunneling electron to enter the π channel, forcing it to tunnel through the remaining σ channel thereby favoring the IET activity of high-frequency stretching modes. Such principles have been successfully extended to more complex systems, such as metallo-porphyrin compounds.

Finally, we can mention that the high sensitivity of IETS to the contact geometry and to the molecular orientation^[42] with respect to the metallic electrodes can provide structural information on the molecular junction, and enables to ascertain that the desired molecule is inside the junction and participates to the conduction process.

I.B.4. Theoretical methods for simulating IET responses of molecular junctions

Several theoretical methods have been proposed in parallel with the experimental developments of IETS, offering an essential complement to assess and interpret the experimental spectra. One of the first and still used model for simulating the inelastic tunneling process in a STM junction was proposed by Tersoff and Hamann^[43], who employed a first-order perturbation theory tunneling Hamiltonian approach using the Bardeen approximation to calculate the tunneling matrix elements. In the limit of low bias voltage, they state that the tunneling current is found to be proportional to the surface local density of states (LDOS) at the Fermi level at the position of the point probe (tip). Among the Tersoff-Hamann based approaches, we can mention works using the Lorente-Persson theory^[44]. It consists in a generalization of the Tersoff Hamann theory for elastic tunneling to inelastic tunneling by considering the many-body LDOS for the electrons interacting with the vibrational modes. The corresponding theoretical formalism is implemented in density functional theory (DFT) calculations. In this approach, the inelastic contribution to the change in conductance is due to the change in the LDOS caused by the electron-vibration coupling. However, it presents limitations related to the independence of the tip electronic structure, since the model assumes a spherical symmetry of the electronic structure of the tip's wave function (wave-functions which constitute the electronic structure of the tip are s-wave), while it has been shown that atomic resolution in STM requires localized metallic p_z or d_z^2 tip states in metal-STM imaging^[45]. An alternative method consists of using Green's functions approaches that explicitly take into account the tip electronic structure. In 1994, Ratner and co-workers^[46] have developed a model to calculate transport properties based on Löwdin's partitioning technique to calculate the Green's function and transition matrix elements, and applied it to STM. It has also been applied by Yalikari et al^[47] for evaluating the influence of molecule-electrode binding on the current-voltage characteristics. In this thesis, the elastic and inelastic properties of the different molecular systems that we have studied have been simulated by using the Quantum Chemistry for Molecular Electronics (QCME) code^[48], which is based on the Green's function formalism introduced by Ratner and co-workers^[46] within the harmonic approximation for evaluating the vibronic couplings. The reliability of this method has been substantiated in several works involving a variety of single molecular devices by reproducing and interpreting experiment^[49], and the formalism will be detailed in sections II.C.2 and II.C.3. Finally, Fig. (I.7) illustrates typical examples of experimental measurements and theoretical simulations of IET spectra of molecular systems of different sizes reported in the literature^[38,50-51].

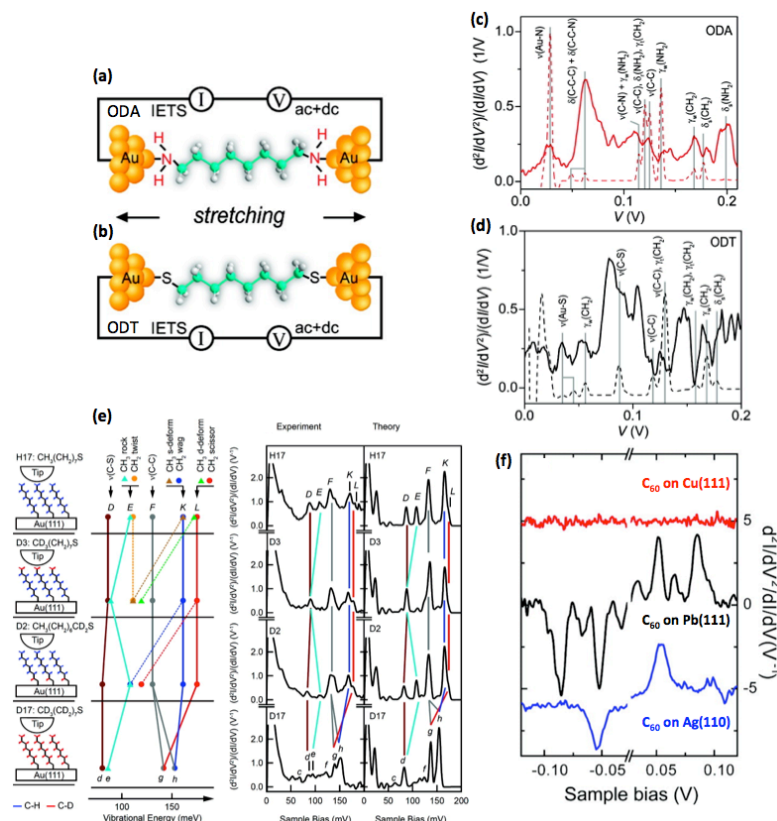


Fig. I.7. Illustration of 1,8 octanediamine (ODA, $\text{H}_2\text{N}-[\text{CH}_2]_8-\text{NH}_2$) (a) and 1,8 octanedithiol (ODT, $\text{HS}-[\text{CH}_2]_8-\text{SH}$) (b) single-molecule junctions. Experimental (solid lines) and theoretical (dashed lines) IET spectra of ODA (c) and ODT (d) single-molecule junctions. These pictures are taken from ref. [50]. (e): Experimental and theoretical IET spectra of deuterated alkanethiol SAM originate from ref. [51]. (f): Experimental IET spectra of a C_{60} molecule on Cu(111), Pb(111) and Ag(110) surfaces taken from ref. [38].

I.C. Objectives

The aim of this thesis carried out within the frame of the ARC proposal TINTIN (Extended- π Conjugated Molecular *TIN*kertoys for OpToelectronics and Sp/*N*tronics), consists in predicting, determining and interpreting the vibrational responses of molecular junctions of interest for molecular electronics, and more particularly their inelastic electron tunneling (IET) spectra by using quantum chemistry methods. This work is also supported by a multidisciplinary approach combining the synthesis of organic π -conjugated systems, and the determination of their properties through a broad range of spectroscopic techniques as well as the device engineering.

IETS is proved to be a promising tool for characterizing devices which integrate functional molecules, and for providing structural information on the molecular junction due to its high sensitivity with respect to several junctions parameters such as the molecule-electrode distance, the orientation of the molecule inside the junction and the molecule-metal bonding. One of the

main goals of this thesis is to assess the effect of these junctions parameters on the IET signatures of molecular junctions of different sizes, going from a simple monocyclic model system to larger systems such as the C_{60} molecule placed between two gold electrodes. This manuscript is structured as follows:

Chapter II presents the theoretical methods used to optimize and calculate the vibrational frequencies of the molecular systems, as well as the formalism of the code employed to get the inelastic transport properties.

The first step of our approach has consisted in selecting an adequate level of calculation presenting the best compromise between the accuracy of the calculated transport properties and the computational cost. The effects of the atomic basis set and of the exchange-correlation (XC) functional on the IET spectra have been investigated by considering the prototypical 1,4-benzenedithiol molecule and are described in Chapter III.

Chapter IV addresses the IET responses of an anil derivative switching between two tautomeric forms via an intramolecular proton transfer, which is a system of interest in the field of molecular electronics. The comparison between the IET spectra of the two forms is performed in order to assess the efficiency of the IET spectroscopy in the characterization of the molecular states of switches.

In Chapter V, we focus on the effect of the molecule-metal bonding on the IET response of molecular junctions based on hydrocarbon molecules of interest for molecular electronics: the 1-undecane thiol (C11) sandwiched between two gold electrodes, and two classes of molecular wires oligo(phenylene ethynylene) (OPE) and oligo(phenylene vinylene) (OPV). In particular, the analysis of the variation of IET signatures by modifying the anchoring of the molecule to the metallic electrodes as well as their size has been carried out.

Chapter VI deals with the IET responses of a molecular junction based on a single C_{60} molecule placed between two gold electrodes, which are compared to experimental measurements in order to get useful insights on the structural information of the molecular junction and help the understanding and assigning of experimental spectra. In addition, IET signatures of two C_{60} -porphyrin based molecules are discussed in Chapter VII. Finally, conclusions and outlooks are given in Chapter VIII.

I.D. References

- [1] Aviram A.; Ratner M. A. Molecular rectifiers *Chem. Phys. Lett.* **1974**, 29, 277-283.
- [2] (a) Nitzan, A. *Ann. Rev. Phys. Chem.* **2001**, 52, 681-750. (b) Agraït, N.; Yeyati, A. L.; van Ruitenbeek, J. M. *Phys. Rep.* **2003**, 377, 81-129. (c) Datta, S. Quantum transport: Atom to transistor, Cambridge University Press, UK, 2005. (d) Cuniberti, G.; Fagas, G.; Richter, K. Introductory Molecular Electronics: A Brief Overview, Springer, Berlin, 2005. (e) Cuevas, J. C.; Scheer, E. Molecular Electronics: An introduction to the Theory and Experiment, World Scientific Publishing, New Jersey, 2010.
- [3] (a) Metzger, R. M.; Chen, B.; Hopfner, U.; Lakshmikantham, M. V.; Vuillaume, D.; Kawai, T.; Wu, X. L.; Tachibana, H.; Hughes, T. V.; Sakurai, H.; Baldwin, J. W.; Hosch, C.; Cava, M. P.; Brehmer, L.; Ashwell, G. J. *J. Am. Chem. Soc.* **1997**, 119, 10455. (b) Ebling, M.; Ochs, R.; Koentopp, M.; Fischer, M.; von Hänisch, C.; Weigend, F.; Evers, F.; Weber, H. B.; Mayor, M.; *Proc. Natl. Acad. Sci. USA* **2005**, 102, 8815. (c) Díez-Pérez, I.; Hihath, J.; Lee, Y.; Yu, L.; Adamska, L.; Kozhushner, M.A.; Oleynik, I. I.; Tao, N. *Nat. Chem.* **2009**, 1, 635.
- [4] (a) Park, H.; Park, J.; Lim, A. K. L.; Anderson, E. H.; Alivisatos, A. P.; McEuen, P. L. *Nature* **2000**, 407, 57. (b) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruna, H. D.; McEuen, P. L.; Ralph, D. C. *Nature* **2002**, 417, 722. (c) Kubatkin, S.; Danilov, A.; Hjort, M.; Cornil, J.; Brédas, J. L.; Stuhr-Hansen, N.; Per Hedegård, P.; Bjørnholm, T. *Nature* **2003**, 425, 698. (d) Song, H.; Kim, Y.; Jang, Y. H.; Jeong, H.; Reed, M. A.; Lee, T. *Nature* **2009**, 462, 1039.
- [5] (a) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; Johnston-Halperin, E.; Delonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shin, Y. S.; Tseng, H.-R.; Stoddart, J. F.; Heath, J. R.; *Nature* **2007**, 445, 414. (b) Lee, J.; Chang, H.; Kim, S.; Bang, G. S.; Lee, H.; *Angew. Chem.* **2009**, 121, 8653.
- [6] (a) Blum, A. S.; Kushmerick, J. G.; Long, D. P.; Patterson, C. H.; Yang, J. C.; Henderson, J. C.; Yao, Y. X.; Tour, J. M.; Shashidhar, R.; Ratna, B. R. *Nat. Mater.* **2005**, 4, 167. (b) Lörtscher, E.; Cizek, J. W.; Tour, J.; Riel, H. *Small* **2006**, 2, 973. (c) Choi, B. Y.; Kahng, S. J.; Kim, S.; Kim, H.; Kim, H. W.; Song, Y. J.; Ihm, J.; Kuk, Y. *Phys. Rev. Lett.* **2006**, 96, 156106. (d) Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L.; *Nat. Nanotechnol.* **2009**, 4, 230. (e) Van Der Molen, S. J.; Liljeroth, P. *J. Phys.: Condens. Matter* **2010**, 22, 133001. (f) Champagne, B.; Plaquet, A.; Pozzo, J. L.; Rodriguez, V.; Castet, F. *J. Am. Chem. Soc.* **2012**, 134, 8101-8103. (g) Castet, F.; Rodriguez, V.; Pozzo, J. L.; Ducasse, L.; Plaquet, A.; Champagne, B. *Acc. Chem. Res.* **2013**, 46, 2656-2665.
- [7] (a) Huang, Z.; Xu, B.; Chen, Y.; Di Ventra, M.; Tao, N. *Nano Lett.* **2006**, 6, 1240-1244. (b) Hsu, B. C.; Amanatidis, I.; Liu, W.-L.; Tseng, A.; Che, Y.-C. *J. Phys. Chem. C* **2014**, 118, 2245-2252.
- [8] (a) Nara, J.; Geng, W. T.; Kino, H.; Kobayashi, N.; Ohno, T. *J. Chem. Phys.* **2004**, 121, 6485; (b) Chen, F.; Li, X.; Hihath, J.; Huang, Z.; Tao, N. *J. Am. Chem. Soc.* **2006**, 128, 15874-15881; (c) Liu, H.; Wang, N.; Zhao, J.; Guo, Y.; Yin, X.; Boey, F. Y. C.; Zhang, H. *ChemPhysChem.* **2008**, 9, 1416-1424; (d) Cho, Y.; Kim, W. Y.; Kim, K. S. *J. Phys. Chem. A* **2009**, 113, 4100-4104.
- [9] (a) Eigler, D. M.; Lutz C. P.; Rudge W. E. *Nature* **1991**, 352, 600-603. (b) Chen, J.; Reed, M.A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, 286, 1550-1552. (c) Zeng, C. G.; Wang, H. Q.; Wang, B.; Yang, J. L.; Hou, J. G. *Appl. Phys. Lett.* **2000**, 77, 3595-3597. (d) Grobis, M.; Wachowiak, A.; Yamachika, R.; Crommie, M. F. *Appl. Phys. Lett.* **2005**, 86, 204102. (e) Zhao, J.; Zeng, C.; Cheng, X.;

Wang, K.; Wang, G.; Yang, J.; Hou, J. G.; Zhu, Q. *Phys. Rev. Lett.* **2005**, *95*, 045502. (f) Lewis, P. A.; Inman, C. E.; Maya, F.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. *J. Am. Chem. Soc.* **2005**, *127*, 17421-17426. (g) Moore, A. M.; Dameron, A. A.; Mantooth, B. A.; Smith, R. K.; Fuchs, D. J.; Cizek, J. W.; Maya, F.; Yao, Y.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **2006**, *128*, 1959-1967. (h) Alemani, M.; Peters, M. V.; Hecht, S.; Rieder, K-H.; Moresco, F.; Grill, L. *J. Am. Chem. Soc.* **2006**, *128*, 14446-14447. (i) Moore, A. M.; Mantooth, B. A.; Donhauser, Z. J.; Yao, Y.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **2007**, *129*, 10352-10353. (j) Liljeroth, P.; Repp, J.; Meyer, G. *Science* **2007**, *317*, 1203-1206. (k) Katano, S.; Kim, Y.; Hori, M.; Trenary, M.; Kawai, M. *Science* **2007**, *316*, 1883-1886. (l) Kumar, A. S.; Ye, T.; Takami, T.; Yu, B-C.; Flatt, A. K.; Tour, J. M.; Weiss, P. S. *Nano Lett.* **2008**, *8*, 1644-1648. (m) Alemani, M.; Selvanathan, S.; Ample, F.; Peters, M. V.; Rieder, K-H.; Moresco, F.; Joachim, C.; Hecht, S.; Grill, L. *J. Phys. Chem. C* **2008**, *112*, 10509-10514.

[10] Willner, I.; Willner, B. *Trends. Biotechnol.* **2001**, *19*, 222-230.

[11] (a) Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* **1998**, *395*, 257-260. (b) Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C-S.; Ree, M. *Nature. Mater.* **2006**, *5*, 197-203.

[12] (a) Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nano Lett.* **2006**, *6*, 458. (b) Baheti, K.; Malen, J. A.; Doak, P.; Reddy, P.; Jang, S-Y.; Tilley, T. D.; Majumdar, A.; Segalman, R. A. *Nano Lett.* **2008**, *8*, 715. (c) Dell'Angela, M.; Kladnik, G.; Cossaro, A.; Verdini, A.; Kamenetska, M.; Tamblyn, I.; Quek, S. Y.; Neaton, J. B.; Cvetko, D.; Morgante, A.; Venkataraman, L. *Nano Lett.* **2010**, *10*, 2470-2474.

[13] (a) Binnig, G.; Rohrer, H. *Helv. Phys. Acta* **1982**, *55*, 725. (b) Hansma, P. K.; Tersoff, J. *J. Apply. Phys.* **1987**, *61*, R1-R23. (c) Vazquez, H.; Skouta, R.; Schneebeli, S.; Kamenetska, M.; Breslow, R.; Venkataraman, L.; Hybertsen, M. S.; *Nat. Nanotechnol.* **2012**, *7*, 663.

[14] Aradhya, S. V.; Frei, M.; Hybertsen, M. S.; Venkataraman, L.; *Nat. Mater.* **2012**, *11*, 872.

[15] (a) Li, X. L.; Hua, S. Z.; Chopra, H. D.; Tao, N. J.; *Micro & Nano Letters* **2006**, *1*, 83. (b) Tian, J. H.; Yang, Y.; Liu, B.; Schollhorn, B.; Wu, D. Y.; Maisonhaute, E.; Muns, A. S.; Chen, Y.; Amatore, C.; Tao, N. J.; Tian, Z. Q. *Nanotechnology* **2010**, *21*, 274012.

[16] (a) Tsutsui, M.; Shoji, K.; Taniguchi, M.; Kawai, T. *Nano Lett.* **2008**, *8*, 345. (b) Baik, J. M.; Lee, S. J.; Moskovits, M. *Nano Lett.* **2009**, *9*, 672. (c) Zhang, H.; Thompson, C. V.; Stellacci, F.; Thong, J. T. L. *Nanotechnology* **2010**, *21*. (d) Johnson, S. L.; Hunley, D. P.; Sundararajan, A.; Johnson, A. T. C.; Strachan, D. R. *IEEE Tran. Nanotechnol.* **2011**, *10*, 806.

[17] (a) Perrin, M. L.; Martin, C. A.; Prins, F.; Shaikh, A. J.; Eelkema, R.; van Esch, J. H.; van Ruitenbeek, J. M.; van der Zant, H. S. J.; Dulic, D. *Beilstein J. Nanotechnol.* **2011**, *2*, 714. (b) Yang, Y.; Chen, Z. B.; Liu, J. Y.; Lu, M.; Yang, D. Z.; Yang, F. Z.; Tian, Z. Q. *Nano Research* **2011**, *4*, 1199. (c) Yoshizawa, K. *Acc. Chem. Res.* **2012**, *45*, 1612. (d) Lörtscher, E.; Gotsmann, B.; Lee, Y.; Yu, L. P.; Rettner, C.; Riel, H. *ACS Nano* **2012**, *6*, 4931.

[18] Ho, W. J. *Chem. Phys.* **2002**, *117*, 11033-11061.

[19] (a) Taniguchi, M.; Tsutsui, M.; Yokota, K.; Kawai, T. *Nanotechnology*, **2009**, *20*, 434008; (b) Tsutsui, M.; Taniguchi, M.; Shoji, K.; Yokota, K.; Kawai, T. *Nanoscale* **2009**, *1*, 164-170; (c) Kim, Y.; Song, H.; Strigl, F.; Pernau, H-F.; Lee, T.; Scheer, E. *Phys. Rev. Lett.* **2011**, *106*, 196804; (d) Fock, J.;

- Sørensen, J. K.; Lörtcher, E.; Vosch, T.; Martin, C. A.; Riel, H.; Kilså, K.; Bjørnholm, van der Zant, H *Phys. Chem. Chem. Phys.* **2011**, *13*, 14325-14332.
- [20] Jaklevic, R. C.; Lambe, J. *Phys. Rev. Lett.* **1966**, *17*, 1139.
- [21] (a) Kirtley, J. *ACS Symp. Ser.* **1980**, *137*, 217. (b) Hansma, P. K. *Tunneling Spectroscopy*, Plenum Press, New York, 1982.
- [22] Gamow, G. *ZP*, **1928**, *51*, 204-212.
- [23] (a) Balantekin, A. B.; Takigawa, N. *Rev. Mod. Phys.* **1998**, *70*, 77 (b) Saha, R.; Markmann, A.; Batista, V. S. *Mol. Phys.* **2012**, *110*, 995.
- [24] (a) Esaki, L. *Phys. Rev.* **1958**, *109*, 603–604. (b) Bedrossian, P.; Chen, D. M.; Mortensen, K; Golovchenko, J. A. *Nature* **1989**, *342*, 258-260.
- [25] Animalu, A. O. E. *Phys. Rev. B*, **1973**, *8*, 4420.
- [26] (a) Griffith, J.E.; Kochanski, G. P. *Annu. Rev. Mater. Sci.* **1990**, *20*, 219-244. (b) Zandvliet, H. J. W.; van Houselt, A. *Annu. Rev. Anal. Chem.* **2009**, *2*, 37-55.
- [27] Lambe, J.; Jaklevic, R. C. *Phys. Rev.* **1968**, *165*, 821.
- [28] Jennings, R. J.; Merrill, J. R.; *J. Phys. Chem. Solids*, **1972**, *33*, 1261.
- [29] Klein, J.; Léger, A.; Belin, M.; Défourneau, D.; Sangster, M. J. L. *Phys. Rev. B* **1973**, *7*, 2336.
- [30] (a) Kroeker, R. M.; Hansma, P. K.; *Surf. Sci.* **1977**, *67*, 362. (b) Mazur, U.; Hipps, K. W. “Inelastic Electron Tunneling Spectroscopy” in: *Handbook of Vibrational Spectroscopy*, Eds: Chalmers, J.; Griffiths, P. John Wiley&Sons, New York, 2002.
- [31] Kirtley, J.; Hansma, P. K. *Surf. Sci.* **1977**, *66*, 125-130.
- [32] (a) Hipps, K. W.; Mazur, U.; Pearce, M. S. *Chem. Phys. Lett.* **1979**, *68*, 433. (b) Hipps, K. W.; Mazur, U. *J. Phys. Chem.* **1980**, *84*, 3162. (c) Hipps, K. W.; William, S. D.; Mazur, U. *Inorg. Chem.* **1984**, *23*, 3500.
- [33] (a) Troisi, A.; Ratner, M. A. *Nano. Lett.* **2006**, *6*, 1784-1788. (b) Troisi, A.; Ratner, M. A. *J. Chem. Phys.* **2006**, *125*, 214709. (c) Troisi, A.; Beebe, J. M.; Picraux, L. B.; van Zee, R. D.; Stewart, D. R.; Ratner, M. A.; Kushmerick, J. G. *PNAS*, **2007**, *104*, 14255-14259.
- [34] (a) Landauer, R. *IBM J. Res. Dev.* **1957**, *1*, 223. (b) Buttiker, M.; Imry, Y.; Landauer, R.; Pinhas, S. *Phys. Rev. B* **1985**, *31*, 6207.
- [35] (a) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science*, **1997**, *278*, 252. (b) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, Jr., D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science*, **2001**, *292*, 2303. (c) James, D. K.; Tour, J. M. *Chem. Mater.* **2004**, *16*, 4423.
- [36] Ramachandran, G. K.; Hopson, T. J.; Rawlett, A. M.; Nagahara, L. A.; Primak, A.; Lindsay, S. M. *Science*, **2003**, *300*, 1413.

- [37] Persson, B. N. J.; Baratoff, A. *Phys. Rev. Lett.* **1987**, *59*, 339.
- [38] Franke, K. J.; Schulze, G.; Pascual, J. I. *J. Phys. Chem. Lett.* **2010**, *1*, 500.
- [39] Pascual, J. I.; Gómez-Herrero, J.; Sánchez-Portal, D.; Rust, H.-P. *J. Chem. Phys.* **2002**, *117*, 9531.
- [40] (a) Grobis, M.; Khoo, K. H.; Yamachika, R.; Lu, X.; Nagaoka, K.; Louie, S. G.; Crommie, M. F.; Kato, H.; Shinohara, H. *Phys. Rev. Lett.* **2005**, *94*, 136802. (b) Liu, N.; Silien, C.; Ho, W.; Maddox, J. B.; Mukamel, S.; Liu, B.; Bazan, G. C. *J. Chem. Phys.* **2007**, *127*, 244711. (c) Wang, Y.; Kioupakis, E.; Lu, X.; Wegner, D.; Yamachika, R.; Dahl, J. E.; Carlson, R. M. K.; Louie, S. G.; Crommie, M. F. *Nature Mater.* **2008**, *7*, 38.
- [41] (a) Burema, S. R.; Bocquet, M. L. *J. Phys. Chem. Lett.* **2012**, *3*, 3007-3011. (b) Burema, S. R.; Bocquet, M. L. *Nanotechnology* **2012**, *23*, 315702. (c) Burema, S. R.; Seufert, K.; Auwärter, W.; Barth, J. V.; Bocquet, M. L. *ACS Nano* **2013**, *6*, 5273-5281.
- [42] (a) Troisi, A.; Ratner, M. A. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2421; (b) Leng, J. C.; Lin, L. L.; Song, X. N.; Li, Z. L.; Wang, C. K. *J. Phys. Chem. C* **2009**, *113*, 18353.
- [43] (a) Tersoff, J.; Hamann, D. R. *Phys. Rev. Lett.* **1983**, *50*, 1998; (b) Tersoff, J.; Hamann, D. R. *Phys. Rev. B* **1985**, *31*, 805.
- [44] (a) Lorente, N.; Persson, M. *Phys. Rev. Lett.* **2000**, *85*, 2997; (b) Lorente, N.; Persson, M.; Lauhon, L. J.; Ho, W. *Phys. Rev. Lett.* **2001**, *86*, 2593; (c) Bocquet, M. L.; Lorente, N. *J. Chem. Phys.* **2009**, *130*, 124702; (d) Bocquet, M. L.; Wang, B. *Prog. Surf. Sci.* **2010**, *85*, 435-459.
- [45] Chen, C. J. *Phys. Rev. Lett.* **1990**, *65*, 448.
- [46] (a) Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 6849; (b) Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 6856.
- [47] Yaliraki, S. N.; Kemp, M.; Ratner, M. A. Conductance of Molecular Wires: Influence of Molecule-Electrode Binding *J. Am. Chem. Soc.* **1999**, *121*, 3428-3434.
- [48] (a) Jiang, J.; Wang, C. K.; Luo, Y. 2006, *Quantum Chemistry for Molecular Electronics* (QCME-V1.1), Royal Institute of Technology, Sweden; (b) Jiang, J.; Kula, M.; Luo, Y. *J. Chem. Phys.* **2006**, *124*, 034708.
- [49] (a) Jiang, J.; Kula, M.; Lu, W.; Luo, Y. *Nano Lett.* **2005**, *5*, 1551 (b) Kula, M.; Jiang, J.; Luo, Y. *Nano Lett.* **2006**, *6*, 1693-1698; (c) Cao, H.; Jiang, J.; Ma, J.; Luo, Y. *J. Phys. Chem. C* **2008**, *112*, 11018-11022; (d) Lin, L. L.; Wang, C. K.; Luo, Y. *ACS Nano* **2011**, *5*, 2257.
- [50] Kim, Y.; Hellmuth, T. J.; Bürkle, M.; Pauly, F.; Scheer, E. *ACS Nano* **2011**, *5*, 4104-4111.
- [51] Okabayashi, N.; Paulsson, M.; Ueba, H.; Konda, Y.; Komeda, T. *Nano Lett.* **2010**, *10*, 2950-2955.

Theoretical and computational methods

II. Theoretical and computational methods

In this chapter, the theoretical principles of the methods used in this thesis are introduced. Section II.A describes the principles of density functional theory, while the different kinds of orbital basis sets used in our calculations are discussed in Section II.B. Then, general principles of quantum scattering theory are introduced in Section II.C, as well as the formalism related to the code used for simulating the inelastic electron tunneling spectra of our different molecular systems.

II.A. Density Functional Theory^[1-2]

II.A.1. General approach

Ab initio methods focus on evaluating the electronic wavefunction, using it as the fundamental quantity from which any property of a chemical system can be determined. However, the fact that a wavefunction depends on the electronic coordinates (considering that each electron is described by 3 spatial- and one spin- coordinates) turns out to be inconvenient as the number of variables to consider to describe large systems can grow drastically making the calculations harder to achieve.

In the frame of Density Functional Theory the fundamental quantity used to describe a system is no longer the wavefunction but the electron density, from which all the fundamental properties can also be derived. The main advantage of this alternative approach resides in the independence of the description of the electron density with regard to the size of the system, as it is always described by no more than 3 spatial- and one spin-coordinates.

II.A.2. The Hohenberg and Kohn theorems

The first theorems which allowed to adapt the formalism and methodologies of quantum chemistry using the electron density as the main variable have been advanced by Hohenberg and Kohn.

The first theorem^[3] considers that the electron density $\rho_0(\vec{r})$ describing the ground state of a many-body system allows to determine the external potential $V_{ext}(\vec{r})$ up to a constant, taking into account the electrostatic interactions between electrons and nuclei as well as interactions between electrons and external electromagnetic fields. As other models

have shown that the kinetic energy of one system can also be derived from its electron density, one can express the ground state energy as a functional of the ground state density $\rho_0(\vec{r})$:

$$E_0[\rho_0(\vec{r})] = \int \rho_0(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + T[\rho_0(\vec{r})] + E_{ee}[\rho_0(\vec{r})] \quad (II.A.1)$$

where T is the kinetic energy functional and E_{ee} is the electron-electron interaction energy functional. These two terms being independent of the system characteristics we can group them in a new term, the Hohenberg-Kohn functional $F_{HK}[\rho_0(\vec{r})]$. Eq. (II.A.2) can then be written as:

$$E_0[\rho_0(\vec{r})] = \int \rho_0(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + F_{HK}[\rho_0(\vec{r})] \quad (II.A.2)$$

$$\text{where } F_{HK}[\rho_0(\vec{r})] = T[\rho_0(\vec{r})] + E_{ee}[\rho_0(\vec{r})]$$

Determining this functional in order to apply the first HK theorem is the finality of every DFT calculation, but new approximations are needed as it is impossible to know the exact form of F_{HK} . These approximations are introduced in the next section.

The second theorem states a variational principle applied to the DFT formalism, as a test electron density $\tilde{\rho}(\vec{r})$ only delivers the lowest ground-state energy of one system provided it corresponds to the real ground-density $\rho_0(\vec{r})$. In other words, the use of any density $\tilde{\rho}(\vec{r})$ different from $\rho_0(\vec{r})$ provides a system energy higher than the minimal energy corresponding to the real ground-state:

$$E_0[\rho_0(\vec{r})] \leq E_0[\tilde{\rho}(\vec{r})] \quad (II.A.3)$$

II.A.3. The Kohn-Sham approach

We have seen that the Hohenberg-Kohn functional $F[\rho(\vec{r})]$ contains the majority of the energetic parameters, in the form of a kinetic term and potential terms describing the interactions between electrons. We can make a distinction between the classical Coulomb term $J[\rho(\vec{r})]$ describing the interelectronic repulsion and a non-classical term $E_{ncl}[\rho(\vec{r})]$ containing the effects of electronic correlation, exchange and self-interaction:

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{ncl}[\rho(\vec{r})] \quad (II.A.4)$$

$$\text{where } J[\rho(\vec{r})] = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

The determination of the exact form of $F[\rho(\vec{r})]$ is mainly constrained by the difficulty to evaluate the kinetic energy for a set of interacting electrons. The formalism proposed by

Kohn and Sham^[4] is based on the splitting of this kinetic energy functional in two parts (Eq. II.A.5): one term T_S that can be calculated exactly and considers electrons as non-interacting particles, and a correlation correction term T_c accounting for electron-electron interactions.

$$T[\rho_S(\vec{r})] = T_S[\rho_S(\vec{r})] + T_c[\rho_S(\vec{r})] \quad (\text{II.A.5})$$

where $\rho_S(\vec{r})$ is the ground-state electron density of the non-interacting system which can be defined within an orbital formulation, introducing atomic orbitals Ψ_n^{KS} denoted as the Kohn-Sham orbitals representing the non-interacting electrons. Note that $\rho_S(\vec{r})$ defined from the Kohn-Sham orbitals must reproduce the ground-state density of the real interacting system $\rho_0(\vec{r})$:

$$\rho_S(\vec{r}) = \sum_{n=1}^N |\Psi_n^{KS}(\vec{r})|^2 = \rho_0(\vec{r}) \quad (\text{II.A.6})$$

Therefore, the Kohn-Sham orbitals allow the calculation of the electron density from Eq. (II.A.6) and constitute also the Slater determinant representing the ground-state wavefunction.

The term T_S introduced in Eq. (II.A.5) can also be defined from the Kohn-Sham orbitals:

$$T_S[\rho_S(\vec{r})] = -\frac{1}{2} \sum_{n=1}^N \langle \Psi_n^{KS}(\vec{r}) | \nabla^2 | \Psi_n^{KS}(\vec{r}) \rangle \quad (\text{II.A.7})$$

From Eq. (II.A.4) and (II.A.5) we can write:

$$F[\rho_S(\vec{r})] = T_S[\{\Psi_n^{KS}(\vec{r})\}] + J[\rho_S(\vec{r})] + E_{XC}[\rho_S(\vec{r})] \quad (\text{II.A.8})$$

where $E_{XC}[\rho_S(\vec{r})] = E_{ncl}[\rho_S(\vec{r})] + T_c[\rho_S(\vec{r})]$ is defined as the exchange-correlation (XC) functional.

In order to determine the Kohn-Sham orbitals and the XC functional, one needs to write and solve the Kohn-Sham equation:

$$\hat{H}^{KS} \Psi_n^{KS}(\vec{r}_i) = \varepsilon_n \Psi_n^{KS}(\vec{r}_i) \quad (\text{II.A.9})$$

$$\left[-\frac{1}{2} \nabla_i^2 + \int \frac{\rho(\vec{r}_j)}{|\vec{r}_{ij}|} d\vec{r}_j + V_{XC}(\vec{r}_i) + V_{ext}(\vec{r}_i) \right] \Psi_n^{KS}(\vec{r}_i) = \varepsilon_n \Psi_n^{KS}(\vec{r}_i)$$

where V_{XC} is the exchange-correlation potential defined as $V_{XC} = \frac{\partial E_{XC}[\rho]}{\partial \rho}$, $\hat{H}^{KS}$ is the Kohn-Sham Hamiltonian and V_{ext} is the external potential introduced in Eq. (II.A.1). Note that the resolution of the Kohn-Sham equation requires a self-consistent procedure since the orbitals, density and XC terms are interdependent. Moreover, thanks to the transformation described in Eq. (II.A.8) the challenge of a DFT calculation is no longer to find the exact

Hohenberg-Kohn functional, but to approximate the exchange-correlation parameter in the best way possible.

Such approximations are generally based on the early division of the XC functional into two separate functionals of the electron density: an exchange functional E_X and a correlation functional E_C , as described in Eq. (II.A.10).

$$E_{XC}[\rho(\vec{r})] = E_X[\rho(\vec{r})] + E_C[\rho(\vec{r})] \quad (\text{II.A.10})$$

II.A.4. Approximations of the exchange-correlation (XC) functional

II.A.4.1 Local Density Approximation (LDA)

The simplest approximation of the exchange-correlation energy assumes that it is defined at any point in space as a function of the electron density at this point only. This approach is therefore called the Local Density Approximation (LDA) and can be applied by locally considering a system of interest as a homogeneous electron gas of similar electron density $\rho(\vec{r})$. The LDA XC energy is defined as:

$$E_{XC}^{LDA}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{XC}^{LDA}(\rho(\vec{r})) d\vec{r} \quad (\text{II.A.11})$$

where ε_{XC}^{LDA} is the exchange-correlation energy per particle in the case of a homogenous electron gas. This value can be split into exchange (ε_X^{LDA}) and correlation (ε_C^{LDA}) contributions, accordingly to Eq. (II.A.10):

$$\varepsilon_{XC}^{LDA}(\rho(\vec{r}_i)) = \varepsilon_X^{LDA}(\rho(\vec{r}_i)) + \varepsilon_C^{LDA}(\rho(\vec{r}_i)) \quad (\text{II.A.12})$$

One of the first formulation of the exchange term in the case of a homogeneous electron gas has been proposed by Dirac^[5], which describes explicitly the dependence of the exchange energy with the local density $\rho(\vec{r})$:

$$\varepsilon_X^{LDA,Dirac}[\rho(\vec{r})] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \rho^{4/3}(\vec{r}) d\vec{r} \quad (\text{II.A.13})$$

Another usual form of the exchange energy is proposed by Slater, extending Eq. (II.A.13) to spin-polarized systems by expressing a dependence between the exchange functional and the Local Spin Densities (LSD) $\rho_\alpha(\vec{r})$ and $\rho_\beta(\vec{r})$ ^[6], as presented in Eq. (II.A.14). Note that the $2^{1/3}$ coefficient appearing in this formulation originates from the spin-scaling relation between spin-compensated and spin-polarized systems ^[6]:

$$\varepsilon_X[\rho_\alpha(\vec{r}), \rho_\beta(\vec{r})] = \frac{1}{2} (\varepsilon_X[2\rho_\alpha(\vec{r})] + \varepsilon_X[2\rho_\beta(\vec{r})]) \quad (\text{II.A.14})$$

$$\varepsilon_X^{LSDA,Slater}[\rho(\vec{r})] = -2^{1/3} \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int (\rho_\alpha^{4/3}(\vec{r}) + \rho_\beta^{4/3}(\vec{r})) d\vec{r}$$

Note that, for a closed-shell system, ρ_α and ρ_β are identical and the LSD expression becomes a standard Local Density functional.

The correlation term is however more difficult to approximate independently from the exchange term in the LDA approach. Various methods and formulations have been proposed, among which the popular Vosko-Wilk-Nusair correlation functional (VWN)^[7] and the Perdew local correlation functional (PL)^[8].

LDA functionals are therefore defined in a simple analytic form, and become less accurate when increasing the inhomogeneity of the described system. Typically, LDA functionals tend normally to overestimate binding energies, whereas they usually underestimate bond lengths, ground-state and ionization energies. Results obtained from LDA approximation tend to improve with the size of the system and are, by definition, better evaluated in the cases of systems presenting small variations of the electron density. Note however that satisfying results have also been obtained by using LDA functionals on several systems with relatively large density gradients, what could be partially explained by the cancellation of errors resulting from the underestimation of the exchange energy and the overestimation of the correlation energy, leading to surprisingly good E_{XC}^{LDA} values.

II.A.4.2 Generalized Gradient Approximation (GGA) and meta-GGA methods

In order to deal with inhomogeneous systems characterized by regions with large electron density gradients, it seems appropriate to incorporate explicitly the density gradient in the approximation of the E_{XC} functional. This is the principle of the “nonlocal” Generalized Gradient Approximation methods (GGAs), which make the exchange and correlation energies dependent on both the electronic density $\rho(\vec{r})$ and the density gradient $\vec{\nabla}\rho(\vec{r})$:

$$E_{XC}^{GGA}[\rho(\vec{r})] = \int \rho(\vec{r}) \varepsilon_{XC}^{GGA}(\rho(\vec{r}), \vec{\nabla}\rho(\vec{r})) d\vec{r} \quad (\text{II.A.15})$$

where the term ε_{XC}^{GGA} can also be split into exchange and correlation contributions. Two different approaches were considered to develop expressions of the exchange-correlation functionals.

The first one is based on numerical fitting procedures with experimental results obtained for large training sets of molecules, which led to the development of the popular Becke88 (B)^[9] and Perdew-Wang (PW)^[10] exchange functionals for example. Such functionals perform well in the evaluation of atomization energies and reaction barriers, but lack accuracy in the description of some important properties in solid-state physics.

The second approach is purely theoretical, based on basic principles derived from quantum mechanics, adding corrections to the description of the electronic density and to the density variations, and trying to satisfy exact relations on the exchange and correlation holes. Following this principle, the Perdew86 (P)^[11] and Perdew-Burke-Ernzerhof (PBE)^[12] exchange functionals have been developed, which generally perform better than the fitted functionals in the prediction of solid-state properties, but on the other hand fail at determining atomization energies and reaction barriers which are well described with the former approach.

Several correlation functionals have been developed following these two approaches, among which we can cite the popular Lee-Yang-Parr (LYP)^[13] and Perdew-Wang91 (PW91)^[14] functionals. Practically, GGA exchange-correlation functionals are built by combining distinct exchange and correlation functionals, e.g. the popular BLYP XC functional, which results from the combination of the exchange Becke88 and the correlation LYP functionals. The GGA functionals constitute a real improvement with respect to the LDA methods, as they generally perform better for the evaluation of bond lengths, ground-state energies, dissociation energies, energy barriers and structural energy differences. They also allow to correct vibrational frequencies of molecules composed of atoms belonging to the two first rows of the periodic table.

However, GGA functionals still fail at describing correctly some chemical aspects, such as Van der Waals interactions, ionization potentials and electron affinities in the solid state, (hyper)polarizabilities and excitation energies. Exchange-correlation functionals then need to be further refined.

A natural improvement of the GGA methods is to make the exchange-correlation energy dependent on higher order electron density gradients and, by extension, on the kinetic energy density, leading to the development of meta-GGA XC functionals. These methods present an improved efficiency but they turn out to be technically challenging and can

present some difficulties in terms of numerical stability. Among the meta-GGA exchange-correlation functionals we can cite TPSS^[15] and B95^[16].

II.A.4.3 Hybrid Density Functional methods

Another solution for improving the efficiency of the GGA functionals is to include a percentage of non local Hartree-Fock (HF) exchange to a standard GGA exchange-correlation functional (Eq. II.A.15) in order to describe the correct asymptotic $-\frac{1}{r}$ behavior of the exchange term, which is not satisfied with the LDA and GGA methods. This new kind of functionals is then denoted as Hybrid-GGA functionals.

In order to optimize the weight of each exchange and correlation term in the final functional one needs to rely on empirical data, as the exact amount of HF exchange to incorporate can not be determined theoretically. Taking the example of the Becke three parameter hybrid functional (B3) presented in Eq. (II.A.16):^[17]

$$E_{XC}^{B3} = aE_X^{HF} + (1 - a)E_X^{Slater} + bE_X^{B88} + cE_C^{PW91} + (1 - c)E_C^{VWN} \quad (\text{II.A.16})$$

where a , b and c are semi-empirical parameters fitted to a set of experimental atomization energies, ionization potentials, proton affinities, total atomic energies and other data. In this case these parameters are equal to $a = 0.2$, $b = 0.72$, $c = 0.81$. The only modification brought to this functional in order to build the popular B3LYP functional consisted in replacing the PW91 correlation functional with the LYP correlation functional, the semi-empirical parameters remaining unchanged. The H-GGA functionals turn out to be more efficient than the GGA functionals, this is why they are so widely used nowadays. Among examples of popular hybrid density functionals that we have used in our calculations, we can mention the B3LYP^[18], B3P86^[9,11,16] and B971^[19] XC functionals which are mostly distinguished by the amount of Hartree-Fock (HF) exchange (varying from 20 % for the B3LYP and B3P86 functionals to 21% for the B971 functional, respectively), and the nature of the DFT exchange and correlation functionals.

Note that, following the same idea, one can build Hybrid-meta GGA functionals which result from the combination of HF exchange with meta-GGA functionals. They depend therefore on the electron density and its gradient, the kinetic energy density and exact HF exchange. In this work we have used the TPSSH functional^[20], which is characterized by an amount of HF exchange equal to 10%.

II.A.4.4. Long-range corrected functionals

As mentioned above, hybrid functionals include a fixed amount ($\sim 20\%$ – $\sim 25\%$) of HF exchange added to the usual density functional exchange. However, it has been shown that a large amount (even 100%) of HF exchange is needed to correctly describe properties that are sensitive to the long-range behavior of exchange-correlation potential, and that the incorrect asymptotic decay of the exchange correlation potential (instead of the correct $-1/r$ asymptotic form one has $-a/r$, where a is the amount of HF exchange in the hybrid) provide qualitatively incorrect predictions for charge-transfer excitations energies^[21], or (hyper)polarizabilities in conjugated systems^[22]. One way to overcome this deficiency has consisted in building functionals that combine generalized-gradient approximation (GGA) exchange functionals in DFT at short range with the ab initio Hartree-Fock exchange at long range by using the standard error function. These range-separated hybrids, which aim to add corrections to the description of long-range interactions correspond to the second set of XC functionals used in our simulations and they are called long-range corrected XC functionals, or range-separated hybrids. Their scheme relies on the splitting of the interelectronic Coulomb operator into short range and long-range parts such as:

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \operatorname{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \operatorname{erf}(\mu r_{12})}{r_{12}} \quad (\text{II.A.17})$$

where the relations $0 \leq \alpha + \beta \leq 1$, $0 \leq \alpha \leq 1$ and $0 \leq \beta \leq 1$ should be satisfied. The first part of Eq. (II.A.17) describes the short-range interactions and is combined with GGA exchange, while the second term accounts for the long-range interactions and is combined with HF exchange. The parameter α enables to incorporate the HF exchange contribution over the whole range by a factor of α , while the parameter β allows its inclusion at long range. Among the range-separated hybrids that we have used in our calculations we can mention the LC-BLYP^[23], CAM-B3LYP^[24] and ω B97x^[25] functionals. Fig. (II.1). illustrates the contributions to exchange from r_{12} apportioned into DFT and HF for the B3LYP, LC-BLYP and CAM-B3LYP functionals. The contributions to exchange in the LC-BLYP functional correspond to pure DFT (B88) at short range and pure HF at long range. In our work, all the calculations performed by using this latter functional are characterized by a range-separation parameter $\mu=0.47 \text{ Bohr}^{-1}$. The CAM-B3LYP functional comprises 19% of HF exchange plus 81% of Becke 1988 (B88) exchange-interaction at short range, 65% of HF plus 35% of B88 at long range, and $\mu=0.33 \text{ Bohr}^{-1}$. Finally, the ω B97x functional is characterized by 16% of HF exchange plus

84% of B97 exchange-interaction at short range, and corresponds to pure HF at long range with a parameter value controlling the partitioning of the interelectronic distance r_{12} equals to 0.3 Bohr^{-1} . Finally, a summary of characteristics of DFT functionals that are discussed in this section and used in our IET simulations is given in Table (II.1).

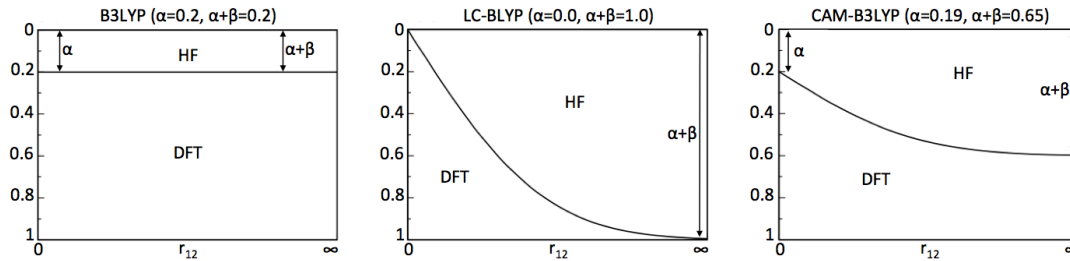


Fig. II.1. Schematic representation of the contributions to exchange from r_{12} apportioned into DFT and HF for the B3LYP, LC-BLYP and CAM-B3LYP functionals (taken from Ref. [24]).

Name	year	type	a
B3LYP	1994	H-GGA	20
B3P86	1993	H-GGA	20
B971	1998	H-GGA	21
BLYP	1988	GGA	0
PBE	1996	GGA	0
PBE0	1996	H-GGA	25
SVWN5	1981	LSDA	0
TPSS	2003	m-GGA	0
TPSSh	2003	Hm-GGA	10
LC-BLYP	2001	RSH-GGA	0-100
CAM-B3LYP	2004	RSH-GGA	19-65
ω -B97x	2008	RSH-GGA	16-100

Table. II.1. Summary of common DFT functionals, where ‘a’ refers to the percentage of HF exchange in the functional, ‘LSDA’ to Local Spin Density Approximation, ‘GGA’ to Generalized Gradient Approximation, ‘H-GGA’ to Hybrid Generalized Gradient Approximation, ‘m-GGA’ to meta Generalized Gradient Approximation, ‘Hm-GGA’ to Hybrid meta Generalized Gradient Approximation, and ‘RSH-GGA’ to Range Separated Hybrid Generalized Gradient Approximation.

II.B. Atomic orbital basis sets

II.B.1. Gaussian basis sets

In order to describe the electronic densities and the wavefunctions, atomic basis sets of various types and sizes have been selected in our simulations. A basis set refers to the set of (non-orthogonal) one-particle functions used to build the molecular orbitals. In the Roothaan-Hall method^[26], the molecular orbitals are described as linear combinations of

known atomic orbitals. Different approaches have been developed to define these sets of functions called “atomic orbital basis sets”, in order to solve a chemical problem within an expected accuracy. Quantum chemical calculations are typically performed within a finite set of basis functions, which describe as well as possible the exact atomic orbitals but are never a perfect representation of these, even in the case of simple hydrogenoids, due to approximations and simplifications of their analytic formulas.

In order to introduce the basic ideas leading to the choice of a basis set we can take the example of two-electron systems requesting only 1s orbitals. Two types of basis functions have been commonly proposed: (i) the normalized 1s Slater-type function centered at R_A having the form:

$$\phi_{1s}^{SF}(\zeta, r - R_A) = (\zeta^3/\pi)^{1/2} e^{-\zeta|r-R_A|} \quad (\text{II.B.1})$$

where ζ corresponds to the Slater orbital exponent, and (ii) the 1s Gaussian-type function centered at R_A which can be expressed as follows:

$$\phi_{1s}^{GF}(\alpha, r - R_A) = (2\alpha/\pi)^{3/4} e^{-\alpha|r-R_A|^2} \quad (\text{II.B.2})$$

where α is the Gaussian orbital exponent. Note that the diffuseness or size of these basis functions is represented by the orbital exponents ζ or α (which are positive numbers larger than zero), so that a small exponent implies a large diffuse function, while a large exponent implies a small dense function. The major differences between these types of functions appear at $r=0$ and at large values of r . Indeed, at $r=0$ the Slater function has a finite slope and the Gaussian function has a zero slope, while for large values of r the Gaussian function $e^{-\alpha r^2}$ decays much more rapidly than the Slater function $e^{-\zeta r}$. For an accurate description of the electronic wavefunctions, a priori one would prefer the Slater form whose description is close to the qualitative features of molecular orbitals. However, the use of Slater functions is limited to the treatment of diatomic molecules since the evaluation of their three and four-center integrals increase the computational time, while it is more easy and less time-consuming by using the Gaussian type functions. Indeed, quantum chemistry calculations involve a lot of products of AO functions in the form of two-electron integrals, which turn out to be more rapidly and efficiently carried when using Gaussian functions since a product of two Gaussian functions provides another Gaussian function, and also because the treatment of Gaussian functions in differential and integral calculations is extensively documented. Defining the basis functions as linear combinations of the primitive Gaussian

functions ϕ_μ^{GF} called *contractions* constitutes a remedy to the II.B.2 form, and leads to the construction of Contracted Gaussian functions (CGF), defined as follows:

$$\phi_\mu^{CGF}(r - R_A) = \sum_{p=1}^L d_{p\mu} \phi_p^{GF}(\alpha_{p\mu}, r - R_A) \quad (\text{II.B.3})$$

where L is the length of the contraction, $d_{p\mu}$ are the contraction coefficients and $\alpha_{p\mu}$ are the contraction exponents. The choice of contracting several Gaussian functions in order to define the basis functions comes from the need to mimic as much as possible the functional behavior of molecular orbitals, and therefore the description of the electronic density. One of the main problems that would arise from a bad approximation of such functions concerns the accurate description of the cusp effect of the wavefunction observed at the nuclear position ($r=0$). Indeed, a single Gaussian function presents a zero gradient at $r=0$, making it unable to describe correctly such cusp behavior, and the use of an optimized contracted function intends to fit as much as possible the primitive wavefunction. Following the optimization of the CGFs and the fixation of the L, d and α parameters giving the best description of the atomic orbital wavefunctions possible, these functions will be practically used as CGTOs (Contracted Gaussian Type Orbitals) in the course of ab initio calculations. An application of this procedure that has been widely used is to fit a Slater-type orbital (STO) to a linear combination of $n=1,2,3,\dots$ primitive Gaussian functions: this is called the STO-nG procedure. Among these CGTO basis sets, we can mention the minimal (in the sense of having the least number of functions per atom required to describe the occupied atomic orbitals of that atom) or “single- ζ ” basis sets for which each atomic orbital is described by a single CGTO, and especially the STO-3G basis set where each basis function is represented by a contraction of three Gaussian functions.

Nowadays the most used CGTO basis set concerns the “split-valence” type developed by Pople and his group, which are optimized at the Hartree-Fock level to minimize the HF energy and improves the flexibility of the valence region. These basis sets construction are directly referenced in their names which follow the “k-nlmG” structure, where k is the number of primitive GTOs (PGTOs) used for representing the core orbitals, and nlm indicates the number of CGTOs the valence orbitals are split into, and how many PGTOs are used for their representation. When the valence AOs are split into two CGTOs we speak of a double- ζ basis set, a split into three CGTOS is associated to a triple- ζ basis set, ... Such extended

descriptions tend to improve the quality of the MO's and of their associated properties, and allows a better description of the electron distribution anisotropy. The definition of these kind of basis sets can be illustrated with the example of the widely used 6-31G basis set, for which the core orbitals are represented by a contraction of 6 PGTOs, the inner part of the valence orbitals is a contraction of 3 PGTOs and the outer part of the valence orbitals is represented by one PGTO^[27].

Polarization functions can also be added to the orbital description in order to improve the flexibility in the angular part of the wave function, and get a more accurate description of the asymmetric charge distribution around the nucleus. For example, in the case of the 6-31G(d) basis set (also called 6-31G*) we take into account unoccupied d orbitals on all the non-hydrogen atoms. Polarization functions can also be added on the hydrogen atoms, as in the example of the 6-31G(d,p)^[28] basis set (6-31G**) where the first * still means that d orbitals are added on all non-hydrogen atoms and the second * indicates that p orbitals are added on all hydrogen atoms.

In order to improve the description of the outer valence region we can also add diffuse functions. They have the form of Gaussian functions which have small exponents and decay slowly with the distance from the nucleus which can be useful for the description of weak bonds or for the calculations of molecular properties depending on the wave function tail (e.g. polarizability). They are usually s- and p- type orbitals, which are indicated by the "+" or "++" symbols. The first term means that one set of diffuse s- and p-functions are added only on heavy atoms, while the second term indicates that a supplementary diffuse s-function is also added to hydrogen atoms. Summarizing these two types of tuning, we take the example of the 6-31+G(d) basis set that is characterized by the additions of one set of diffuse sp-functions and a single d-type polarization function on heavy atoms only.

The use of Gaussian functions can be taken one step further to define basis sets able to evaluate the electron correlation corrections to the energy in the best possible way. The general idea is to define a set of virtual orbitals, called *correlating orbitals*, that will be described along the occupied canonical orbitals obtained from atomic Hartree-Fock calculations. A major concern is to match the correlation corrections obtained with the new basis with the corrections obtained in the Complete Basis Set (CBS) limit.

A first proposition is to generate the correlating orbitals by carrying correlated atomic calculations in the full canonical basis of the occupied and virtual orbitals generated

by a HF calculation. By diagonalizing the virtual part of the resulting one-electron density matrix, we select the Atomic Natural Orbitals (ANOs) which have the largest associated occupation numbers, which depict the contribution that each natural orbital make to the correlated wavefunction. These selected virtual natural orbitals are defined as our correlating natural orbitals and, together with the occupied canonical orbitals obtained from the previous HF calculation, will be used as a basis for correlated molecular calculations. This kind of basis set is known as an ANO basis^[29]. In spite of their efficiency, the large number of PGFs needed to describe ANO basis makes their applications rather expensive in computational time, especially if we want to converge the corrections obtained within the CBS limit.

In this context, Dunning^[30] has proposed an alternative way defining smaller basis sets able to reproduce the accuracy of the corrections obtained with ANO basis. Instead of defining the correlating orbitals following an occupation number criterion, we focus here on an energy criterion: the correlating orbitals are defined as single PGFs, whose respective exponents are optimized in order to maximize the contribution of each correlating orbital to the correlation energy in atomic valence CISD calculation. This approach is called “correlation-consistent”: shells of correlating orbitals lowering the total energy by similar amounts are added systematically to a set of occupied HF orbitals. Such basis sets defined as “correlation-consistent polarized valence basis sets” take the general form “cc-pVXZ”, where X is a cardinal number referencing the successive additions of correlating orbital shells.

This can be illustrated with the example of atomic calculations carried on the carbon atom. Belonging to the first row, its occupied orbitals contain two s-type and one p-type functions, each of them being a contraction of a set of PGFs. The first shell of correlating orbitals is added for X=2, corresponding to the cc-pVDZ basis set, and consists of one s-type, one p-type and one d-type primitive correlating orbital. The cc-pVDZ basis set will thus describe three s-type, two p-type and one d-type orbitals, as shown in Table (II.2). After getting a final set of orbitals for a given cc-pVXZ method, incrementing the X value by 1 will consist in adding a different shell of correlating orbitals. Table (II.2) reports the structures of the different cc-pVXZ basis sets for [B-Ne] atoms.

In order to get more flexibility in the description of diffuse electron distribution, we can add diffuse functions to the cc-pVXZ basis set in the form of primitive functions whose exponents have been optimized by minimizing the energy of atomic anions. In the case of

augmented correlation-consistent basis sets (aug-cc-pVXZ) we add one single diffuse function for each angular momentum present in the root set, as illustrated in Table (II.2).

In opposition to the Pople basis sets, which were designed to get the best HF energy possible from the occupied orbitals contributions, the addition of diffuse functions to correlation-consistent basis sets aim to maximize the contributions of the occupied and correlating orbitals to the correlation energy. This is made possible by the addition of diffuse functions for every angular momentum present in the basis set. Finally, the basis sets composition for a selection of atoms involved in our IET simulations is given in Table (II.3).

X	cc-pVXZ	N _v	aug-cc-pVXZ		N _{aug}
D	[3s2p1d]	14	+1s1p1d	[4s3p2d]	23
T	[4s3p2d1f]	30	+1s1p1d+1f	[5s4p3d2f]	46
Q	[5s4p3d2f1g]	55	+1s1p1d+1f+1g	[6s5p4d3f2g]	80
5	[6s5p4d3f2g1h]	91	+1s1p1d+1f+1g+1h	[7s6p5d4f3g2h]	127

Table II.2. Structure of the cc-pVXZ and aug-cc-pVXZ basis sets for the [B-Ne] atoms. N_v and N_{aug} refer to the total numbers of contracted orbitals in the cc-pVXZ and aug-cc-pVXZ basis sets, respectively.

Basis set		Hydrogen		Carbon, Nitrogen, Oxygen		Sulfur	
Name	Quality	Contracted	Primitive	Contracted	Primitive	Contracted	Primitive
STO-3G	SZ	1s	3s	2s1p	6s3p	3s2p	9s6p
6-31G	DZ	2s	4s	3s2p	10s4p	4s3p	16s10p
6-31G(d)	DZ	2s	4s	3s2p1d	10s4p1d	4s3p1d	16s10p1d
6-31+G(d)	DZ*	2s	4s	4s3p1d	11s5p1d	5s4p1d	17s11p1d
6-31+G(d,p)	DZ*	2s1p	4s1p	4s3p1d	11s5p1d	5s4p1d	17s11p1d
6-311G(d)	TZ	3s	5s	4s3p1d	11s5p1d	6s5p1d	13s9p1d
6-311+G(d)	TZ*	3s	5s	5s4p1d	12s6p1d	7s6p1d	14s10p1d
cc-pVDZ	DZ	2s1p	4s1p	3s2p1d	9s4p1d	4s3p2d	12s8p2d
cc-pVTZ	TZ	3s2p1d	5s2p1d	4s3p2d1f	10s5p2d1f	5s4p3d1f	15s9p3d1f
cc-pVQZ	QZ	4s3p2d1f	6s3p2d1f	5s4p3d2f1g	12s6p3d2f1g	6s5p4d2f1g	16s11p4d2f1g
aug-cc-pVDZ	DZ*	3s2p	5s2p	4s3p2d	10s5p2d	5s4p3d	13s9p3d
aug-cc-pVTZ	TZ*	4s3p2d	6s3p2d	5s4p3d2f	11s6p3d2f	6s5p4d2f	16s10p4d2f

Table. II.3. Basis sets composition for a selection of atoms involved in our IET simulations. Note that the symbol * refers to basis sets including diffuse functions, while ‘DZ’, ‘TZ’ and ‘QZ’ mean ‘Double Zeta’, ‘Triple-Zeta’ and ‘Quadruple Zeta’, respectively.

II.B.2. Effective Core Potential (ECP) Basis Sets

In the treatment of molecular systems containing heavy elements, two main problems arise: the large number of electrons increases significantly the computational time,

which evolves as N^4 (where N is the number of electrons), and neglecting the relativistic effects can have a significant impact on the accuracy of the calculated properties^[31]. These latter effects originate from the increase of the core electron speed (essentially s and p orbitals) due to the large atomic number of the heavy element, what induces a relativistic increase of their masses and then a contraction of the inner s and p orbitals. Moreover, electrons with large angular momentum (d and f orbitals) weakly suffer from this mass-velocity effect but, as the contraction of the s and p orbital increases the shielding of the nuclear charge, the outer-core orbitals tend to be destabilized and more expanded.

The numerical resolution of the Dirac equation taking into account these relativistic effects would be the most rigorous approach to describe this kind of systems, but it would not reduce the computational cost of our calculations^[32]. An economical alternative consists in using relativistic effective core potential method (RECP), *i.e.* in replacing the chemically inert core electrons with an effective potential mimicking the interactions between core and valence electrons. The main advantages of this approach are that i) we can afford the use of larger basis sets to describe the valence electrons as the number of electrons to describe explicitly has drastically decreased and ii) the incorporation of relativistic effects in the RECP prevents from using a relativistic hamiltonian in the calculations. Such a simplification is justified by the fact that the chemical and physical properties mostly depend on the valence orbitals, but one needs to ensure that the simplification of the numerical description of the core-valence interactions does not alter the energetic and structural characteristics obtained in an all-electron calculation. In this frame, the final goal is to develop and apply the valence-only Hamiltonian.

The development of the Los Alamos National Laboratory 2-Double-Zeta (LANL2DZ) ECP used in this work has been advanced by Hay^[33] and coworkers. The first step consisted in defining in the best way possible the “core” orbitals to be replaced by an effective potential: these core orbitals are denoted ϕ_C^R while the remaining valence orbitals are labelled ϕ_V^R . The total relativistic wavefunction of a N -electron system can be expressed as a product of core and valence orbitals:

$$\Psi^R(1,2 \dots N) = A[\phi_C^R(1,2 \dots n_c)\phi_V^R(n_c + 1, \dots, N)] \quad (\text{II.B.4})$$

where A is the antisymmetrization and normalization operator, and n_c refers to the number of core electrons. The total energy associated to the relativistic Hamiltonian can also be separated into contributions due to core, valence and core-valence interaction energies:

$$E_T^R = \langle \psi^R | H^{rel} | \psi^R \rangle = E_C^R + E_V^R + E_{CV}^R \quad (II.B.5)$$

Since the focus is on the explicit description of valence electrons, Eq. (II.B.5) is reduced to a valence-only form:

$$E_V + E_{CV} = \langle \phi_V^R | H_V^{rel} | \phi_V^R \rangle \quad (II.B.6)$$

where H_V^{rel} is the modified Hamiltonian and can be expressed as follows:

$$H_V^{rel} = \sum_{v=n_c+1}^N \left(-\frac{1}{2} \nabla_v^2 - \frac{Z}{r_v} \right) + \sum_{v=n_c+1}^N \sum_{v'>v}^N U_{vv'}^{val} + \sum_{c=1}^{n_c} \sum_{v=n_c+1}^N U_{cv}^{core-val} + W^{rel} \quad (II.B.7)$$

where the second term refers to the interactions between valence electrons, the third term to interactions between core and valence electrons and the fourth includes the relativistic mass-velocity and Darwin terms. This latter is associated to the decrease of the attraction potential energy due to the increased shielding of the nuclear charge and concerns only the s electrons whose density is non zero in the vicinity of the nucleus.

The goal of the RECP theory is to replace the last two terms by a single relativistic effective potential (RECP) noted U^{RECP} . The Phillips-Kleinman theory^[34] allows to define a local REP respecting the orthogonality between core and valence orbitals, what is essential to prevent the valence wavefunctions collapsing in the core region. In order to determine U^{RECP} a reduced Hamiltonian focusing on the core-valence interactions is defined as follows:

$$H_{PK}^{rel} = \sum_{v=n_c+1}^N \left(-\frac{1}{2} \nabla_v^2 - \frac{Z}{r_v} \right) + U^{RECP} \quad (II.B.8)$$

Using this incomplete Hamiltonian with standard orbitals would not satisfy the orthogonality condition $\langle \phi_V^R | \phi_C^R \rangle = 0$. The respect of this condition imposes to replace the standard orbitals ϕ_V^R with pseudo-orbitals χ_V^R characterized by the same energies ε_V , in order to make the following equation valid:

$$H_{PK}^{rel} \chi_V^R = \varepsilon_V \chi_V^R \quad (II.B.9)$$

In the shape-consistent approach^[35] we adopt here, these pseudo-orbitals have to be nodeless since they must correspond to the first solution of the valence Hamiltonian for a given symmetry, and also because we need to avoid singularities in the definition of the potential where $\chi_V^R = 0$ outside the origin. An important feature of the core-valence interactions is that electrons contained in atomic orbitals presenting different symmetries feel the core effects in different ways. This means that a different RECP has to be generated

for every angular momentum l of the valence orbitals, and each χ_l pseudo-orbital defines a unique effective core potential U_l^{RECP} .

Christiansen^[36] and co-workers have proposed a method for constructing pseudo-orbitals respecting two conditions described in Eq. (II.B.10):

- In the core region, the valence pseudo-orbitals can be expressed as a polynomial function to ensure their regular growth;
- In the valence region, the valence pseudo-orbitals must be close to their orbital counterparts obtained in all-electron calculations, so that the overlaps between valence orbitals as well as valence-valence interactions are well reproduced.

$$\chi_l = \begin{cases} \sum_i C_i r^i & r \leq r_c \\ \phi_l & r \geq r_c \end{cases} \quad (\text{II.B.10})$$

where r_c represents the limit radius of the core region. The polynomial coefficients C_i are determined by matching the value and the first three derivatives of χ_l and ϕ_l at the r_c position, respecting the condition that χ_l is normalized. Starting from Eq. (II.B.7) to write the one-electron symmetry eigenvalue equation, we obtain:

$$\left(-\frac{1}{2} \nabla_i^2 - \frac{Z_{eff}}{r_i} + W'_{li} + U_{li}^{RECP} \right) \chi_{li} = \varepsilon_{li} \chi_{li} \quad (\text{II.B.11})$$

where $Z_{eff} = Z - n_c$ is the effective nuclear charge and W'_{li} is the valence-valence interaction term evaluated with the pseudo-orbitals χ_{li} . We can easily deduce the effective potential from Eq. (II.B.11):

$$U_{li}^{RECP} = \frac{\left(\frac{1}{2} \nabla_i^2 + \frac{Z_{eff}}{r_i} - W'_{li} + \varepsilon_{li} \right) \chi_{li}}{\chi_{li}} \quad (\text{II.B.12})$$

Practically, the numerical effective core potentials U_l^{RECP} are then derived for each l by demanding that the χ_l is a solution in the field of U_l^{RECP} with the same orbital energy ε_l as the orbital ϕ_l . The numerical potentials are fit in analytical form as Gaussian functions:

$$\sum_k d_k r^{n_k} \exp[-\zeta_k r^2] \quad (\text{II.B.13})$$

where $n_k = 0, 1$, or 2 . Table (II.4) reports the LANL2DZ ECP parameters n_k, ζ_k and d_k defined for every l we have used for describing Au atoms.

The numerical pseudo-orbitals χ_{li} are also fit with Gaussian functions to obtain basis sets able to describe the molecular structures.

We have seen that the definition of the valence hamiltonian and U_i^{RECP} depend on the definition of the valence pseudo-orbitals. Since we focus in this work on single molecules embedded between gold electrodes, our requirements need to be refined. Indeed, the large size of gold atoms make the distinction between their core and valence regions difficult. For such atoms, the 5s and 5p orbitals are in principle core orbitals but since their extent is similar to the 5d valence orbitals we can not replace them by ECP's as, in this case, the distinction between spatial core and valence regions would be confusing. These outermost core orbitals then need to be treated on an equal footing with the 5d and 6s valence orbitals, being defined explicitly as Gaussian-type functions. Moreover, the 6s pseudo-orbital is defined with a node in the vicinity of the 5d orbital, in the same way as the Hartree-Fock 6s orbital. We expect this similarity in the nodal structure to improve the accuracy of the two-electron integrals calculated with our ECP approach, with respect to all-electron calculations. The symmetries considered to describe the total effective potential of gold atoms range from s- to g-type orbitals, the latters being the lowest valence angular momentum not represented in the core.

As a final remark, one could legitimately question the impact of modifying the orbitals description when using an ECP, since the absence of core electrons modify the value of the correlation energy with respect to the one determined in an all-electron calculation. Hopefully, it has been proven that the errors in the estimation of the correlation effects are of the same order of magnitude as the errors induced by the use of a finite basis set^[37].

n_k	ζ_k	d_k
g potential		
1	622.6287956	-60.0000000
2	136.2843607	-555.5292312
2	33.1549781	-168.0019785
2	9.9894895	-63.0399875
2	3.0481312	-4.2516681
s-g potential		
0	194.7374304	3.0000000
1	351.5327447	38.6020880
2	122.3270402	864.8370727
2	32.0914617	374.9935520
2	5.2451812	289.7910100
2	4.4916223	-152.4532773
p-g potential		
0	420.6158801	2.0000000
1	109.4417815	73.8885625
2	34.1714280	326.6729872
2	5.9879750	126.5814591
d-g potential		
0	219.2666158	3.0000000
1	122.7297786	55.6793149
2	63.1063369	449.1987335
2	18.3684520	215.0269091
2	4.4972844	64.0840995
f-g potential		
0	108.5506037	4.0000000
1	56.4795527	51.8065335
2	29.2069159	231.2183113
2	9.5440543	119.0047386
2	2.8965118	15.3424188

Table II.4. LANL2DZ ECP parameters n_k , ζ_k and d_k defined for every l we have used for describing Au atoms.

II.C. Quantum scattering theory

II.C.1. Basics on Green's Function^[38]

In this section, we describe the properties of Green's functions and the closely Green's operators which are crucial to treat scattering problems in quantum mechanics. We begin by deriving the Lippmann-Schwinger equation, a formulation of the scattering problem which is central to all further developments. Then we introduce the operator Green's function G , the solutions of inhomogeneous differential equations, and the transition operator T and establish their role in scattering theory, their physical meaning and discuss their mathematical properties. Note that the Green's function basics discussed here are detailed in reference [38].

At first, let us consider the problem of an electron undergoing an external potential in an one-dimensional system, which is described by the Schrödinger equation:

$$H(x)\Psi(x) = E\Psi(x) \quad (\text{II.C.1})$$

where:

$$H(x) = H_0 + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad (\text{II.C.2})$$

and $V(x)$ refers to an external potential acting on the electron. Eq. (II.C.1) can be rearranged in the following form:

$$[E - H_0(x)] \Psi(x) = V \Psi(x) \quad (\text{II.C.3})$$

In the Dirac's notation, the Schrödinger equation for the full Hamiltonian H can be written as:

$$(E - H_0)|\Psi\rangle = V|\Psi\rangle \quad (\text{II.C.4})$$

and we can express $|\Psi\rangle$ as the sum of the incident and the scattered wavefunctions (corresponding to the non-perturbed wavefunction and its perturbation contribution), so that:

$$|\Psi\rangle = |\phi\rangle + |\Psi^{sc}\rangle \quad (\text{II.C.5})$$

The eigenstates $|\phi\rangle$ of H_0 can also be introduced so that we have:

$$H_0|\phi\rangle = E|\phi\rangle \quad (\text{II.C.6})$$

The insertion of Eq. (II.C.5) into Eq. (II.C.4) and the use of Eq. (II.C.6) lead to:

$$(E - H_0)|\Psi^{sc}\rangle = V|\Psi\rangle. \quad (\text{II.C.7})$$

Multiplying both sides of Eq. (II.C.7) by $(E - H_0)^{-1}$, we get:

$$|\Psi^{sc}\rangle = (E - H_0)^{-1}V|\Psi\rangle \quad (\text{II.C.8})$$

and adding $|\phi\rangle$ to both sides of Eq. (II.C.8), we obtain:

$$|\Psi\rangle = |\phi\rangle + (E - H_0)^{-1}V|\Psi\rangle \quad (\text{II.C.9})$$

which is called the Lippmann-Schwinger equation. Starting from this equation, we can introduce the concept of ‘Green’s function’, where the free particle’s and the full Green’s operators can be respectively defined as:

$$G_0 = (E - H_0)^{-1} \text{ and } G = (E - H)^{-1} \quad (\text{II.C.10})$$

Using this definition, the Lippmann-Schwinger equation assumes its standard form as:

$$|\Psi\rangle = |\phi\rangle + G_0V|\Psi\rangle \quad (\text{II.C.11})$$

Thereby solving the Lippmann-Schwinger equation for $|\Psi\rangle$ is formally simple, giving:

$$|\Psi\rangle = (1 - G_0V)^{-1}|\phi\rangle \quad (\text{II.C.12})$$

A similar equation to Eq. (II.C.11) can be obtained in terms of the full Green’s function. For this purpose, we use Eq. (II.C.5) in the r.h.s. of Eq. (II.C.7) to get:

$$(E - H_0 - V)|\Psi^{sc}\rangle = V|\phi\rangle \leftrightarrow |\Psi^{sc}\rangle = GV|\phi\rangle \quad (\text{II.C.13})$$

Adding $|\phi\rangle$ to both sides of the above equation and using Eq. (II.C.5) we obtain:

$$|\Psi\rangle = |\phi\rangle + GV|\phi\rangle = (1 + GV)|\phi\rangle \quad (\text{II.C.14})$$

We can also mention that the iteration method can be another way to solve the Lippmann-Schwinger equation and in this case Eq. (II.C.11) can be rewritten as:

$$|\Psi_{new}\rangle = |\phi\rangle + G_0V|\Psi_{old}\rangle \quad (\text{II.C.15})$$

The procedure starts by considering the zeroth order approximation so that: $|\Psi_{old}\rangle = |\phi\rangle$ and by using Eq. (II.C.15) to generate a better approximation: $|\Psi_{new}\rangle = (1 + G_0V)|\phi\rangle$. Using this latter expression as $|\Psi_{old}\rangle$ then leads to a better approximation and $|\Psi_{new}\rangle = (1 + G_0V + G_0VG_0V)|\phi\rangle$. After an infinite number of iterations, the following expression of $|\Psi\rangle$ is found:

$$|\Psi\rangle = (1 + G_0V + G_0VG_0V + \dots)|\phi\rangle \quad (\text{II.C.16})$$

which is known as the Born series. Eq. (II.C.16) can be written as an integral equation and the Born-series for the wavefunction $\Psi(x) = \langle x|\Psi\rangle$ is given by:

$$\begin{aligned} \Psi(x) = & \phi(x) + \int G_0(x, x')V(x')\phi(x')\delta^3x' + \\ & \int G_0(x, x')V(x')G_0(x', x'')V(x'')\phi(x'')\delta^3x'\delta^3x'' + \dots \end{aligned} \quad (\text{II.C.17})$$

where we have defined $\phi(x) = \langle x|\phi\rangle$ and $G_0(x, x') = \langle x|G_0|x'\rangle$. This expression can be understood from a simple experimental situation: considering a moving particle which can

be detected from the collision with a device placed at position x , the collision probability is supposed to be independent of the path followed by the particle and will be proportional to the square of the total wavefunction $|\Psi(x)|^2$. The terms of the developed form presented in Eq. (II.C.17) then correspond to all possible trajectories by which the particle can reach the detector, i.e. depending on the number of collisions the scattered particle underwent before detection. For example, the first term of the development corresponds to the probability amplitude that a particle reaches position x without scattering (i.e. we assume $V=0$). The second term corresponds to a situation where the particle scatters only once at position x' , and is then propagated as a free-spherical wave to reach the detector with a probability amplitude modulated by a factor $V(x')$. The integral form means that we sum over all possible collision positions. Following the same idea, the third term will describe a particle scattering twice at positions x' and x'' , summing over both collision positions, etc.

Let us now discuss the properties of the Green's function and those of the closely Green's operator. To solve Eq. (II.C.1) we require a Green's function for the operator $[E - H(x)]$, which is a function that satisfies:

$$[E - H(x)]G(x, x') = \delta(x - x') \quad (\text{II.C.18})$$

We can notice that the Green's function is a complex function that depends both on the spatial coordinates and on the energy E , where x is a spatial position variable and x' is a parameter which corresponds to the position of the point source. In order to understand the physical meaning of the Dirac delta function $\delta(x - x')$, let us recall a typical example coming from electrostatics dealing with the expression of a charge density $\rho(x)$ of a point charge q at x' so that $\rho(x) = q\delta(x - x')$. In this case, the use of this Dirac delta function enables to ensure i) a zero value of the charge density everywhere except at $x = x'$ since there is no charge anywhere except at this point, ii) an infinite value of the charge density at x' due to the presence of a finite charge in an infinitively small volume.

In the case of a free electron, $V(x) = V_0$ (constant value) and the Green's function (or propagator) is defined as follows:

$$\left[E - V_0 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] G(x, x') = \delta(x - x') \quad (\text{II.C.19})$$

We can mention that Eq. (II.C.19) just looks like the Schrödinger equation:

$$\left[E - V_0 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] \Psi(x) = 0 \quad (\text{II.C.20})$$

except for the source term $\delta(x - x')$ on the right hand side. Therefore, one can consider the Green's function $G(x, x')$ as a wavefunction centered at position x resulting from an excitation applied at x' . Practically, we can expect that this wavefunction will expand in all directions from the position x' . Fig. (II.2) presents the example of a one-dimensional situation where two resulting waves expand from position x' , where A^+ and A^- are the respective amplitudes.

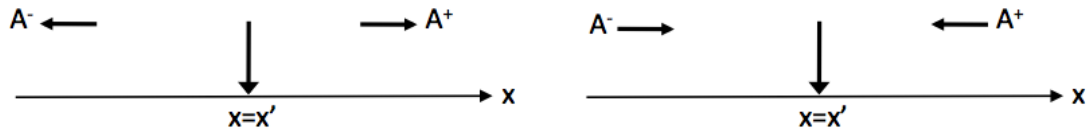


Fig. II.2. Illustration of the retarded (left) and advanced (right) Green's function for an infinite 1-D wire.

In this specific case, the Green's function can be obtained exactly. We can write:

$$\begin{aligned} G(x, x') &= A^+ e^{[ik(x-x')]} & x > x' \\ G(x, x') &= A^- e^{[-ik(x-x')]} & x < x' \end{aligned} \quad (\text{II.C.21})$$

where $k = \frac{(2m(E-V_0))^{1/2}}{\hbar}$. These solutions satisfy Eq. (II.C.19) at all positions $x \neq x'$, independently of the amplitudes A^+ and A^- . As appears from the situation defined in Fig. (II.2), we must define a continuity condition in order to satisfy Eq. (II.C.19) at the peculiar position $x = x'$:

$$[G(x, x')]_{x=x'+} = [G(x, x')]_{x=x'-} \quad (\text{II.C.22})$$

while the derivative must be discontinuous by $2m/\hbar^2$, leading to:

$$\left[\frac{\partial G(x, x')}{\partial x} \right]_{x=x'+} - \left[\frac{\partial G(x, x')}{\partial x} \right]_{x=x'-} = \frac{2m}{\hbar^2} \quad (\text{II.C.23})$$

Replacing the expression of $G(x, x')$ from Eq. (II.C.21) into Eq. (II.C.22) and (II.C.23), we obtain:

$$A^+ = A^- \quad \text{and} \quad ik[A^+ + A^-] = \frac{2m}{\hbar^2} \quad (\text{II.C.24})$$

giving:

$$A^+ = A^- = -\frac{i}{\hbar v} \quad \text{and} \quad v = \frac{\hbar k}{m} \quad (\text{II.C.25})$$

Thereby, the retarded $G^R(x, x')$ and advanced $G^A(x, x')$ Green's functions can be expressed as follows:

$$G^R(x, x') = -\frac{i}{\hbar v} \exp[ik|x - x'|] \quad (\text{II.C.26})$$

$$G^A(x, x') = +\frac{i}{\hbar v} \exp[-ik|x - x'|] \quad (\text{II.C.27})$$

where:

$$k = \frac{\sqrt{2m(E - V_0)}}{\hbar} \quad \text{and} \quad v = \frac{\hbar k}{m} \quad (\text{II.C.28})$$

These two formulations both satisfy Eq. (II.C.19) but correspond to two different situations: Eq. (II.C.26) describes retarded Green's functions corresponding to waves expanding from the excitation point x' , while Eq. (II.C.27) describes advanced Green's functions corresponding to waves expanding from a distant source towards position x' where they will disappear. In the following methodology we will use retarded Green's functions, that can be seen as the relative probability amplitude that a particle created at the position x' will reach position x . This corresponds for example to the case of a STM experiment, where electrons leave the tip to reach the sample molecule.

The addition of an infinitesimal imaginary part Γ ($\Gamma > 0$) to the energy enables to incorporate the boundary conditions into the equation itself and to define the function in the case of E is an eigenvalue of H . Thus, Eq. (II.C.19) involving the retarded function $G^R(x, x')$ becomes:

$$\left[E - V_0 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + i\Gamma \right] G^R(x, x') = \delta(x - x') \quad (\text{II.C.29})$$

and by considering the advanced function $G^A(x, x')$, we obtain:

$$\left[E - V_0 + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - i\Gamma \right] G^A(x, x') = \delta(x - x') \quad (\text{II.C.30})$$

The small imaginary part of the energy introduces a positive imaginary component to the wavenumber defined in Eq. (II.C.28), and makes the advanced function grow indefinitely as we move from the point of excitation. This makes the retarded Green's function the only acceptable solution, since an appropriate solution must be bounded. We can also write Eq. (II.C.29) in an alternative form in terms of the eigenfunctions and eigenvalues of the

Hamiltonian operator H of the system with $H|\Psi_\eta\rangle = \varepsilon_\eta|\Psi_\eta\rangle$ and $1 = |\Psi_\eta\rangle\langle\Psi_\eta|$ where $|\Psi_\eta\rangle$ denotes the orthonormal basis set of eigenvectors with energy ε_η , we obtain:

$$G^R(E) = \sum_{\eta} \frac{|\Psi_\eta\rangle\langle\Psi_\eta|}{E - \varepsilon_\eta + i\Gamma} \quad (\text{II.C.31})$$

We can notice that the knowledge of the Green's function operator $G(E)$ for all values of E of a Hamiltonian H is equivalent to the knowledge of a complete solution of the corresponding eigenvalue problem.

In addition, another property of the Green's function concerns the relation between the imaginary part of the Green's function and the density of states of the system. As we know, the density of states is a function of energy that measures the number of states available in a given energy range per unit length. The density per energy value ε is $\sum_{\eta} \delta(E - \varepsilon_\eta)$ where ε_η is an eigenvalue of the Hamiltonian. The DOS then is a product of this density per energy level and the corresponding wavefunction probability $|\Psi_\eta^2(x)|$:

$$\rho(x, E) = \sum_{\eta} \delta(E - \varepsilon_\eta) |\Psi_\eta^2(x)| \quad (\text{II.C.32})$$

Using the identity: $\lim_{y \rightarrow 0^+} \frac{1}{x \pm iy} = P\left(\frac{1}{x}\right) \mp i\pi\delta(x)$ where P denotes a Cauchy principle value, we can recast the retarded Green's function. Defining $x = E - \varepsilon_\eta$ and $y = \Gamma$ one arrives at:

$$G^R(x, x', E) = P \sum_{\eta} \frac{\Psi_\eta(x)\Psi_\eta^*(x')}{E - \varepsilon_\eta} - i\pi \sum_{\eta} \delta(E - \varepsilon_\eta) \Psi_\eta(x)\Psi_\eta^*(x') \quad (\text{II.C.33})$$

and therefore:

$$\rho(x) = -\frac{1}{\pi} \text{Im}[G^R(x, x', E)] \quad (\text{II.C.34})$$

This demonstrates the close link between Green's functions and the DOS.

Referring to the general equation (II.C.2), let us now consider the case where H_0 is the Hamiltonian of a problem for which the Green's functions are known, and V is an arbitrary single-particle perturbation. We want to express the Green's function of the full problem in terms of the unperturbed Green's functions. The retarded Green's functions $G_0(z)$ and $G(z)$ associated to H_0 and H , respectively are expressed as follows with $z = E + i\Gamma$:

$$G_0(z) = (z - H_0)^{-1} \quad \text{and} \quad G(z) = (z - H)^{-1} \quad (\text{II.C.35})$$

From Eq. (II.C.35), we can rewrite $G(z) = (z - H)^{-1}$ as follows:

$$\begin{aligned}
G(z) &= (z - H_0 - V)^{-1} = \{(z - H_0)[1 - (z - H_0)^{-1}V]\}^{-1} \\
G(z) &= [1 - (z - H_0)^{-1}V]^{-1}(z - H_0)^{-1} \\
G(z) &= [1 - G_0(z)V]^{-1}(G_0(z))
\end{aligned} \tag{II.C.36}$$

The expansion of $[1 - G_0(z)V]^{-1}$ in a power series leads to:

$$G(z) = G_0(z) + G_0(z)V G_0(z) + G_0(z)V G_0(z)V G_0(z) + \dots \tag{II.C.37}$$

and Eq. (II.C.37) can be expressed in a compact form, so that we get:

$$\begin{aligned}
G(z) &= G_0(z) + G_0(z)V[G_0(z) + G_0(z)V G_0(z) + \dots] \\
&= G_0(z) + G_0(z)V G(z)
\end{aligned} \tag{II.C.38}$$

or:

$$\begin{aligned}
G(z) &= G_0(z) + [G_0(z) + G_0(z)V G_0(z) + \dots]V G_0(z) \\
&= G_0(z) + G(z)V G_0(z)
\end{aligned} \tag{II.C.39}$$

The relationship between $G_0(z)$ and $G(z)$ shown in Eq. (II.C.38) and (II.C.39) is called the Lippmann-Schwinger equation for $G(z)$.

At this point we can introduce the so-called transition operator T playing an important role in scattering theory and which directly relates $G^R(z)$ and $G_0^R(z)$, as:

$$T(z) = V + V G(z) V \tag{II.C.40}$$

An important identity relating the operators T , G and G_0 is obtained by multiplying Eq. (II.C.40) on the left by G_0 :

$$G_0(z)T(z) = [G_0(z) + G_0(z)V G(z)]V = G(z)V \tag{II.C.41}$$

since according the Lippmann-Schwinger equation, $G(z) = G_0(z) + G_0(z)V G(z)$. Similarly, multiplying on the right we find that:

$$T(z)G_0(z) = V G(z) \tag{II.C.42}$$

This means that the knowledge of $T(z)$ implies the one of $G(z)$. As a first application of these identities we can get an expression of $G(z)$ in terms of $T(z)$. According to the Lippmann-Schwinger equation, we have: $G(z) = G_0(z) + G_0(z)V G(z)$, thus by replacing $V G(z)$ by $T(z)G_0(z)$, we find that:

$$G(z) = G_0(z) + G_0(z)T(z)G_0(z) \tag{II.C.43}$$

Eq.(II.C.40) gives $T(z)$ in terms of the unknown Green's operator $G(z)$. If we use the identity gives in Eq. (II.C.41) to replace $G(z)V$ by $G_0(z)T(z)$, we obtain the equation for $T(z)$ in terms of known operator $G_0(z)$:

$$T(z) = V + VG_0(z)T(z) \quad (\text{II.C.44})$$

This equation is known as the Lippmann-Schwinger equation for $T(z)$. The solution of this Lippmann-Schwinger equation, is often not simple to get, and one may need to resort to approximation methods. One approximation often used at weak potentials V or high energies is the Born approximation. To get the series, we iterate Eq. (II.C.44) to get in operator form, the Born series given by:

$$T(z) \approx V + VG_0(z)V + VG_0(z)VG_0(z)V + \dots \quad (\text{II.C.45})$$

Each term of this series takes into account different powers of the perturbation potential, and the series is expected to converge for weak potentials or high energies. To exemplify the latter case in atomic physics, we can consider in the case of an electron scattering that “high” corresponds to an energy larger than 10^3 eV, while for proton scattering in nuclear physics we consider a “high” energy is larger than 10^3 MeV. This series can be interpreted as a sequence of transition operators describing the interactions between the particle with a potential V , whose propagation evolves according to $(E - H_0 + i\Gamma)^{-1}$.

II.C.2. Elastic Scattering theory

As we have mentioned in the introduction, the IET signatures of the different molecular systems studied in this thesis have been simulated by using the QCME code^[39] that implements a generalized quantum chemical model for the elastic and inelastic transport in molecular junction. It is based on the Green’s function formalism developed in section II.C.1 and derives from previous works of Ratner and co-workers^[40]. In our simulation, each molecular device is divided into three parts: two electron reservoirs constituted by metallic atoms, called the source (S) and the drain (D), and the molecule connecting them (Fig. (II.3)). However, only a small part of the metallic atoms can be considered in the quantum chemistry calculations due to heavy computational costs. This approximation leads to the modeling of an ‘extended molecule’ for representing the scattering region but it has been proved to be sufficient for having an accurate description of the metal-molecule-metal interface interactions because only the metallic atoms that are close to the molecule contribute significantly to the coupling coefficients^[41]. Moreover, we also know that the main contribution to the IET response comes from the molecular part. Concerning our simulated devices, the metallic electrodes are characterized by a continuum of energy levels whereas the molecule has discrete levels, also called molecular orbitals. In

particular, one can distinguish between a set of filled levels (below the Fermi level) and a set of empty levels (above the Fermi level). Thereby, different levels of theory are applied for these two subsystems. The extended molecule is treated at the density functional theory (DFT) level while the electronic states of the source and the drain are described within the effective mass approximation^[42], which considers that the important excitations will occur nearby the extrema of the bands (i.e. at the minimum of the conduction band and at the maximum of the valence band). The electrons can flow when one molecular level is nearby the Fermi level. This is in general not the case since the lowest unoccupied molecular orbital (LUMO) is separated from the highest occupied molecular orbital (HOMO) by a gap of typically a few eV. However, under the application of a bias voltage (V), a change of the energy levels of the reservoirs with respect to the molecular levels occurs, allowing electron transfer. Indeed, the energy levels of the electrodes shift with respect to the Fermi energy while the molecular orbital levels remain at the same position and an energy window of width equal to eV opens. As soon as the first molecular orbital is included in this window, electrons tunnel from the source to the molecule and from the molecule to the drain.

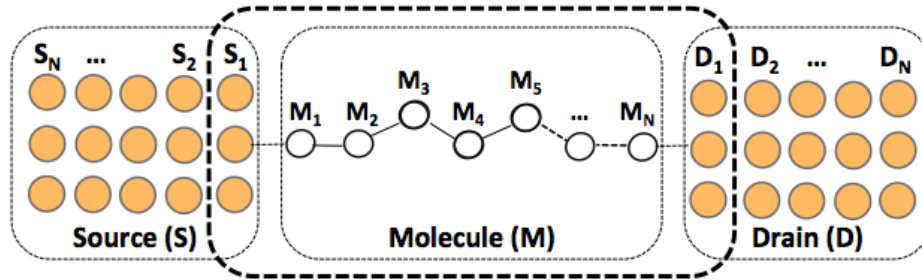


Fig. II.3. Illustration a molecular junction.

The Schrödinger equation of the whole system reads:

$$H|\Psi_\eta\rangle = \varepsilon_\eta|\Psi_\eta\rangle \quad (\text{II.C.46})$$

where H is the Hamiltonian of the system and is defined by:

$$H = H^{SS} + H^{MM} + H^{DD} + V$$

and can be also expressed in a matrix format as follows:

$$H = \begin{pmatrix} H^{SS} & V^{SM} & V^{SD} \\ V^{MS} & H^{MM} & V^{MD} \\ V^{DS} & V^{DM} & H^{DD} \end{pmatrix} \quad (\text{II.C.47})$$

where $H^{SS} + H^{MM} + H^{DD}$ is the Hamiltonian of the noninteracting subsystems S , M and D and V indicates the interaction potential. H^{SS} can be expressed in terms of the corresponding one-particle states (assumed orthonormal) as:

$$H^{SS} = \sum_i^S \varepsilon_i^{SS} |S_i\rangle\langle S_i| \quad (\text{II.C.48})$$

and we can define Ψ_η^S the wavefunction of the subsystem S as follows:

$$|\Psi_\eta^S\rangle = \sum_i^S c_{i,\eta}^S |S_i\rangle \quad (\text{II.C.49})$$

In the same way, we can express H^{DD} as:

$$H^{DD} = \sum_i^D \varepsilon_i^{DD} |D_i\rangle\langle D_i| \quad (\text{II.C.50})$$

with:

$$|\Psi_\eta^D\rangle = \sum_i^D c_{i,\eta}^D |D_i\rangle \quad (\text{II.C.51})$$

and

$$H^{MM} = \sum_i^M \varepsilon_i^{MM} |M_i\rangle\langle M_i| \quad (\text{II.C.52})$$

with:

$$|\Psi_\eta^M\rangle = \sum_i^M c_{i,\eta}^M |M_i\rangle \quad (\text{II.C.53})$$

The interaction energy term V is expressed as follows:

$$\begin{aligned} V = & \sum_{S,M} \sum_{\eta} V_{SM,\eta} |S_\eta\rangle\langle M_\eta| + \sum_{M,S} \sum_{\eta} V_{MS,\eta} |M_\eta\rangle\langle S_\eta| \\ & + \sum_{D,M'} \sum_{\eta} V_{DM',\eta} |D_\eta\rangle\langle M'_\eta| + \sum_{M',D} \sum_{\eta} V_{M'D,\eta} |M'_\eta\rangle\langle D_\eta| \\ & + \sum_{S,S'} \sum_{\eta} V_{SS',\eta} |S_\eta\rangle\langle S'_\eta| + \sum_{D,D'} \sum_{\eta} V_{DD',\eta} |D_\eta\rangle\langle D'_\eta| \end{aligned} \quad (\text{II.C.54})$$

where M and M' run over all the atomic sites of the molecular subsystem between M_1 and M_N which are the end sites making the contact with the Source and Drain reservoirs, as illustrated in Fig. (II.3). We can neglect the coupling between the source and the drain due to the distance separating them and due to the screening effect caused by the molecule.

As we have discussed in the previous section, the transition operator T defined as follows: $T = V + VG^0T = V + VGV$ is crucial for calculating the current density through molecular junctions since the square of the absolute value is proportional to the probability for an electron to go from one state to another. In Green's function theory, the transition

matrix element at energy level for an electron scattered from the initial states $|S_\eta\rangle$ of reservoir S to the final states $|D_\eta\rangle$ of reservoir D is defined as:

$$\begin{aligned} T_{DS,\eta} &= \sum_S \sum_D \langle D_\eta | T | S_\eta \rangle \\ &= \sum_S \sum_D \langle D_\eta | V | S_\eta \rangle + \sum_S \sum_D \langle D_\eta | V G V | S_\eta \rangle \end{aligned} \quad (\text{II.C.55})$$

where the first term can be neglected since there is no direct coupling between the Drain and Source reservoirs. By replacing the interaction term V from Eq. (II.C.54) into Eq. (II.C.55) we can write this transition operator as:

$$T_{DS,\eta} = \sum_S \sum_D \sum_{M,M'} V_{DM',\eta} g_{M'M}^\eta V_{MS,\eta} \quad (\text{II.C.56})$$

where $V_{DM',\eta}$ ($V_{MS,\eta}$) refers to the coupling energy between Drain layers (Source layers) and the atomic sites of the molecule, and can be calculated as:

$$\begin{aligned} V_{DM',\eta} &= \sum_{i=1}^{\in D} \sum_{j=1}^{\in M'} c_{i\eta}^D c_{j\eta}^{M'} \langle \chi_i^D | V | \chi_j^{M'} \rangle \\ V_{MS,\eta} &= \sum_{i=1}^{\in M} \sum_{j=1}^{\in S} c_{i\eta}^M c_{j\eta}^S \langle \chi_i^M | V | \chi_j^S \rangle \end{aligned} \quad (\text{II.C.57})$$

In our quantum chemistry calculations, only a small number of gold atoms can be considered for describing the metallic electrodes as it has been shown that one layer of atoms is sufficient to get accurate transport properties^[41]. Therefore we define one extended molecule as the junction of the molecular system and the first layer of the Source (Drain) denoted S_1 (D_1), as illustrated in Fig. (II.3). Indeed, as the coupling energy between the molecule and the electrodes decreases with the interatomic distance, one can assume that the gold atoms that are not part of the first layer *i.e.* atoms not directly connected to the molecule, will contribute little to the electron tunneling process. $g_{M'M}^\eta$ refers to the Green's function describing the carrier-conduction contribution which is defined for a given scattering channel ε_ξ :

$$g_{M'M}^\eta = \sum_\xi \frac{\langle M'_\eta | \Psi_\xi \rangle \langle \Psi_\xi | M_\eta \rangle}{z_\eta - \varepsilon_\xi} = \sum_\xi \frac{\langle M'_\eta | \Psi_\xi \rangle \langle \Psi_\xi | M_\eta \rangle}{(E_\eta - \varepsilon_\xi) + i\Gamma_\eta} \quad (\text{II.C.58})$$

where the parameter z_η is a complex variable: $z_\eta = E_\eta + i\Gamma_\eta$, E_η being equal to the energy of the tunneling electron. For an elastic scattering process it is equal to the energy when it enters the scattering region from the source and when the drain collects it. Γ_η refers to the level broadening of the energy state Ψ_η and can be defined thanks to the Fermi golden rule, as follows:

$$\Gamma_\eta = \pi n^S(E_f) V_{DM'}^2 |\langle M'_\eta | \Psi_\eta \rangle|^2 + \pi n^D(E_f) V_{MS}^2 |\langle \Psi_\eta | M_\eta \rangle|^2 \quad (\text{II.C.59})$$

To explain this broadening we can consider a scattering channel constituted of molecular orbitals which are characterized by discrete energy levels as long as it remains isolated. When coupling this channel to the source and drain contacts which have a continuous distribution of states, the initial sharp density of states of the channel will broaden into a more diffuse structure. Such broadening occurs because of the overlap between energy-fixed molecular states and contact states covering wide energy ranges.

From Eq. (II.C.56), the transition intensity can be expressed as follows:

$$T = |T|^2 = \left| \sum_\eta T_{DS,\eta} \right|^2 \quad (\text{II.C.60})$$

II.C.3. Inelastic Scattering theory

As mentioned previously, under the application of a bias voltage, electrons can migrate from the source to the drain inelastically by inducing vibrational excitations in the molecule provided the bias voltage matches a vibrational transition energy. This inelastic process leads to changes of the current-voltage I-V characteristics that are taken into account with the introduction of a new term in the Hamiltonian. In the adiabatic Born-Oppenheimer approximation, the electronic Hamiltonian of the whole molecular system can be considered to depend parametrically on the vibrational normal modes Q and the Schrödinger equation becomes:

$$H(Q, \vec{r}) |\Psi_\eta(Q, \vec{r})\rangle |\theta_v(Q)\rangle = \left[\varepsilon_\eta + \sum_k \hbar \omega_k \left(n_k^v + \frac{1}{2} \right) \right] |\Psi_\eta(Q, \vec{r})\rangle |\theta_v(Q)\rangle \quad (\text{II.C.61})$$

where $\Psi_\eta(Q, \vec{r})$ and $\theta_v(Q)$ represent the electronic and vibrational wavefunctions, respectively. ε_η refers to the energy of the eigenstate $|\Psi_\eta\rangle$, $\hbar \omega_k$ is equal to the frequency of k^{th} vibrational normal mode Q_k and n_k^v is the quantum number associated to the k^{th} normal mode for the v state. Note that the vibrational index v implicitly depends on the

electronic state η . The nuclear-motion-dependent wavefunction can be expanded in a power series of the vibrational normal mode, such as:

$$|\Psi_\eta(Q, \vec{r})\rangle = \left| (\Psi_\eta)_{Q=0} + \sum_k \left(\frac{\partial \Psi_\eta(Q, \vec{r})}{\partial Q_k} \right)_{Q=0} Q_k + \dots \right| \quad (\text{II.C.62})$$

We will only conserve the first derivative $\frac{\partial \Psi_\eta(Q, \vec{r})}{\partial Q_k}$ in this expansion since we only consider the electronic off-resonant case and adopt the harmonic approximation. The carrier-contribution $g_{M'M}^{\eta,v}$ expressed in Eq. (II.C.58) becomes:

$$g_{M'M}^{\eta,v} = \sum_\xi \sum_{v'} \frac{\langle \theta_v(Q) | \langle M'_\eta(Q, \vec{r}) | \Psi_\xi(Q, \vec{r}) \rangle | \theta_{v'}(Q) \rangle \langle \theta_{v'}(Q) | \langle \Psi_\xi(Q, \vec{r}) | M_\eta(Q, \vec{r}) \rangle | \theta_v(Q) \rangle}{z_{\eta v} - \varepsilon_{\xi v'}} \quad (\text{II.C.63})$$

where $z_{\eta v} = E_\eta + i\Gamma_\eta + \sum_k \hbar\omega_k \left(n_k^v + \frac{1}{2} \right)$. In the following, we consider that $\theta_0(Q)$ refers to the vibrational ground state ($v = 0$) since most of the IET experiments are performed at low temperatures, and $\theta_1(Q)$ refers to the first excited vibrational state ($v' = 1$). The numerator of Eq. (II.C.63) is decomposed into two terms:

$$\langle \theta_0(Q) | \langle M'_\eta(Q, \vec{r}) | \Psi_\xi(Q, \vec{r}) \rangle | \theta_1(Q) \rangle \text{ and } \langle \theta_1(Q) | \langle \Psi_\xi(Q, \vec{r}) | M_\eta(Q, \vec{r}) \rangle | \theta_0(Q) \rangle$$

To evaluate the first term of Eq. (II.C.63), the following substitutions are carried out:

$$\langle M'_\eta(Q, \vec{r}) | = \left\langle M'_{\eta, Q=0} + \sum_k \left(\frac{\partial M'_\eta}{\partial Q_k} \right)_{Q=0} Q_k \right|$$

and

$$|\Psi_\xi(Q, \vec{r})\rangle = \left| \Psi_{\xi, Q=0} + \sum_k \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} Q_k \right|$$

so that we obtain:

$$\begin{aligned} & \left\langle \theta_0(Q) \left| \left\langle M'_{\eta, Q=0} + \sum_k \left(\frac{\partial M'_\eta}{\partial Q_k} \right)_{Q=0} Q_k \right| \Psi_{\xi, Q=0} + \sum_k \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} Q_k \right| \theta_1(Q) \right\rangle = \\ & \langle \theta_0(Q) | \theta_1(Q) \rangle \langle M'_{\eta, Q=0} | \Psi_{\xi, Q=0} \rangle + \left\langle M'_{\eta, Q=0} \left| \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} \right\rangle Q_{k,01} \right. \\ & + \left\langle \left(\frac{\partial M'_\eta}{\partial Q_k} \right)_{Q=0} \left| \Psi_{\xi, Q=0} \right\rangle Q_{k,01} + \left\langle \theta_0(Q) \left| \left(\frac{\partial M'_\eta}{\partial Q_k} \right)_{Q=0} \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} \right| \theta_1(Q) \right\rangle \end{aligned} \quad (\text{II.C.64})$$

with:

$$Q_{k,01} = \langle \theta_0(Q) | Q_k | \theta_1(Q) \rangle = \sqrt{\hbar/2\omega_k} \quad (\text{II.C.65})$$

$$\langle \theta_0(Q) | \theta_1(Q) \rangle \langle M'_{\eta, Q=0} | \Psi_{\xi, Q=0} \rangle = 0 \quad (\text{II.C.66})$$

$$\left\langle \theta_0(Q) \left| \left\langle \left(\frac{\partial M'_{\eta}}{\partial Q_k} \right)_{Q=0} \left| \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} \right\rangle \right| \theta_1(Q) \right\rangle = 0 \quad (\text{II.C.67})$$

Here we consider that the term $\left\langle \left(\frac{\partial M'_{\eta}}{\partial Q_k} \right)_{Q=0} \left| \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} \right\rangle$ presents a very small amplitude and so can be neglected. It leads to:

$$\begin{aligned} \langle \theta_0(Q) | \langle M'_{\eta}(Q, \vec{r}) | \Psi_{\xi}(Q, \vec{r}) | \theta_1(Q) \rangle = \\ \sqrt{\frac{\hbar}{2\omega_k}} \left[\left\langle M'_{\eta, Q=0} \left| \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} \right\rangle + \left\langle \left(\frac{\partial M'_{\eta}}{\partial Q_k} \right)_{Q=0} \left| \Psi_{\xi, Q=0} \right\rangle \right] \end{aligned} \quad (\text{II.C.68})$$

In the same way the calculation of the second term of the numerator of Eq. (II.C.63):

$$\langle \theta_1(Q) | \langle \Psi_{\xi}(Q, \vec{r}) | M_{\eta}(Q, \vec{r}) | \theta_0(Q) \rangle$$

By replacing:

$$\langle \Psi_{\xi}(Q, \vec{r}) | = \left\langle \Psi_{\xi, Q=0} + \sum_k \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} Q_k \right|$$

and:

$$|M_{\eta}(Q, \vec{r})\rangle = \left| M_{\eta, Q=0} + \sum_k \left(\frac{\partial M_{\eta}}{\partial Q_k} \right)_{Q=0} Q_k \right\rangle$$

We obtain:

$$\begin{aligned} \left\langle \theta_1(Q) \left| \left\langle \Psi_{\xi, Q=0} + \sum_k \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} Q_k \right| M_{\eta, Q=0} + \sum_k \left(\frac{\partial M_{\eta}}{\partial Q_k} \right)_{Q=0} Q_k \right\rangle \right| \theta_0(Q) \right\rangle = \\ \langle \theta_1(Q) | \theta_0(Q) \rangle \langle \Psi_{\xi, Q=0} | M_{\eta, Q=0} \rangle + \left\langle \Psi_{\xi, Q=0} \left| \left(\frac{\partial M_{\eta}}{\partial Q_k} \right)_{Q=0} \right\rangle Q_{k,10} \right. \\ \left. + \left\langle \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} \left| M_{\eta, Q=0} \right\rangle Q_{k,10} + \left\langle \theta_1(Q) \left| \left\langle \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} \left| \left(\frac{\partial M_{\eta}}{\partial Q_k} \right)_{Q=0} \right\rangle \right| \theta_0(Q) \right\rangle \right. \end{aligned} \quad (\text{II.C.69})$$

with:

$$Q_{k,10} = \langle \theta_1(Q) | Q_k | \theta_0(Q) \rangle = \sqrt{\hbar/2\omega_k} \quad (\text{II.C.70})$$

$$\langle \theta_1(Q) | \theta_0(Q) \rangle \langle \Psi_{\xi, Q=0} | M_{\eta, Q=0} \rangle = 0 \quad (\text{II.C.71})$$

$$\left\langle \theta_1(Q) \left| \left\langle \left(\frac{\partial \Psi_{\xi}}{\partial Q_k} \right)_{Q=0} \left| \left(\frac{\partial M_{\eta}}{\partial Q_k} \right)_{Q=0} \right\rangle \right| \theta_0(Q) \right\rangle = 0 \quad (\text{II.C.72})$$

At the end, we obtain:

$$\langle \theta_1(Q) | \langle \Psi_\xi(Q, \vec{r}) | M_\eta(Q, \vec{r}) | \theta_0(Q) \rangle = \sqrt{\frac{\hbar}{2\omega_k}} \left[\left\langle \Psi_{\xi, Q=0} \left| \left(\frac{\partial M_\eta}{\partial Q_k} \right)_{Q=0} \right\rangle + \left\langle \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} \left| M_{\eta, Q=0} \right\rangle \right] \quad (\text{II.C.73})$$

Finally, the numerator of Eq. (II.C.63) considering the vibrational ground state ($v = 0$ and $v' = 1$) can be written to describe the inelastic contribution in the form:

$$\begin{aligned} & \langle \theta_0(Q) | \langle M'_\eta(Q, \vec{r}) | \Psi_\xi(Q, \vec{r}) | \theta_1(Q) \rangle \langle \theta_1(Q) | \langle \Psi_\xi(Q, \vec{r}) | M_\eta(Q, \vec{r}) | \theta_0(Q) \rangle \\ &= \frac{\hbar}{2\omega_k} (A + B) \times (C + D) \end{aligned} \quad (\text{II.C.74})$$

with:

$$(A + B) = \left\langle M'_{\eta, Q=0} \left| \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} \right\rangle + \left\langle \left(\frac{\partial M'_\eta}{\partial Q_k} \right)_{Q=0} \left| \Psi_{\xi, Q=0} \right\rangle \quad (\text{II.C.75})$$

and:

$$(C + D) = \left\langle \Psi_{\xi, Q=0} \left| \left(\frac{\partial M_\eta}{\partial Q_k} \right)_{Q=0} \right\rangle + \left\langle \left(\frac{\partial \Psi_\xi}{\partial Q_k} \right)_{Q=0} \left| M_{\eta, Q=0} \right\rangle \quad (\text{II.C.76})$$

By applying the same procedure, we obtain for the elastic contribution (with $v = 0$ and $v' = 0$):

$$\begin{aligned} & \langle \theta_0(Q) | \langle M'_\eta(Q, \vec{r}) | \Psi_\xi(Q, \vec{r}) | \theta_0(Q) \rangle \langle \theta_0(Q) | \langle \Psi_\xi(Q, \vec{r}) | M_\eta(Q, \vec{r}) | \theta_0(Q) \rangle \\ &= \langle M'_{\eta, Q=0} | \Psi_{\xi, Q=0} \rangle \langle \Psi_{\xi, Q=0} | M_{\eta, Q=0} \rangle \end{aligned} \quad (\text{II.C.77})$$

Looking at Eq. (II.C.63) above, we can now interpret the different terms as follows: the terms in Eq. (II.C.77) provide the elastic contribution and the other terms of Eq. (II.C.75) and (II.C.76) contribute to the inelastic parts associated to the exchange energy between the electron and the vibrational mode. In the off-resonance regime the inelastic terms directly depend on the vibronic excited states contributions. This means that the current can be decomposed into two parts: the elastic (I_{el}) and inelastic (I_{inel}) as: $I = I_{el} + I_{inel}$. Practically, only a small fraction of the tunnelling electrons (the cross-section for such an excitation is very small due to the short traversal time of the electrons compared to the typical oscillation period of the molecular vibrations) contribute to the inelastic-tunneling process. The

conductance change induced by the electron-vibronic coupling will then be very small, what forces us to rely on second derivative measurements d^2I/dV^2 to really detect them. Sketching d^2I/dV^2 vs. V will represent the IET spectra obtained in our simulations.

The task of a theory of scanning tunnelling microscopy is to calculate the current flowing from the tip to the sample surface or vice versa depending on the applied voltage. In a single-particle picture this can be viewed as a scattering process where an electron incident from the interior of the tip metal scatters from the barrier and has certain probability of penetrating into the sample surface. The transition probability per unit time from initial state $|i\rangle$ to final state $|f\rangle$, under the application of a perturbation V is given by:^[43]

$$\frac{2\pi}{\hbar} |T_{fi}|^2 \rho(E_f) \quad (\text{II.C.78})$$

where $\rho(E_f)$ refers to the density of final states, and $T_{fi} = \langle f|T|i\rangle$, and T is the transition operator described in the previous section. The current from initial state $|i\rangle$ to final state $|f\rangle$ is expressed as follows:

$$i = \frac{2\pi e}{\hbar} \sum_{i,f} |T_{fi}|^2 f(E_i) [1 - f(E_f)] \delta(E_i - E_f) \quad (\text{II.C.79})$$

where $f(E)$ is the Fermi function given by: $f(E) = \frac{1}{e^{[(E-E_F)/k_B T]} + 1}$ and the sum runs over the states of the reservoirs. The delta function δ describes the conservation of energy for the case of an elastic tunneling process, while the initial and final particles are respectively populated with the equilibrium distribution function $f(E_i)$ and $f(E_f)$. The total current defined as the sum of all partial currents from left to right states and vice versa is:

$$i = \frac{2\pi e}{\hbar} \sum_{i,f} |T_{fi}|^2 [f(E_i) - f(E_f)] \delta(E_f - E_i) \quad (\text{II.C.80})$$

This expression is the simplest version of the so-called Landauer formula and highlights the relationship between the current and the transition probability.

Electron transport through a molecular wire can often be considered as a one-dimensional process. In this case the current is defined as:^[44]

$$\begin{aligned} i &= \frac{2\pi e}{\hbar} \sum_{i,f} |T_{fi}|^2 [f(E_i - eV) - f(E_f)] \delta(E_f - E_i) \\ &= \frac{2\pi e}{\hbar} \int_0^\infty |T(E, V)|^2 [f(E - eV) - f(E)] n^S(E) n^D(E) dE \end{aligned} \quad (\text{II.C.81})$$

where $n^S(E)$ and $n^D(E)$ refer to the density of states of the source and drain reservoirs, respectively. However, the metal electrodes can have different dimensionalities depending

on the geometrical and electronic structures of the electrodes (1D: molecular wire, 2D: metal film). Wang et al.^[45] have evaluated the effect of the dimensionalities of the energy distribution of metal contacts on the I-V characteristics of a model system constituted by a 1,4-benzene-dithiolate embedded between two gold electrodes. It has been shown that they have a strong effect on the shape of the conductance curves and the best agreement with the experimental measurements is found when considering a three-dimensional energy distribution to evaluate the current flowing from the source to the drain, and this model will be adopted in our simulations.

We assume that the molecule is aligned along the z direction, which corresponds also to the direction of current transport. In a three-dimensional energy system, when energies in both x and y directions are continuous, the current density is evaluated as follows.^[45,46]

$$i^{3D} = \frac{2\pi em^* k_B T}{\hbar^3} \int_0^\infty \ln \left\{ \frac{1 + \exp[(E_F + eV - E_z)/k_B T]}{1 + \exp[(E_F - E_z)/k_B T]} \right\} \times |T(E_z, V)|^2 n^S(E_z) n^D(E_z) dE_z \quad (\text{II.C.82})$$

The total conduction current is $I_{3D} = A i_{3D}$ where A corresponds to the effective injection area, and $A \approx \pi r_{3s}^2$. Here, r_{3s}^2 is associated to the radius of the sphere whose volume is equal to the one per conduction electron and is equal to: $r_{3s}^2 = [3/(4\pi N_{3D})]^{1/3}$ and the density of electron is defined as: $N_{3D} = (2m^* E_F)^{3/2} / (3\hbar^3 \pi^2)$. We can mention that the effective mass gives a convenient way to describe the motion of band electrons subjected to an external force. The electrons can therefore be treated as if they were free but with an effective mass which contains all of the necessary information about the way in which the electron's motion is modified by the lattice potential through which it moves.

To summarize, the simulation of an IET spectrum involves different steps, as sketched in Fig. (II.4). First, at the DFT level, the optimization of the geometrical structure is performed, and therefore the characteristics of the frontier orbitals are obtained. Then, at the same level of approximation, the vibrational frequencies of the extended molecule as well as the first-order derivatives of the wavefunction with respect to the normal mode coordinates are calculated. All these quantum chemical calculations are performed with the Gaussian 09 package^[47]. From these molecular properties, the IET spectrum ($\partial^2 I / \partial V^2$) is then simulated for a given temperature by using the QCME code. This latter evaluates the current intensity I in the molecular junction, *i.e.* from the source to the drain electrode for a voltage V , as expressed in Eq. (II.C.82). This evaluation requires the calculation of the

molecule-electrode couplings written in Eq. (II.C.57) and of the transition probability for an electron to go from an initial state in the source electrode to a final state in the drain electrode, as defined in Eqs. (II.C.56) and (II.C.60).

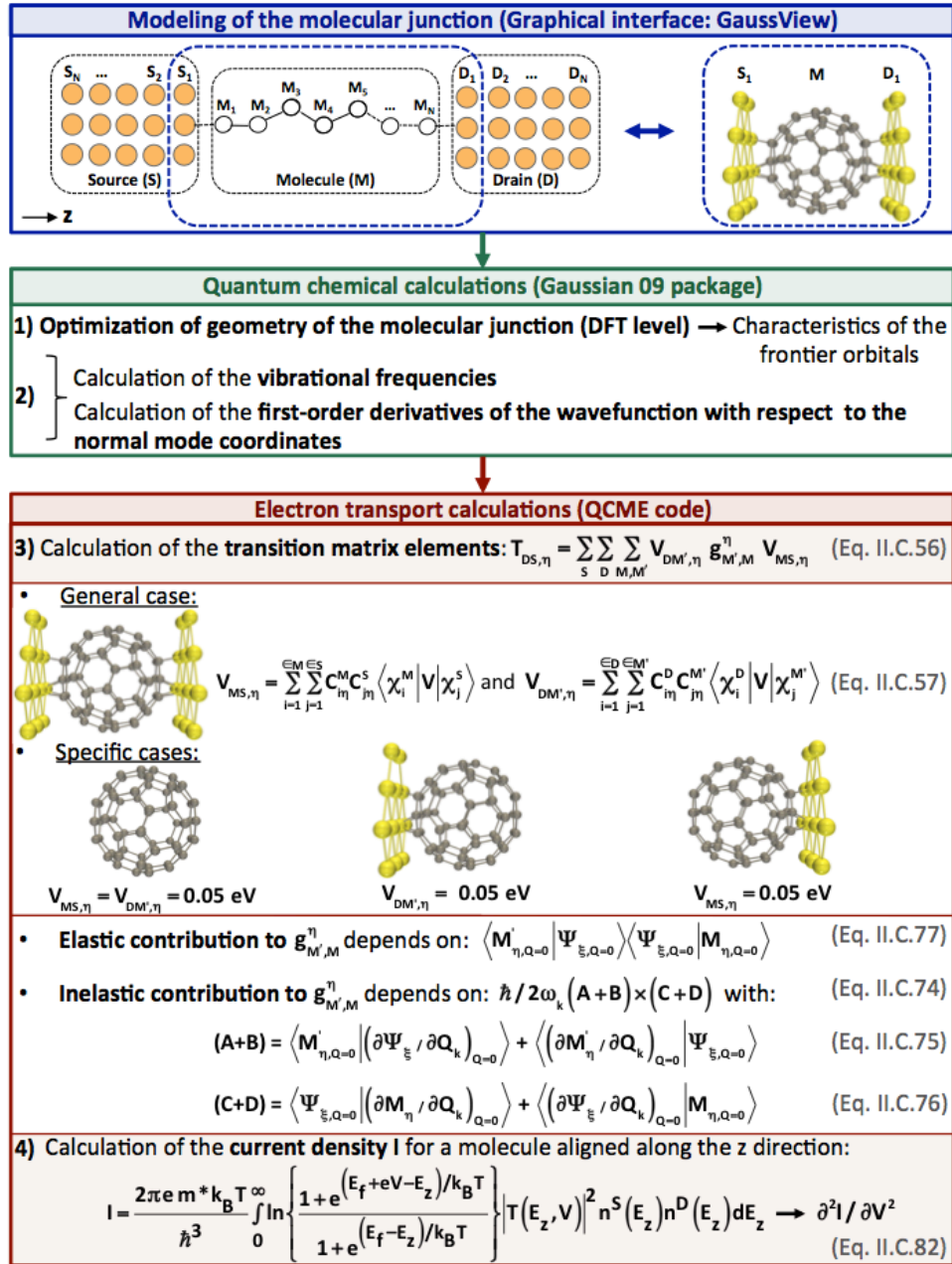


Fig. II.4. Schematic representation of the different steps involved in the simulation of an IET spectrum.

II.D. References

- [1] Koch, W.; Holthausen, M. *A chemist's Guide to Density Functional Theory*, Wiley-VCH, 2001.
- [2] Cramer, C.J. *Essentials of Computational Chemistry, Theories and Models*, Wiley, second edition, 2004.
- [3] Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864-871.
- [4] Kohn, W.; Sham, L.J. *Phys. Rev. A* **1965**, *140*, 1133-1138.
- [5] Dirac, P. *Proc. Cambridge Philos. Soc.* **1930**, *26*, 376-385.
- [6] Scuseria, G.E.; Staroverov, V.N. in *Theory and Applications of Computational Chemistry: The First 40 Years (A Volume of Technical and Historical Perspectives)* (Elsevier, Amsterdam) 669-724, 2005.
- [7] Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200-1211.
- [8] Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23*, 5048-5079.
- [9] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.
- [10] Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1986**, *33*, 8800.
- [11] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822-8824.
- [12] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- [13] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
- [14] Perdew, J. P. in *Electronic Structure of Solids '91*, Ed. P. Ziesche and H. Eschrig (Akademie Verlag, Berlin) 11-20, 1991.
- [15] Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- [16] Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040-1046.
- [17] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- [18] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623-11627.
- [19] Hamprech, F. A.; Cohen, A.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264-6271.

- [20] Staroverov, V. N.; Scuseria, G. E.; Tao J.; Perdew J. P. *J. Chem. Phys.* **2003**, *119*, 12129-12137.
- [21] Dreuw, A.; Weisman, J. L.; Head-Gordon, M. *J. Chem. Phys.* **2003**, *119*, 2943.
- [22] (a) McDowell, S. A. C.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1995**, *235*, 4. (b) Champagne, B.; Perpète, E. A.; van Gisbergen, S. J. A.; Baerends, E.-J.; Snijders, J. G.; *J. Chem. Phys.* **1998**, *109*, 10489.
- [23] (a) Leininger, T.; Stoll, H.; Werner, H.-J.; Savin, A. *Chem. Phys. Lett.* **1997**, *275*, 151; (b) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, *115*, 3540.
- [24] Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51-57.
- [25] Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, *128*, 084106.
- [26] (a) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69. (b) Hall, G. G. *Proc. R. Soc. Lond. A* **1951**, *205*, 541-552.
- [27] (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- [28] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- [29] (a) Almlöf, J.; Taylor, P. R. *J. Chem. Phys.* **1987**, *86*, 4070. (b) Almlöf, J.; Taylor, P. R. *Adv. Quantum Chem.* **1991**, *22*, 301.
- [30] Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- [31] (a) Desclaux, J. P.; Kim, Y. K. *J. Phys. B: At. Mol. Phys.* **1975**, *8*, 1177. (b) Pyykkö, P. *Adv. Quantum Chem.* **1978**, *11*, 353. (c) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271 (d) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276. (e) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (f) Schwarz, W. H. E. *Fundamentals of relativistic effects in chemistry*, Springer, Berlin, 1990. (g) Christoffersen, R. E.; Hall, G. G. *Theor. Chim. Acta* **1996**, *4*, 250 (h) Pyykkö, P. *Annu. Rev. Phys. Chem.* **2012**, *63*, 45-64.
- [32] Dolg, M. *Theor. Chim. Acta*, **1996**, *93*, 141.
- [33] (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
- [34] Phillips, J. C., Kleinman, L. *Phys. Rev.* **1959**, *116*, 287.
- [35] (a) Durand, P.; Barthelat, J. C.; *Theor. Chim. Acta*. **1975**, *38*, 283. (b) Lee, Y. S.; Ermiler, W. C.; Pitzer, K. S. *J. Chem. Phys.* **1977**, *67*, 5861.
- [36] Christiansen, P. A.; Lee, Y. S.; Pitzer, K. S. *J. Chem. Phys.* **1979**, *71*, 4445.

- [37] Teichteil, C.; Malrieu, J. P.; Barthelat, J. C. *Molec. Phys.* **1977**, *33*, 181.
- [38] Economou, E. N. *Green's Functions in Quantum Physics*, Springer, Berlin, 1990 ; (b) Taylor J. R. *Scattering Theory*, Wiley, New York, 1972. (c) Datta, S. *Electronic transport in mesoscopic systems*, Cambridge university press, 1995.
- [39] Jiang, J.; Wang, C. K.; Luo, Y. 2006, *Quantum Chemistry for Molecular Electronics* (QCME-V1.1), Royal Institute of Technology, Sweden.
- [40] Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 6849.
- [41] Evers, F.; Weigend, F.; Koentopp, M. *Phys. Rev. B* **2004**, *69*, 235411.
- [42] Sham, L. J. Nakayama, M. *Phys. Rev B* **1979**, *20*, 734.
- [43] Davydov, A. S. *Quantum Mechanics*, NEO press, Ann. Arbor, 1966.
- [44] Tersoff, J.; Hamann, D. R. *Phys. Rev. B* **1985**, *31*, 805.
- [45] Wang, C-K.; Luo. Y. *J. Chem. Phys.* **2003**, *119*, 4923
- [46] Duke, C. B. *Tunneling in Solids*, Academic Press, Inc., New York, 1969.
- [47] Frisch, M. J et al. Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

Effects of the Basis Set and of the Exchange-Correlation Functional on the Inelastic Electron Tunneling Signatures of 1,4-benzenedithiol

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III. Effects of the Basis Set and of the Exchange-Correlation Functional on the Inelastic Electron Tunneling Signatures of 1,4-benzenedithiol.

III.A. Introduction

As we have mentioned in introduction Inelastic Electron Tunneling (IET) Spectroscopy is a recent technique to probe the structure and properties of molecules adsorbed on metallic surfaces or between metallic electrodes^[1]. Provided the applied voltage is high enough to excite a molecular vibration, IET appears in electron transport experiments through molecular junctions in addition to the dominating elastic processes. Since IET highlights vibrational transitions of molecules, it can be used to analyze the molecular properties, including its changes due to interactions with the metal. The experimental measurements are often accompanied by quantum mechanical modeling to help unraveling the junction properties^[2].

Like for simulating and interpreting more traditional vibrational signatures (IR, Raman, hyper-Raman, VCD, VROA, resonant Raman)^[3], these modeling rely on successive approximations to make the calculations feasible while accounting for the dominant physico-chemical phenomena. In the case of IET, the approximations concern i) the description of the metallic electrodes, ii) the theory of inelastic scattering, iii) the anharmonicity of the potential energy hypersurface, and iv) the level of approximation adopted to determine the electronic wavefunctions and/or the electron densities. In this paper, we focus on the last point by simulating and analyzing the IET signatures of a model system, 1,4-benzenedithiol, at different levels of theory, namely with several atomic basis sets and with different exchange-correlation (XC) functionals. Those include hybrid XC functionals and long-range corrected (LC) functionals. In addition, we also concentrate on the IR spectra and on the impact of the level of approximation on the IR intensities, allowing us to make a comparison between the two techniques and their specificities with respect to the level of calculation.

III.B. Theoretical and Computational Methods

Following the procedure described in Section II.C, the simulation of the IET spectrum of the 1,4-benzenedithiol has been performed by considering the isolated molecule weakly coupled to fictive electrodes. In this model, the coupling between the molecule and the electrodes is defined as a constant parameter set to 0.05 eV, and the temperature is fixed to 4.2 K.

In order to describe the electronic densities and the wavefunctions, atomic basis sets of various types and sizes were selected. Since it is broadly used in computational vibrational spectroscopy, the first basis set is the split-valence double- ζ 6-31G(d) basis set^[4]. Then, to assess basis set convergence, we employed the Dunning's correlation consistent valence-polarized basis sets^[5] optimized for a better description of the electron correlation effects: cc-pVDZ, cc-pVTZ, and cc-pVQZ, aug-cc-pVDZ and aug-cc-pVTZ basis sets. The third type consists in pseudo potential basis sets^[6] (LANL2DZ and LANL2DZdp), where the core (inner) orbitals are described by an effective potential and the valence orbitals are described as contractions of Gaussian functions. Here these are double- ζ contractions with (LANL2DZdp) or without (LANL2DZ) p and d polarization functions.

The electronic structures were determined using density functional theory (DFT) in combination with a range of XC functionals. These include hybrid functionals, i.e. B3LYP^[7], B3P86^[7a,7c,8], B971^[9] and TPSSH^[10]. The second set of XC functionals includes range-separated hybrids also called long-range corrected XC functionals, such as the LC-BLYP^[11], CAM-B3LYP^[12] and ω B97x^[13] functionals.

In order to compare results obtained at different levels of approximation, the overlaps between the IET active vibrational modes are evaluated. For a fragment (molecule) F , the $O_{p'p}^{AB,F}$ overlap between mode p' of method A and mode p of method B is defined as the square of the scalar product between the two normal modes:

$$O_{p'p}^{AB,F} = \left\langle Q_{p'}^{A,F} \middle| Q_p^{B,F} \right\rangle^2 = \left(\sum_{i\alpha}^F Q_{i\alpha,p'}^A Q_{i\alpha,p}^B \right)^2$$

$Q_{i\alpha,p}$ is the mass-weighted Cartesian displacement of atom i in direction α for the p^{th} normal mode. Each Q_p is normalized so that $\sum_{i\alpha}^{3N} (Q_{i\alpha,p})^2 = 1$. This quantity is dimensionless and its value ranges from 0 (*i.e.* the two modes are totally different) to 1 (*i.e.* the two modes are identical). This analysis is carried out using the PyVib2 program^[14].

III.C Results and Discussion

III.C.1. Effect of the basis set

In this section, we analyze the impact of the basis set on the IET response using the B3LYP exchange-correlation functional. The choice of this hybrid functional is justified by the fact that it predicts (quantitatively) very well the relative IR and Raman activities in small and also medium-size molecules^[15]. Fig. (III.1) reports the IET spectra of 1,4-benzenedithiol with several basis sets.

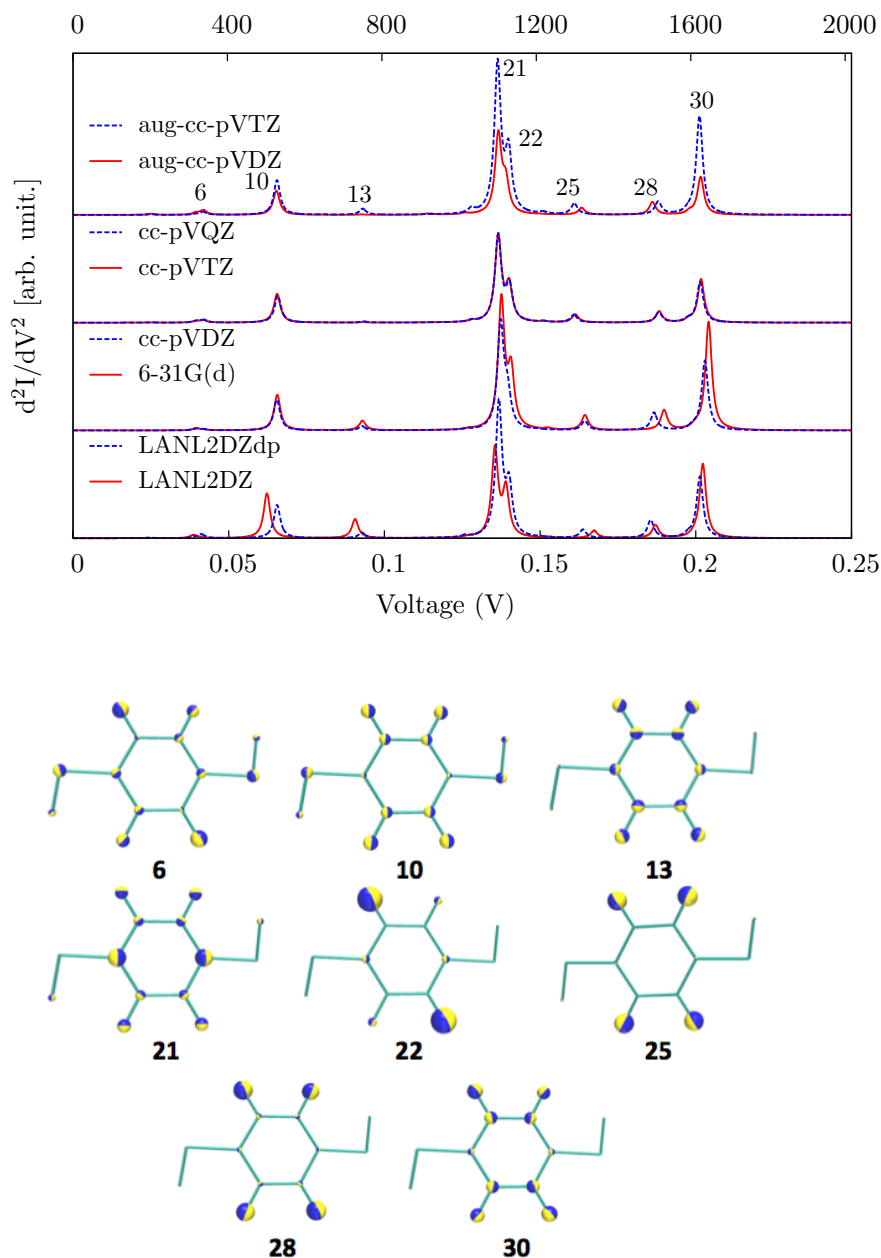


Fig. III.1. (top) IET spectrum of the 1,4-benzenedithiol calculated at the B3LYP level with different basis sets; (bottom) Representation of the numbered vibrational modes corresponding to the most intense peaks of the IET spectrum. The direction of an atomic displacement is given by the line joining the two poles of distinct colors and its amplitude is proportional to the radius of the sphere. The sum of the surfaces of the spheres is always constant. The FWHM is set to 20 cm^{-1} .

For all basis sets, the IET spectrum of the 1,4-benzenedithiol is composed of 8 major vibrational signatures. The most intense (**10**, **21**, **22**, and **30**) correspond to longitudinal motions and more precisely by in-plane C=C stretchings. In these modes, the atoms move in the same direction as the tunneling current. These vibrations are coupled to the frontier orbitals along the main tunneling path and thereby lead to an important IET activity^[1a,1d,16]. The other peaks are associated with in-plane bendings of the 4 C-H bonds of the phenyl ring and correspond to modes **6**, **13**, **25** and **28**. Table (III.1) reports the number, transition potential (V) (corresponding to the frequency of a vibrational transition), and IET intensity values (arb. unit) of the vibrational modes dominating the IET spectrum of 1,4-benzenedithiol calculated with the different basis sets. Note that a peak appearing at a potential of 0.1 V corresponds to a wavenumber of 806.6 cm^{-1} or that a difference of 10 cm^{-1} equals a potential shift of 1.24 mV. In order to evaluate their effects on the IET spectra, we can focus on three specific features: the frequency shifts, the relative IET intensities, and the nature of the vibrational modes in terms of overlaps between any pair of modes calculated with different basis sets.

Considering the vibrational frequencies, no scaling factor was applied since their variations as a function of the basis set are not significant at the B3LYP level of theory^[17]. If we consider the four most intense peaks, the 6-31G(d) basis set gives the highest frequency values, while the LANL2DZ basis set leads to the smallest ones, except for mode **30**. Peaks **22** and **21** present the smallest frequency variations between two basis sets, as they amount to 14 cm^{-1} (1.7 mV) and 17 cm^{-1} (2.1 mV), respectively. For modes **6**, **10**, **13**, and **30**, this difference is about 25 cm^{-1} (3.1 mV), while for modes **25** and **28**, which are characterized by in-plane bending motions of the C-H bonds, it amounts to 50 cm^{-1} (6.2 mV) and 35 cm^{-1} (4.3 mV), respectively. These effects have been quantified by performing linear regressions between sets of vibrational frequencies obtained with different basis sets [Fig. (III.2)]. The aug-cc-pVTZ basis set was chosen as reference. As expected, excellent correlations are obtained between the aug-cc-pVTZ basis set and the cc-pVTZ and cc-pVQZ basis sets, while the LANL2DZ pseudo potential basis set gives the largest deviations.

Basis set	LANL2DZ		LANL2DZdp		6-31G(d)		cc-pVDZ		cc-pVTZ		cc-pVQZ		aug-cc-pVDZ		aug-cc-pVTZ	
Mode Number	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I
6	0.0387	0.037	0.0413	0.029	0.0396	0.018	0.0394	0.018	0.0395	0.025	0.0396	0.024	0.0419	0.060	0.0418	0.020
10	0.0624	0.479	0.0655	0.238	0.0656	0.261	0.0655	0.276	0.0655	0.321	0.0658	0.305	0.0653	0.286	0.0655	0.222
13	0.0906	0.207	0.0927	0.041	0.0930	0.071	0.0928	0.040	0.0931	0.007	0.0933	0.015	0.0927	0.006	0.0930	0.040
21	0.1355	1.000	0.1368	1.000	0.1376	1.000	0.1373	1.000	0.1366	1.000	0.1365	1.000	0.1366	1.000	0.1364	1.000
22	0.1390	0.612	0.1400	0.472	0.1407	0.537	0.1395	0.522	0.1400	0.496	0.1401	0.491	0.1390	0.542	0.1399	0.484
25	0.1673	0.084	0.1639	0.062	0.1644	0.114	0.1643	0.088	0.1613	0.095	0.1608	0.091	0.1633	0.084	0.1610	0.074
28	0.1870	0.147	0.1855	0.132	0.1898	0.152	0.1866	0.163	0.1882	0.129	0.1881	0.120	0.1861	0.153	0.1879	0.088
30	0.2023	0.802	0.2013	0.443	0.2041	0.797	0.2029	0.628	0.2017	0.485	0.2014	0.458	0.2016	0.450	0.2012	0.635
I_{max} (10⁻⁴)	8.61		12.94		12.65		10.32		8.34		8.24		7.87		14.49	
# of basis functions	82		170		140		150		332		628		246		514	

Table III.1. Numbers, potentials (V), and IET intensities (arb. unit) of the vibrational normal modes dominating the IET spectrum of the 1,4-benzenedithiol calculated at different levels of approximation. This table lists the relative intensities as well as the maximum intensity (corresponding to mode **21**).

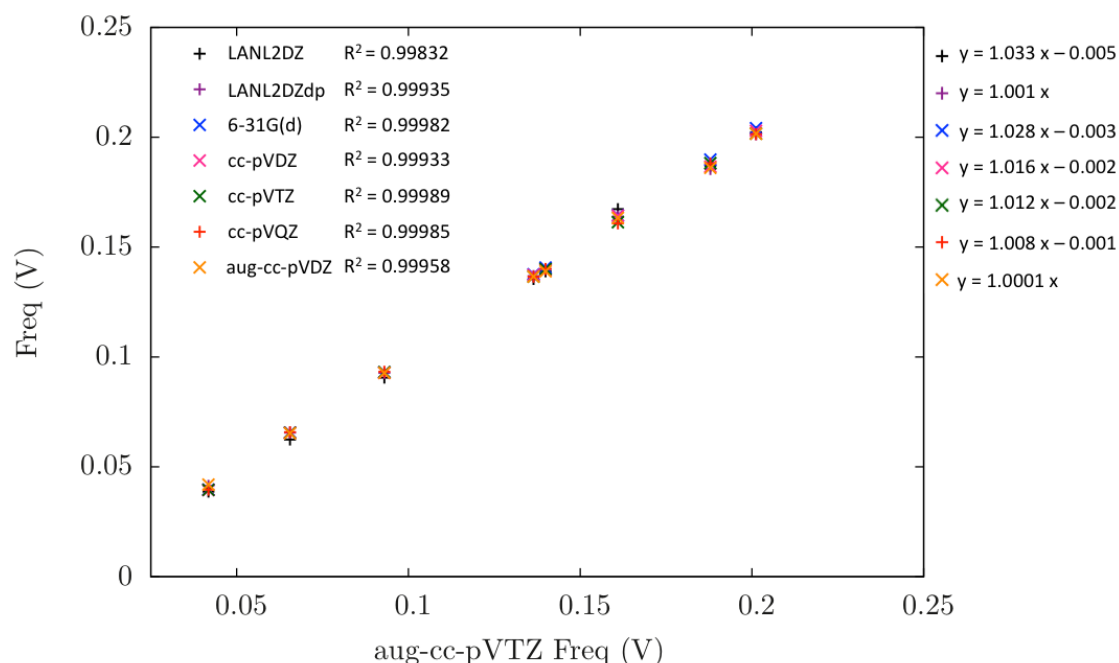


Fig. III.2. Representation of the correlation between the aug-cc-pVTZ frequency values and those calculated with different basis sets, using the B3LYP hybrid functional. In the caption, x refers to the aug-cc-pVTZ frequency values.

When going from the aug-cc-pVTZ to the aug-cc-pVDZ basis set, the largest frequency variations are observed for vibrational modes involving in-plane bending motions of the 4 C-H bonds, which increase by 19 cm^{-1} for mode **25** and decrease by 15 cm^{-1} and 7 cm^{-1} for modes **28** and **22**, respectively. For the other IET active modes the frequency variations are smaller than 3 cm^{-1} . Adding diffuse functions to the triple- and double- ζ leads to a small decrease of the frequency values for all the vibrational modes (except for mode **6**). Such differences are more important with the double- ζ basis set case: for example, if we consider modes **21**, **25** and **30** the cc-pVDZ/aug-cc-pVDZ (cc-pVTZ/aug-cc-pVTZ) differences are respectively 6 cm^{-1} (2 cm^{-1}), 8 cm^{-1} (2 cm^{-1}) and 10 cm^{-1} (4 cm^{-1}). In addition to that, frequency values from the triple- ζ to the double- ζ basis set increase for the two modes having the largest IET intensities (modes **21** and **30**), as their values respectively increase by about 6 cm^{-1} (0.7 mV) and 10 cm^{-1} (1.2 mV). One can observe a similar trend when going from quadruple- ζ to triple- ζ basis set, the frequency values increasing by about 1 cm^{-1} (0.1 mV) and 2 cm^{-1} (0.2 mV) for modes **21** and **30**, respectively, even if this difference is smaller with respect to the comparison between the cc-pVDZ and cc-pVTZ basis sets. Moreover, for modes **25**, **28** and **30** the cc-pVDZ/cc-pVTZ (cc-pVTZ/cc-pVQZ) differences attain respectively: 24 cm^{-1} (4 cm^{-1}), 13 cm^{-1} (1 cm^{-1}) and 10 cm^{-1} (2 cm^{-1}). Finally, the cc-pVDZ, cc-pVTZ, and cc-pVQZ sequence displays a nice convergence of the frequencies with respect to the basis set size.

Concerning the IET intensity values, for most of the active vibrational modes the 6-31G(d) basis set provides the largest intensities. This is mostly verified for modes in the 0.16-0.21 V range *i.e.* for modes **25**, **28** and **30**. On the contrary, for the majority of IET peaks, the aug-cc-pVDZ basis set leads to the smallest IET intensity values and modes **10**, **13**, **21**, **25**, and **30** are more particularly concerned. The most intense peaks present the largest IET intensity variations between two basis sets, which attain 1.87×10^{-4} , 6.62×10^{-4} , 2.97×10^{-4} and 6.54×10^{-4} arb. units, for modes **10**, **21**, **22** and **30**, respectively. For the less intense peaks (except mode **13**), this difference is smaller than 1×10^{-4} arb. units. These effects have been quantified by performing linear regressions between sets of intensities obtained with different basis sets [Fig. (III.3)].

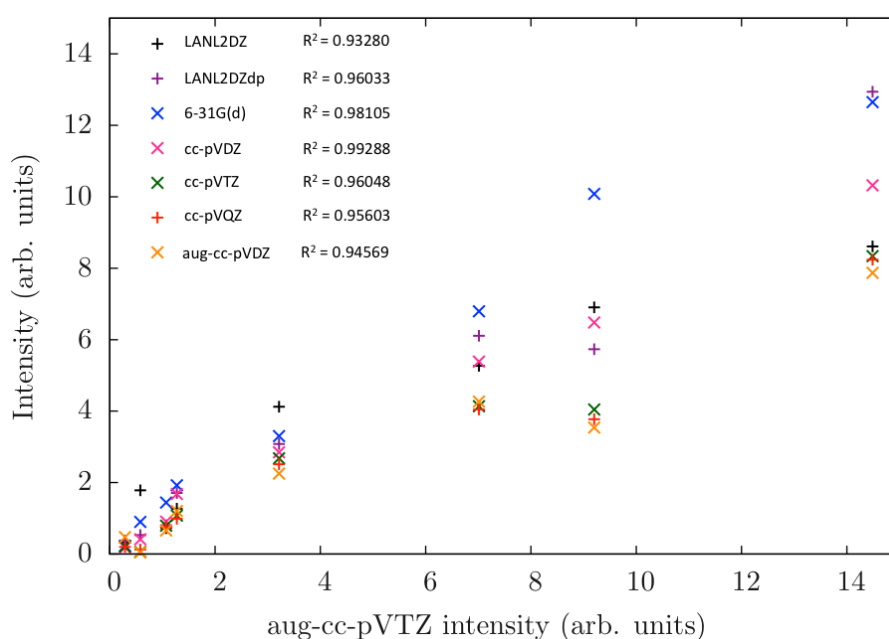


Fig. III.3. Correlation between the aug-cc-pVTZ IET intensity values and those calculated with different basis sets, using the B3LYP hybrid functional. The intensity values are multiplied by 10^4 arb. units.

For all the IET active modes (except mode **6**), when going from the aug-cc-pVTZ to the aug-cc-pVDZ basis set, we observe a decrease of the intensities. Modes **13**, **30** and **21**, involving in-plane stretchings between the two carbon atoms bonded to the sulfur atoms, present the largest variations, as their values decrease by 92%, 62%, and 46% respectively. Adding diffuse functions to cc-pVTZ leads to an important increase of the intensities for all the vibrational modes whereas in the case of cc-pVDZ, the opposite is observed (except for mode **6**) and the variations are more important in the latter case. In addition to that, the calculation of the IET intensity values from the cc-pVDZ to the cc-pVTZ basis set leads to a decrease of the IET activity for all the vibrational modes (except for mode **6**), as their values respectively decrease by about 0.17×10^{-4} , 0.35×10^{-4} , 1.98×10^{-4} ,

1.25×10^{-4} , 0.12×10^{-4} , 0.61×10^{-4} and 2.44×10^{-4} arb. units, for modes **10**, **13**, **21**, **22**, **25**, **28** and **30**, respectively. A similar behavior is observed going from the cc-pVTZ to the cc-pVQZ basis set (except for mode **13**), the IET intensity values decreasing respectively by about 0.01×10^{-4} , 0.16×10^{-4} , 0.10×10^{-4} , 0.09×10^{-4} , 0.04×10^{-4} , 0.09×10^{-4} and 0.27×10^{-4} arb. units for modes **6**, **10**, **21**, **22**, **25**, **28** and **30**, even if this difference is smaller with respect to the comparison between the cc-pVDZ and cc-pVTZ basis sets, as previously observed for the frequency values as well. So, the cc-pVTZ, cc-pVQZ, and aug-cc-pVDZ basis sets provide consistent data whereas the aug-cc-pVTZ intensities are much larger. This could originate from spurious MO levels originating from the many diffuse atomic orbitals as pointed out by Herrmann *et al.*^[18]. Indeed, such large basis sets can lead to an inaccurate description of the low-energy virtual MO's and thereof to artificially high transmission. Herrmann *et al.*^[18] explained this failure by a non-negligible transmission obtained from transport calculations in which all the junction atoms were removed, while their corresponding atomic basis functions were included in the basis set ("ghost atoms").

Further analysis of this effect was carried out by performing additional calculations with standard Pople extended basis sets, 6-311+G(2d,p) and 6-311++G(2df,2pd) as well as basis sets obtained from the aug-cc-pVTZ basis set by removing the *d*, or *f*, or *d* and *f* diffuse functions [Fig. (III.4)]. Results demonstrate that the *d* diffuse functions are responsible for this spurious enhancement effect, whereas the Pople basis sets provide intensity values in close agreement with those obtained with the cc-pVTZ basis set.

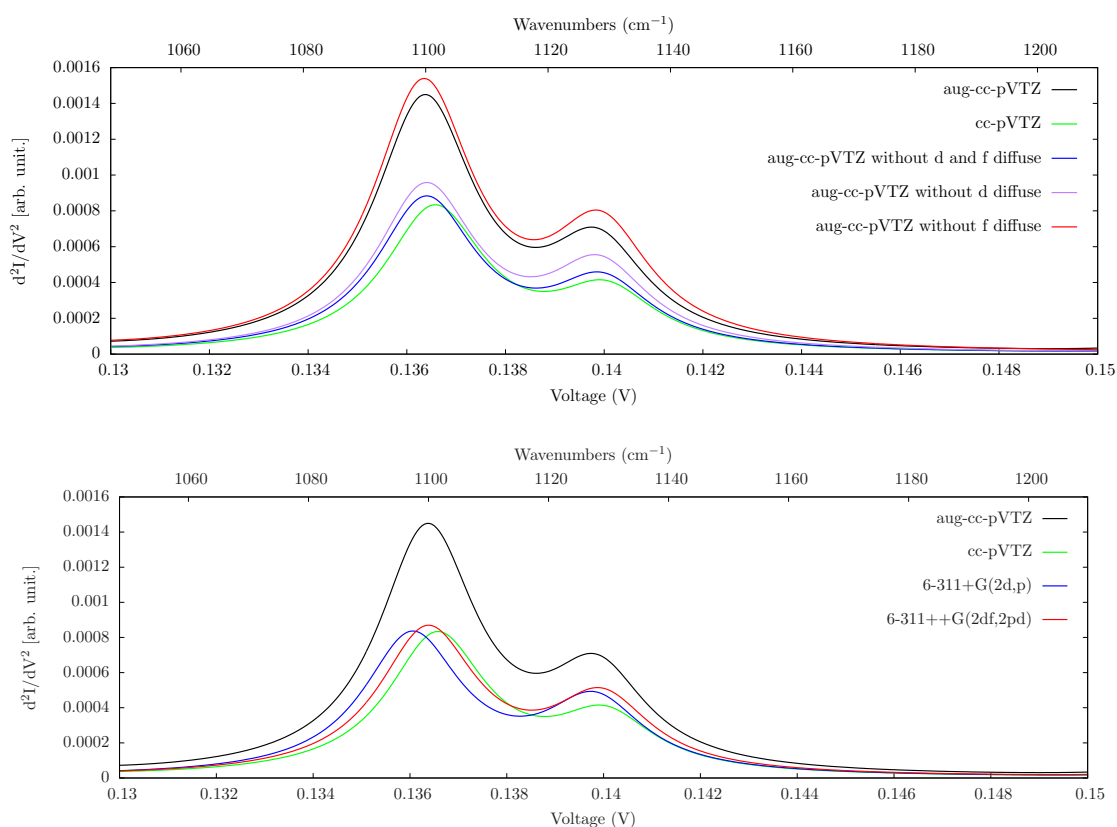


Fig. (III.4). IET spectrum (0.13-0.15 V) of 1,4-benzenedithiol calculated at the B3LYP level with extended basis sets in comparison to those obtained with the conventional cc-pVTZ and aug-cc-pVTZ basis set. (top) the basis sets were obtained from aug-cc-pVTZ by subtracting the *d*, *f*, or *d* and *f* diffuse functions; (bottom) the basis sets are the conventional 6-311+G(2d,p) and 6-311++G(2df,2pd) basis sets. The FWHM is set to 20 cm⁻¹.

Based on the overlap values reported in Table (III.2), one can observe a perfect correlation between the vibrational modes evaluated with the cc-pVTZ basis set and those obtained with more extended basis sets. Indeed, all the overlap values are equal to 1 when considering the correlation between the vibrational modes obtained with the B3LYP/cc-pVQZ and B3LYP/aug-cc-pVTZ levels, while they are slightly smaller in the case of pseudo potential basis sets, especially for modes **6** and **22** that both involve in-plane bendings of the C-H bonds of the phenyl ring. Finally, the double- ζ 6-31G(d) and cc-pVDZ basis sets describe the vibrational modes in a really good agreement with respect to the reference case. Therefore, the differences of IET intensities discussed above should not be explained in terms of changes of the vibrational normal modes but rather by modifications of the coupling between the electronic structure and the molecular vibrations as well as by modifications of the unoccupied molecular orbitals.

From these observations, one can state that, for evaluating the inelastic electron tunneling response of the 1,4-benzenedithiol, the cc-pVTZ basis set gives a good compromise between

accuracy and needs in computational resources and that too many diffuse functions can lead to artificially high IET intensities.

Basis set	LANL2DZ	LANL2DZdp	6-31G(d)	cc-pVDZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ
6	0.976	0.994	0.992	0.999	1.000	0.990	1.000
10	0.999	1.000	1.000	1.000	1.000	1.000	1.000
13	0.997	1.000	1.000	1.000	1.000	1.000	1.000
21	0.997	1.000	1.000	1.000	1.000	1.000	1.000
22	0.973	0.989	0.992	0.990	1.000	0.993	1.000
25	0.998	0.998	0.999	0.998	1.000	0.998	1.000
28	1.000	0.999	1.000	0.998	1.000	0.999	1.000
30	0.999	0.999	1.000	0.999	1.000	0.999	1.000

Table III.2. Overlap values between the IET active vibrational modes calculated with the B3LYP functional and a selection of basis sets, taking as reference the B3LYP/cc-pVTZ results.

III.C.2. Effect of the exchange-correlation (XC) functional

The effects of the XC functional were assessed with two basis sets, the LANL2DZ pseudo potential, usually employed for the description of the Au atoms in simulations of the conducting properties of molecular junctions^[2f,2h,19] and the cc-pVTZ basis set, giving the best balance between accuracy and computational costs as discussed in the previous paragraph. Fig. (III.5) displays the IET spectra of the 1,4-benzenedithiol evaluated with different XC functionals and these two basis sets. To remain consistent with our previous discussion on the basis set effects, our investigation will be performed along the same three steps as in Section III.C.1, taking as reference the hybrid B3LYP functional. Tables (III.3) and (III.4) report the number, frequency/potential (V), and IET intensities (arb. unit) of the vibrational modes dominating the IET spectrum of the 1,4-benzenedithiol.

XC functional	B3LYP		B3P86		B971		TPSSh		ω B97x		LC-BLYP		CAM-B3LYP	
Mode number	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I
6	0.0387	0.037	0.0391	0.027	0.0383	0.038	0.0382	0.027	0.0401	0.021	0.0408	0.023	0.0396	0.030
10	0.0624	0.479	0.0639	0.439	0.0618	0.502	0.0623	0.466	0.0666	0.380	0.0677	0.380	0.0646	0.443
13	0.0906	0.207	0.0916	0.206	0.0898	0.212	0.0896	0.225	0.0943	0.151	0.0959	0.154	0.0929	0.182
21	0.1355	1.000	0.1377	1.000	0.1346	1.000	0.1352	1.000	0.1415	1.000	0.1448	1.000	0.1394	1.000
22	0.1390	0.612	0.1406	0.606	0.1383	0.638	0.1389	0.612	0.1443	0.579	0.1463	0.583	0.1424	0.596
25	0.1673	0.084	0.1708	0.057	0.1664	0.092	0.1688	0.073	0.1662	0.094	0.1658	0.105	0.1671	0.096
28	0.1870	0.147	0.1881	0.154	0.1864	0.149	0.1872	0.131	0.1918	0.187	0.1946	0.235	0.1904	0.181
30	0.2023	0.802	0.2050	0.742	0.2012	0.839	0.2017	0.733	0.2107	0.814	0.2157	0.876	0.2081	0.857
$I_{\max} (10^{-4})$	8.61		7.82		8.77		8.77		9.58		9.72		9.07	

Table III.3. Numbers, potentials (V), and IET intensities (arb. unit) of the vibrational modes dominating the IET spectrum of the 1,4-benzenedithiol calculated with different functionals and using the LANL2DZ pseudo potential basis set. This table lists the relative intensities as well as the maximum intensity (corresponding to mode **21**).

XC functional	B3LYP		B3P86		B971		TPSSh		ω B97x		LC-BLYP		CAM-B3LYP	
Mode number	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I	Potential	I
6	0.0395	0.025	0.0394	0.035	0.0393	0.032	0.0386	0.035	0.0405	0.036	0.0412	0.038	0.0402	0.036
10	0.0655	0.321	0.0671	0.278	0.0656	0.292	0.0660	0.274	0.0687	0.265	0.0700	0.283	0.0674	0.321
13	0.0931	0.007	0.0940	0.010	0.0925	0.011	0.0924	0.004	0.0959	0.034	0.0980	0.036	0.0952	0.022
21	0.1366	1.000	0.1389	1.000	0.1362	1.000	0.1367	1.000	0.1419	1.000	0.1456	1.000	0.1404	1.000
22	0.1400	0.496	0.1411	0.452	0.1393	0.509	0.1399	0.467	0.1446	0.504	0.1473	0.605	0.1429	0.366
25	0.1613	0.095	0.1654	0.074	0.1608	0.098	0.1636	0.088	0.1592	0.123	0.1580	0.114	0.1604	0.112
28	0.1882	0.129	0.1883	0.148	0.1869	0.132	0.1877	0.125	0.1917	0.196	0.1953	0.224	0.1913	0.173
30	0.2017	0.485	0.2038	0.487	0.2005	0.502	0.2011	0.463	0.2089	0.651	0.2142	0.613	0.2071	0.582
$I_{\max} (10^{-4})$	8.34		7.21		8.65		8.71		8.41		8.56		8.14	

Table III.4. Numbers, potentials (V), and IET intensities (arb. unit) of the vibrational modes dominating the IET spectrum of the 1,4-benzenedithiol calculated with different functionals and using the cc-pVTZ basis set. This table lists the relative intensities as well as the maximum intensity (corresponding to mode **21**).

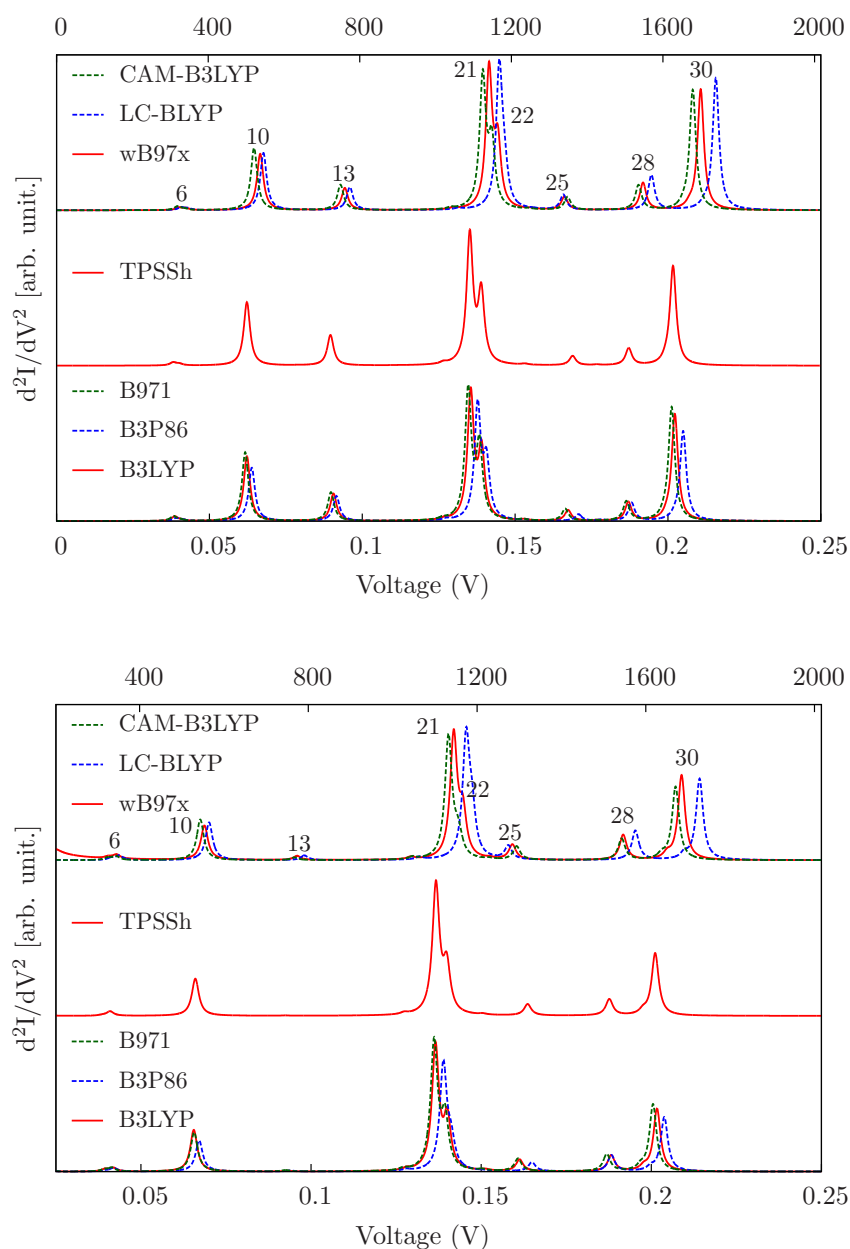


Fig. III.5. IET spectra of the 1,4-benzenedithiol calculated with several hybrid XC functionals in combination with the LANL2DZ pseudo potential basis set (top) and the cc-pVTZ basis set (bottoms). The FWHM is set to 20 cm^{-1} .

First, systematic frequency shifts are observed between the different functionals, which is consistent with the early study by Scott and Radom demonstrating that the scaling factor gets closer and closer to 1 when the amount of HF exchange decreases^[17] [Figs. (III.6) and (III.7)]. Therefore, these systematic frequency shifts can be attributed to the lack of using scaling factors. So, for all the IET active modes (except mode **25**), the TPSSH, B971, and B3LYP functionals give the smallest frequency values, while the functionals LC-BLYP, ω B97x, and CAM-B3LYP including long-range corrections give the largest ones. The most intense peaks (**21** and **30**) present the highest frequency variations between two XC functionals using a given basis set, as they are respectively

equal to 76 cm^{-1} (9.4 mV) and 110 cm^{-1} (13.7 mV) with the cc-pVTZ basis set, and to 82 cm^{-1} (10.2 mV) and 117 cm^{-1} (14.5 mV) with the LANL2DZ pseudo potential basis set. Then, these variations decrease when going towards lower frequency modes.

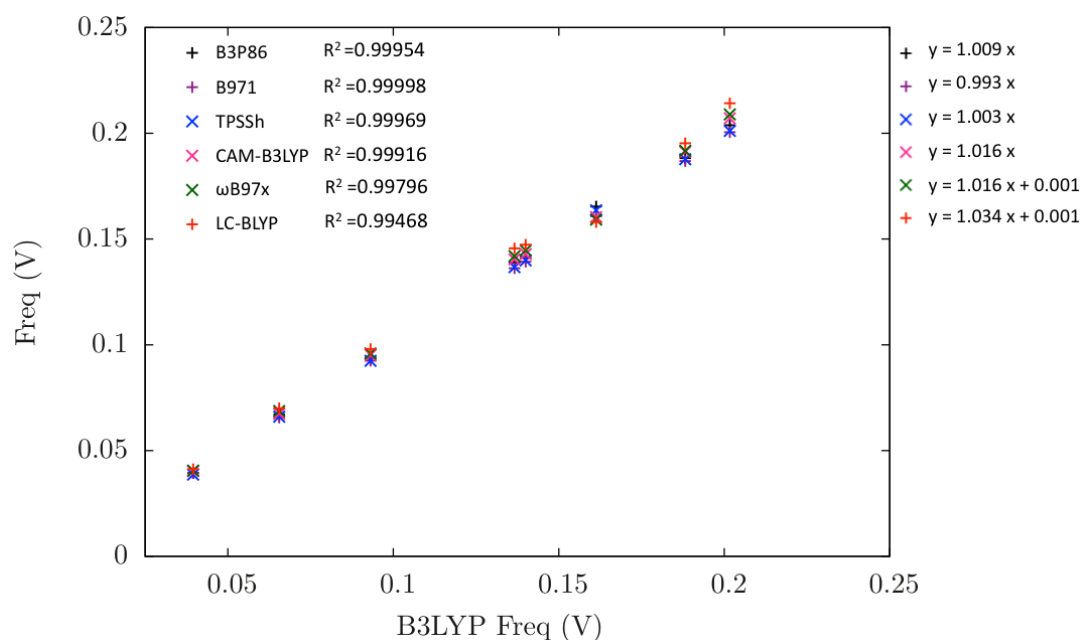


Fig. III.6. Correlation between the B3LYP frequency values and those calculated with different XC functionals with the cc-pVTZ basis set. In the caption, x refers to the B3LYP frequency values.

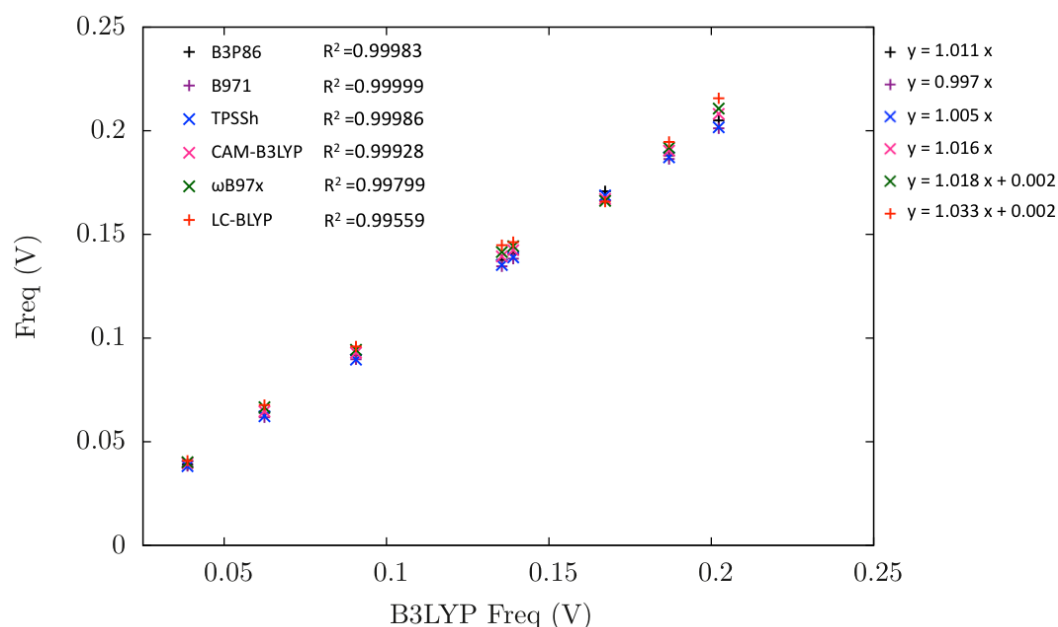


Fig. III.7. Correlation between the B3LYP frequency values and those calculated with different XC functionals with the LANL2DZ pseudo potential basis set. In the caption, x refers to the B3LYP frequency values.

For calculating the IET intensities, the functional has a smaller impact than the basis set. This is illustrated with mode **21** ($I_{\max}$ quantities in Tables (III.3) and (III.4)) for which the largest intensity variation between two different basis sets (aug-cc-pVDZ and aug-cc-pVTZ) is equal to 6.62×10^{-4} arb. units, while it only amounts to 1.35×10^{-4} arb. units when we consider the largest variation between two functionals (B3P86 and TPSSh using the cc-pVTZ basis set). Moreover, for each IET peak, we notice that the difference of intensities between the two extreme values (obtained with two different functionals) is smaller with the cc-pVTZ basis set than with LANL2DZ. For example, using the cc-pVTZ (LANL2DZ) basis set, they are equal to 0.67×10^{-4} (0.97×10^{-4}), 1.50×10^{-4} (1.90×10^{-4}), and 1.96×10^{-4} (2.71×10^{-4}) arb. units, for modes **10**, **21**, and **30**, respectively.

The analysis on the XC effects starts with results obtained with the cc-pVTZ basis set. As shown in Fig. (III.8), there is a good consistency between the intensities calculated with different XC functionals. When looking into the details, one observes that for modes **25**, **28**, and **30**, the LC-BLYP and ω B97x functionals provide the largest intensities, while B3P86 gives the smallest ones. For the other modes, the impact of the XC functional on the IET intensities with respect to the peak frequency is less obvious. Slightly different conclusions can be drawn when using the LANL2DZ basis set [Fig. (III.9)], *i.e.* i) for modes **6**, **10**, and **13** the ω B97x and B3P86 functionals give the smallest intensities, while the B971 functional give the largest ones and ii) for the 0.13-0.22 V modes, the LC-BLYP and ω B97x functionals give the largest values and the B3P86 and TPSSh functionals give the smallest ones.

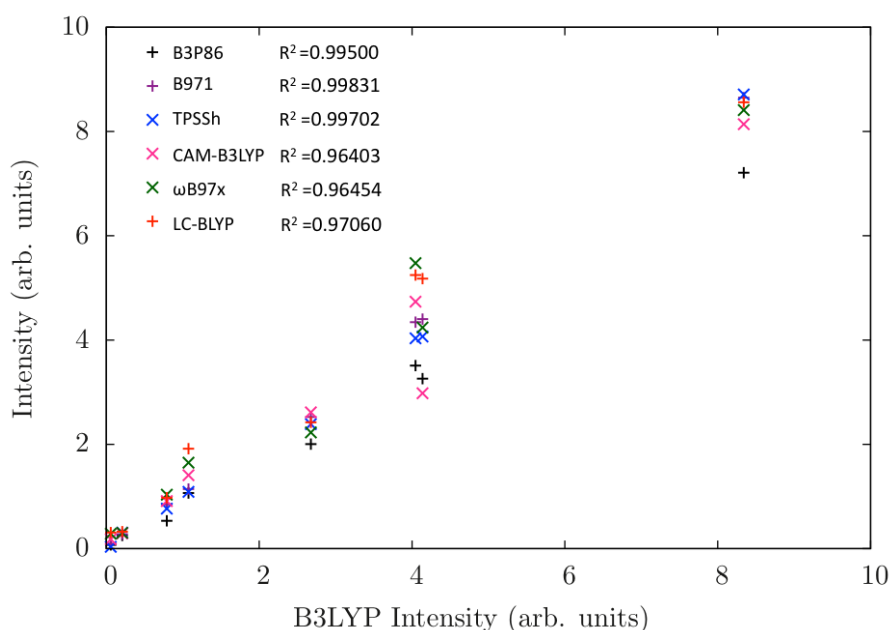


Fig. III.8. Correlation between the B3LYP IET intensity values and those calculated with different XC functionals with the cc-pVTZ basis set. The intensity values are multiplied by 10^4 (arb. units).

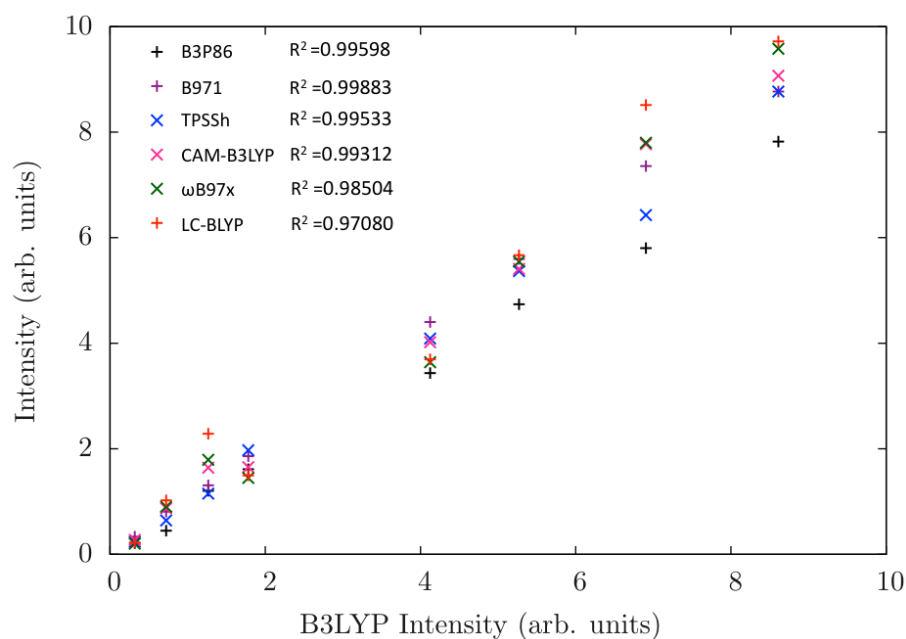


Fig. III.9. Correlation between the B3LYP IET intensity values and those calculated with different exchange-correlation functionals with the LANL2DZ pseudo potential basis set. The intensity values are multiplied by 10^4 (arb. units).

For the B3LYP and B971 functionals, when going from the cc-pVTZ to the LANL2DZ basis set, one can observe an increase of the IET intensity values (except for mode **25**), and for the LC-BLYP functional only the intensity value of mode **6** decreases. In addition to that, the use of the B3P86, TPSSh, CAM-B3LYP, and ω B97x functionals leads to the same tendency (increase) concerning the IET intensity values, except for modes **6** and **25**. Finally, for both basis sets, we notice a good correlation between the intensities obtained with the B3LYP functional and those calculated with the B971 functional, while the CAM-B3LYP and LC-BLYP provide the largest differences with respect to the B3LYP functional when using the cc-pVTZ and LANL2DZ basis sets, respectively [Figs. (III.8) and (III.9)]. Intensity differences can also be investigated from the viewpoint of relative intensities or intensity ordering. Considering the four most intense modes, all functionals predict the same **10** < **22** < **30** < **21** intensity ordering provided the LANL2DZ basis set is used whereas, using the cc-pVTZ basis set, the ordering is either **10** < **22** < **30** < **21** or **10** < **30** < **22** < **21**. This highlights the need of using a sufficiently flexible atomic basis set and also the fact that the XC functional should be carefully chosen. On the basis of these sole theoretical results, it is not possible to tell which XC functional is the best.

For both basis sets, we have evaluated the overlaps between the IET active vibrational modes calculated with the different XC functionals, reported in Tables (III.5) and (III.6), taking as reference the B3LYP/cc-pVTZ and the B3LYP/LANL2DZ results, respectively. For both basis sets, we

can observe a very good correlation between the vibrational modes evaluated with the B3LYP functional and those obtained with the B971 functional. Based on the overlap values, CAM-B3LYP and LC-BLYP are different and probably less appropriate for describing the vibrational modes (mostly for mode **22**, characterized by in-plane bendings of the C-H bonds), in comparison with the other functionals. This is evidenced by the smaller overlap values with respect to the B3LYP functional [overlap of 0.670 for LC-BLYP/B3LYP using LANL2DZ and of 0.693 for CAM-B3LYP/B3LYP using cc-pVTZ]. These small overlaps originate from the fact that using the CAM-B3LYP and LC-BLYP functionals the B3LYP mode **22**, involving in-plane bending motions of the 4 CH bonds of the benzene ring (C₂H, C₃H, C₅H and C₆H), is split into two contributions. So, at the CAM-B3LYP level, one mode involves in-plane bendings of the C₂H and C₅H bonds, while another is characterized by in-plane bendings of the C₃H and C₆H bonds. The frequencies associated to these modes are respectively equal to 1180 cm⁻¹ (0.1463 V) and 1185 cm⁻¹ (0.1470 V) at the LC-BLYP/LANL2DZ level and to 1153 cm⁻¹ (0.1429 V) and 1159 cm⁻¹ (0.1437 V) at the CAM-B3LYP/cc-pVTZ level. Their IET intensities are equal to 5.67×10⁻⁴ and 4.06×10⁻⁴ arb. units at the LC-BLYP/LANL2DZ level and to 2.98×10⁻⁴ and 2.39×10⁻⁴ arb. units at the CAM-B3LYP/cc-pVTZ level. This appears as a kind of accidental degeneracy, which has no impact on the spectral pattern because both modes contribute to the IET intensity at a very similar transition frequency. Finally, even if the overlap values between the modes evaluated with the B3P86 and TPSSh functionals are slightly smaller than the B971 ones, these functionals describe the vibrational modes in a good agreement with respect to the B3LYP.

XC functional	B3P86	B971	TPSSh	ωB97x	LC-BLYP	CAM-B3LYP
6	0.967	0.997	0.935	0.993	0.988	0.997
10	1.000	1.000	1.000	0.999	0.999	1.000
13	0.999	1.000	0.999	0.998	0.998	1.000
21	0.999	1.000	1.000	0.998	0.995	0.999
22	0.887	1.000	0.983	0.839	0.888	0.693
25	0.996	1.000	0.998	0.982	0.945	0.993
28	0.999	1.000	1.000	0.997	0.990	0.998
30	0.999	1.000	1.000	0.997	0.995	0.999

Table III.5. Overlap values between the IET active vibrational modes calculated with several XC functionals and the cc-pVTZ basis set, taking as reference the B3LYP/cc-pVTZ level.

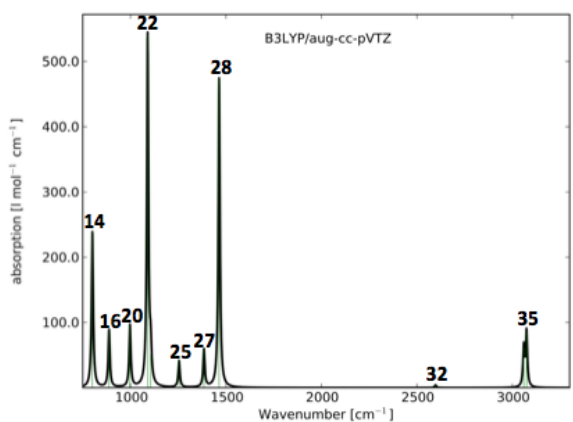
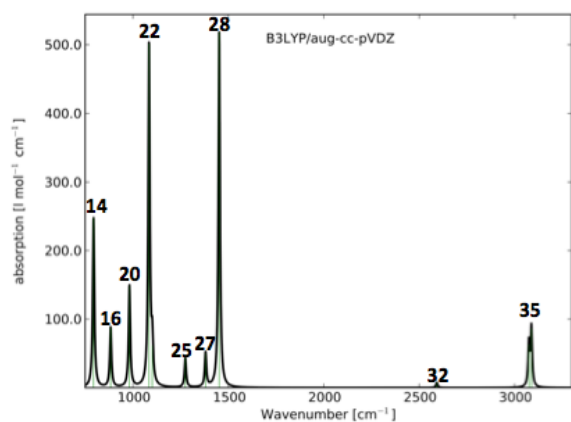
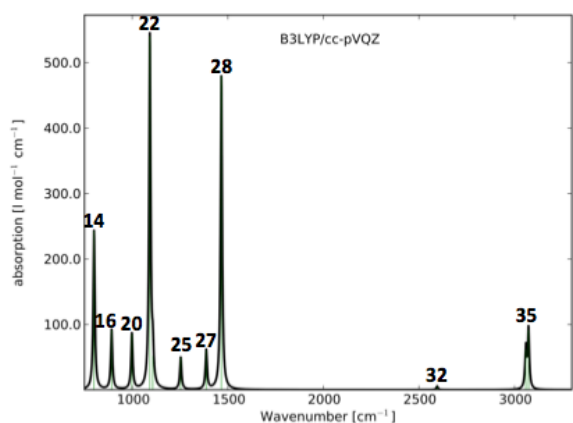
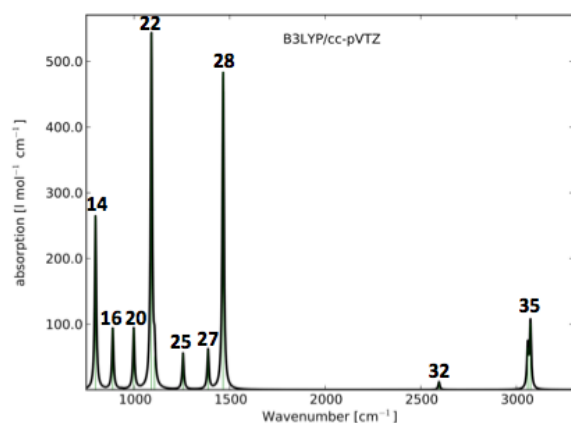
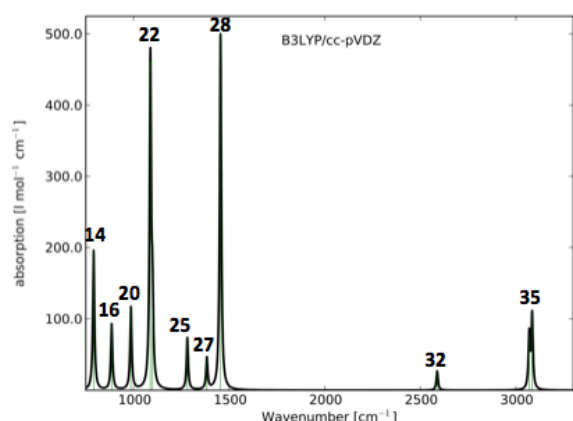
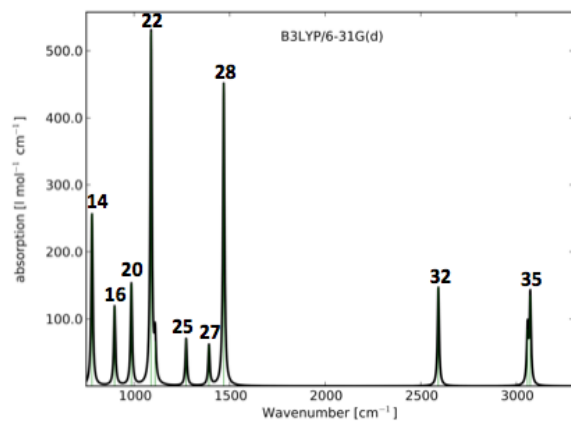
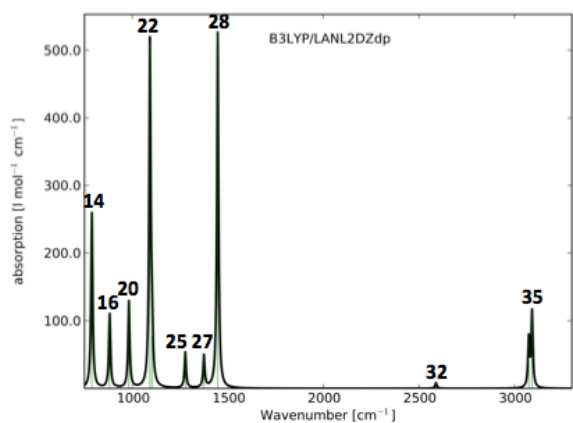
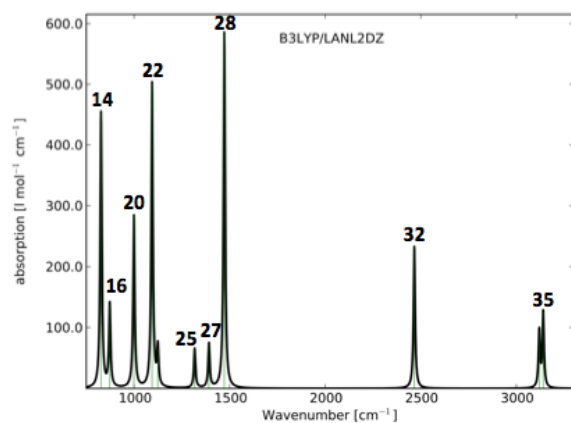
XC functional	B3P86	B971	TPSSh	ω B97x	LC-BLYP	CAM-B3LYP
6	0.981	0.999	0.976	0.952	0.965	0.994
10	1.000	1.000	1.000	0.999	0.999	1.000
13	1.000	1.000	1.000	0.997	0.997	1.000
21	1.000	1.000	1.000	0.997	0.997	0.999
22	0.999	1.000	0.999	0.986	0.670	0.994
25	1.000	1.000	1.000	0.999	0.998	1.000
28	0.999	1.000	1.000	0.997	0.990	0.998
30	0.999	1.000	1.000	0.998	0.996	0.999

Table III.6. Overlap values between the IET active vibrational modes calculated with several XC functionals and the LANL2DZ basis set, taking as reference the B3LYP/LANL2DZ level.

In summary, besides frequency shifts that can be accounted for using an appropriate scaling factor, these calculations have highlighted very small differences between the IET signatures calculated with a set of exchange-correlation functionals, demonstrating there is no advantage of not using the traditional B3LYP XC functional. A similar conclusion was also drawn in a recent work on the sum-frequency generation methyl signature^[15d].

III.C.3. IR spectra of the 1,4-benzenedithiol

In order to further assess the impact of the method of calculation to characterize the IET vibrational signatures of 1,4-benzenedithiol, IR absorption spectra were simulated [Fig. (III.10)], either by using several basis sets with the B3LYP hybrid functional, and by varying the XC functional in combination with the cc-pVTZ basis set. The vibrational IR active modes, which are IET inactive, are represented in Fig. (III.11).



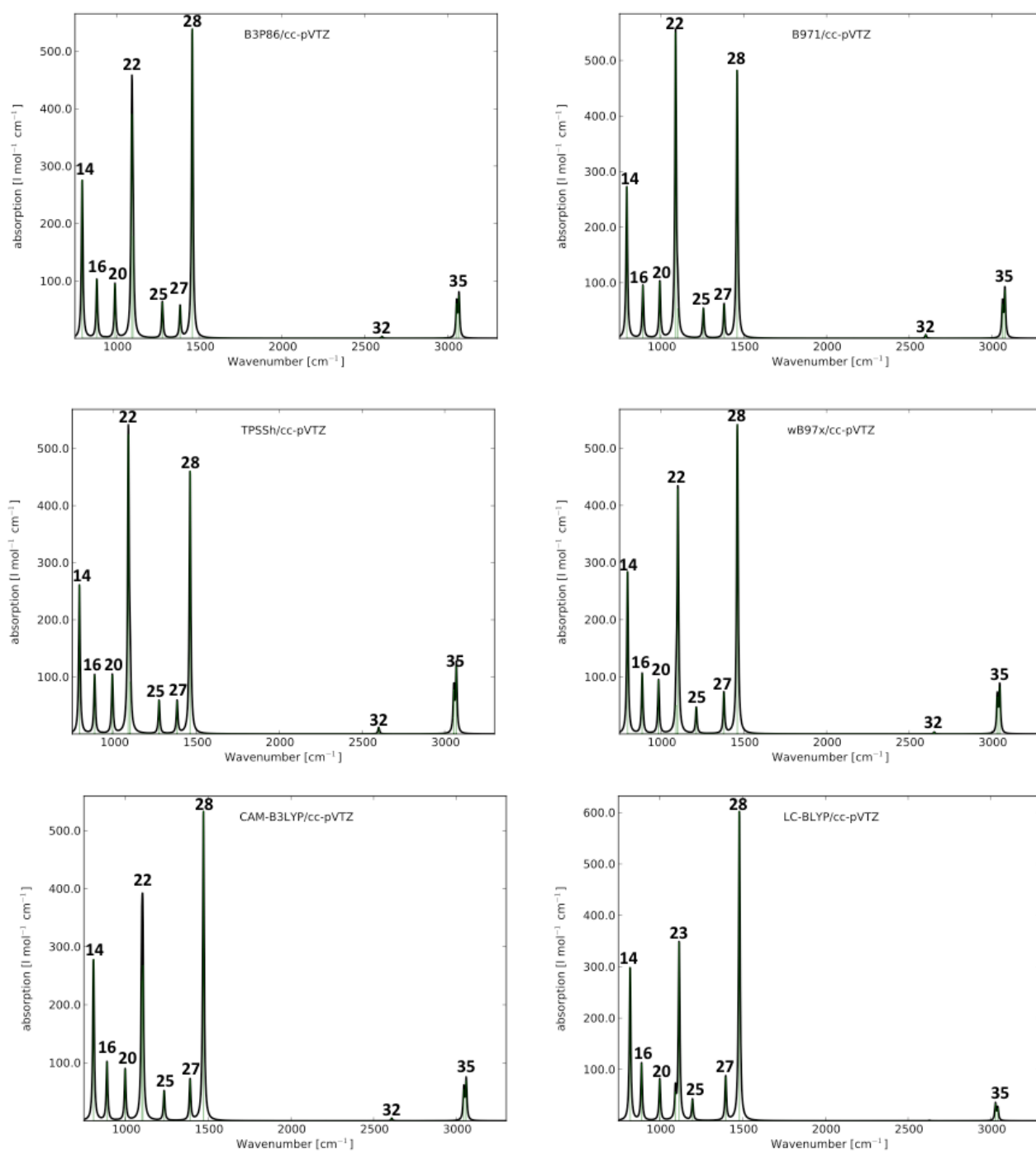


Fig. III.10. IR absorption spectra of the 1,4-benzenedithiol calculated at different levels of approximation. Lorentzian functions with a FWHM of 10 cm^{-1} were employed for simulating the IR spectra.

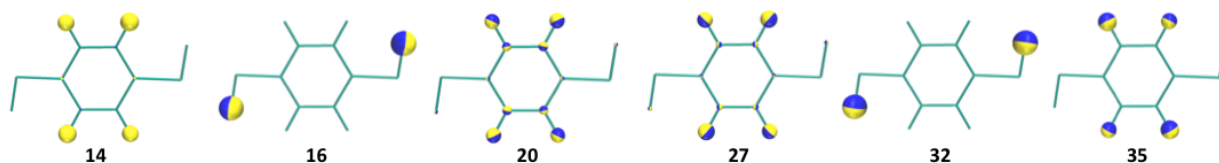


Fig. III.11. Sketch of IR active modes of 1,4-benzenedithiol which are IET inactive. See caption of Fig. (III.1) for more information.

Before analyzing the IR intensities, the availability of experimental vibrational frequencies^[20] enables to assess the reliability of the different theoretical schemes to predict the vibrational frequencies.

Calculated harmonic vibrational frequencies overestimate the experimental fundamental frequencies, due to the neglect of anharmonicity, the approximate treatment of electronic correlation, and the use of a finite basis set. This is also illustrated in Figs. (III.12) and (III.13).

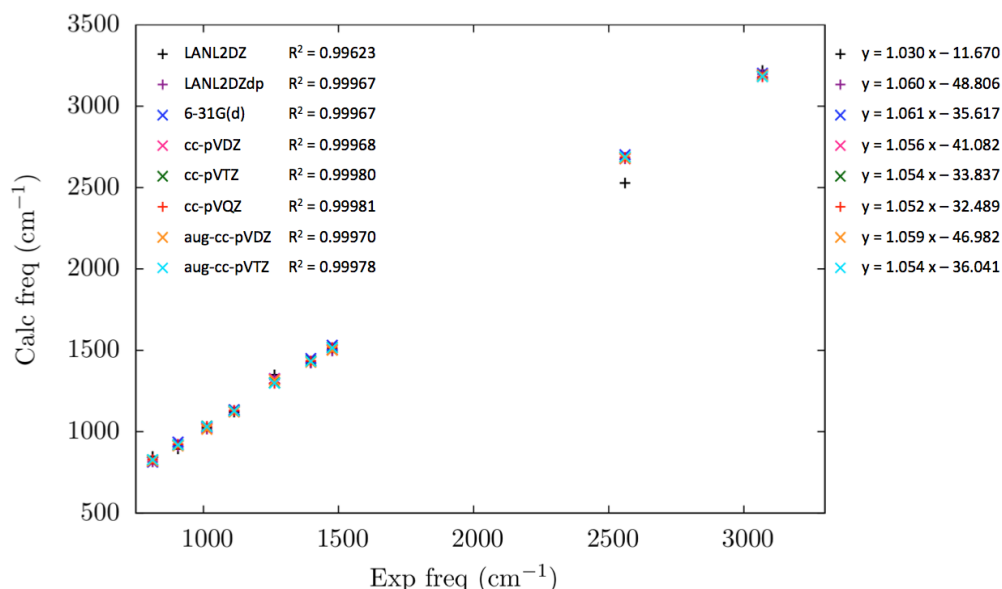


Fig. III.12. Correlation between the experimental fundamental and calculated harmonic frequencies for different basis sets and the hybrid B3LYP functional. In the caption, x refers to the experimental fundamental frequencies.

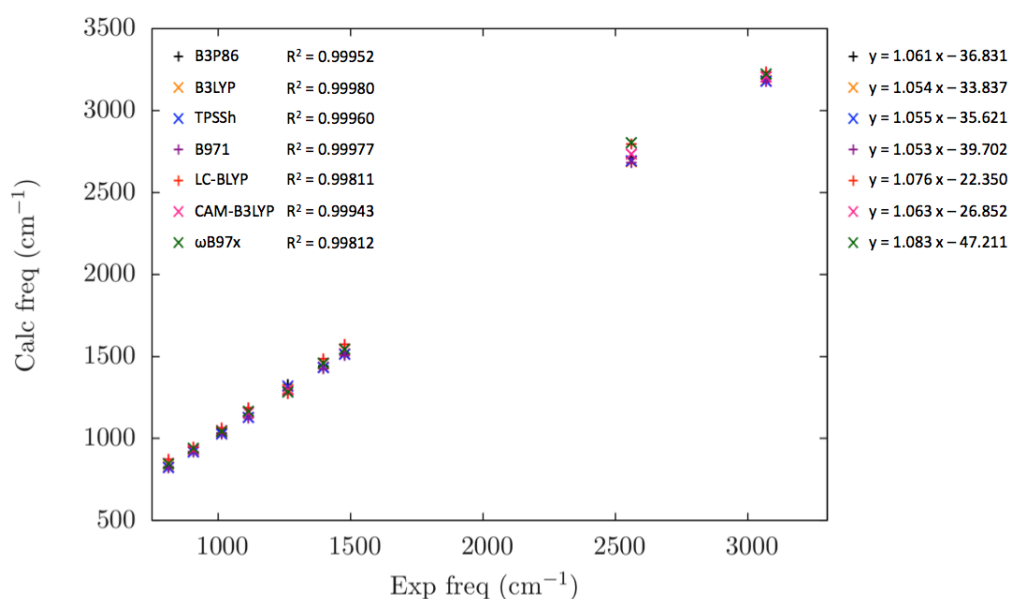


Fig. III.13. Correlation between the experimental fundamental and calculated harmonic frequencies for different XC functionals and the cc-pVTZ basis set. In the caption, x refers to the experimental fundamental frequencies.

To correct for these effects, the harmonic vibrational frequencies are scaled by a factor, which is method dependent. In the present study, we consider a uniform scaling of the frequencies over the whole set of IR active vibrational modes. Please note that more refined methods have already been proposed in the literature^[21], consisting in the application of a local scaling factor for each vibrational mode presenting a significant interest with regards to the molecular structure. However, in the frame of our investigation, such detailed analysis would not bring any additional significant information. Following Ref. [17a], scaling factors (λ) were determined for the different levels of calculation by considering the vibrational frequencies of the IR active normal modes of 1,4-benzenedithiol:

$$\lambda = \sum_i^{\text{all}} \omega_i^{\text{theor}} \nu_i^{\text{expt}} / \sum_i^{\text{all}} (\omega_i^{\text{theor}})^2$$

where ω_i^{theor} is the calculated i^{th} harmonic frequency, ν_i^{expt} is the corresponding experimental fundamental frequency [Table (III.7)]. For the LC-BLYP, ω B97x, and CAM-B3LYP functionals including long-range corrections, the scaling factor ranges from 0.9397 to 0.9539, while for the other functionals, they go from 0.9600 (B3P86) to 0.9687 (B971). The λ value for B3LYP/6-31G(d) calculations amounts to 0.9596 but it increases when keeping the same functional and extending the basis set (0.9656 with cc-pVTZ to 0.9675 with aug-cc-pVDZ). These results are consistent with previous studies^[17,22]. The scaled theoretical harmonic frequencies determined for different basis sets (with the hybrid B3LYP functional) and XC functionals (using the cc-pVTZ basis set) are listed in Tables (III.8) and Table (III.9), respectively. Moreover, the root mean squares errors, after scaling, are given in Table (III.7). They highlight the better performance of triple- ζ basis sets over double- ζ (in fact, quadruple- ζ are even slightly better) as well as the good performance of B3LYP.

The experimental IR spectrum of 1,4-benzenedithiol is displayed in Fig. (III.14) and is characterized by about ten peaks in the 800-3200 cm^{-1} region. Its dominant signatures are well reproduced by all levels of calculations. The experimental spectrum presents two intense transitions at 1477 cm^{-1} and at 812 cm^{-1} [Fig. (III.14)] arising from in-plane and out-of-plane bendings of the C-H bonds, respectively. These correspond to modes **28** and **14** in Fig. (III.10) (mode **14** is IET inactive). Another strong IR band at 1114 cm^{-1} is attributed to in-phase in-plane bendings of the C-H bonds combined with small C-S stretchings (mode **22**). Experimentally, the intensities increase in the order **22** < **14** < **28** whereas the calculations – which predict that these three modes have the highest intensities – give other ordering, either **14** < **22** < **28** or **14** < **28** < **22**, highlighting also the subtle balance between the level of calculation and the relative IR intensities.

Let's point out that the **14** < **28** < **22** ordering is predicted by the B3LYP/cc-pVTZ, B3LYP/cc-pVQZ, and B3LYP/aug-cc-pVTZ calculations but that the **28** < **22** ordering is reversed using the B3P86, CAM-B3LYP, ω B97x, and LC-BLYP XC functionals.

The experimental spectrum is also characterized by three medium intensity peaks: one at 2560 cm⁻¹ and two at 1397 cm⁻¹ and 1013 cm⁻¹ presenting similar IR intensities [Fig. (III.14)]. They correspond to the IET inactive vibrational mode **32** involving in-plane S-H stretchings, to mode **27** arising from out-of-phase C-H bendings combined with small C=C stretchings, and to mode **20** related to in-plane distortions of the phenyl ring associated with small C-S stretchings, respectively. However, the several basis sets and XC functionals considered in this study present some limitations for predicting the relative IR intensities: i) too small IR intensities are predicted for peak **32** (except using the LANL2DZ and 6-31G(d) basis sets), ii) the relative intensities of modes **20** and **27** with respect to mode **28** are overestimated.

Finally, three other weaker IR bands are observed experimentally, at 906 cm⁻¹, 1263 cm⁻¹, and 3069 cm⁻¹. These are associated with vibrational mode **16** involving in plane-bendings of the S-H bonds, mode **25** arising from in-plane bendings of the C-H bonds, and mode **35** characterized by in-plane stretchings of the C-H bonds, respectively. To a large extent, these signatures are well reproduced by the calculations.

As discussed in detail hereabove, the dominant signatures of the experimental IR spectrum are well reproduced by most levels of calculation but some differences remain. In addition, part of the differences originates from the lack of anharmonicity effects considered in the theoretical calculations as well as from the lack of surrounding effects. Though beyond the scope of this study, calculations describing the effects of the solvent using the polarizable continuum model were carried out and do not show substantial improvement, demonstrating that specific solute-solvent interactions between the molecules might be the source of differences.

Level of approximation	Scaling factor λ	rms _{mol}
B3LYP/LANL2DZ	0.9757	46
B3LYP/LANL2DZdp	0.9672	25
B3LYP/6-31G(d)	0.9596	20
B3LYP/cc-pVDZ	0.9666	22
B3LYP/cc-pVTZ	0.9656	18
B3LYP/cc-pVQZ	0.9662	17
B3LYP/aug-cc-pVDZ	0.9675	24
B3LYP/aug-cc-pVTZ	0.9660	19
B3P86/cc-pVTZ	0.9600	23
B971/cc-pVTZ	0.9687	20
TPSSH/cc-pVTZ	0.9655	21
ω B97x/cc-pVTZ	0.9453	38
LC-BLYP/cc-pVTZ	0.9397	34
CAM-B3LYP/cc-pVTZ	0.9539	21

Table III.7. Scaling factors and corresponding root mean square errors (rms) for different levels of calculation, as obtained from the main IR signatures of 1,4-benzenedithiol.

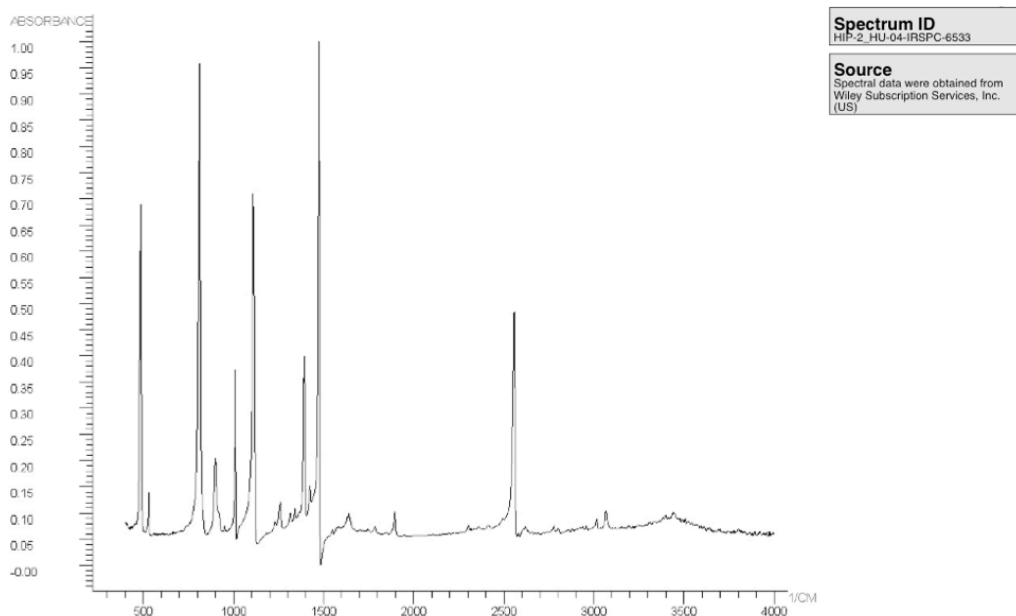


Fig. III.14. Experimental IR absorption spectrum of the 1,4-benzenedithiol from SciFinder (CAS Registry Number : 624-39-5) Refs. Mietrach, A.; Muesmann, T. W. T.; Christoffers, J.; Wickleder, M. S. Eur. J. Inorg. Chem. 2009 (2009), 5328) & WSS: Spectral data were obtained from Wiley Subscription Services, Inc. (US)

Mode number	Experiment	LANL2DZ	LANL2DZdp	6-31G(d)	cc-pVDZ	cc-pVTZ	cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ
14	812	827	788	780	791	799	800	793	800
16	906	872	882	898	885	888	892	883	888
20	1013	999	983	986	986	998	998	982	997
22	1114	1094	1092	1089	1087	1090	1092	1085	1090
25	1263	1317	1278	1272	1281	1256	1253	1274	1254
27	1397	1391	1375	1391	1383	1387	1386	1381	1384
28	1477	1472	1447	1469	1455	1466	1466	1452	1464
32	2560	2467	2589	2592	2588	2596	2595	2592	2598
35	3069	3141	3092	3073	3084	3074	3073	3088	3075

Table III.8. Comparison between experimental and scaled theoretical values (using the corresponding scaling factors of Table (III.7)) for calculations performed with the B3LYP XC functional and different atomic basis sets. The frequencies are given in cm^{-1} .

Mode number	experiment	B3LYP	B3P86	B971	TPSSh	ω B97x	LC-BLYP	CAM-B3LYP
14	812	799	793	794	794	799	820	808
16	906	888	881	891	885	888	890	889
20	1013	998	991	994	992	986	1000	999
22	1114	1090	1092	1089	1089	1102	1116	1106
25	1263	1256	1277	1256	1274	1214	1197	1234
27	1397	1387	1384	1381	1384	1380	1397	1391
28	1477	1466	1457	1460	1462	1461	1480	1472
32	2560	2596	2604	2599	2601	2651	2627	2609
35	3069	3074	3068	3078	3069	3047	3041	3058

Table III.9. Comparison between experimental and scaled theoretical values (using the corresponding scaling factors of Table (III.7)) for calculations performed with the cc-pVTZ atomic basis set and different XC functionals. The frequencies are given in cm^{-1} .

III.D. Conclusions

The effects of the atomic basis set and of the exchange-correlation (XC) functional on the inelastic electron tunneling (IET) spectra have been investigated by considering the prototypical 1,4-benzenedithiol molecule. These studies have been completed by tackling the reliability of the same methods for predicting the IR absorption spectrum of the same molecule. The main conclusions are i) the B3LYP XC functional is suitable to predict the relative vibrational frequencies, ii) provided a scaling factor is used, the root mean square error on the vibrational frequencies goes down to 18 cm^{-1} , iii) the cc-pVTZ basis set is a good compromise between accuracy and computational needs, iv) basis set effects on the IET intensities are larger than those of the XC functional, v) the cc-pVTZ, cc-pVQZ, and aug-cc-pVDZ basis sets provide consistent IET intensities. Further analysis of the impact of the basis set and XC functional will however require making comparisons with experimental results, which depend on the way the molecules interact with the surfaces/electrodes.

III.E. References

- [1] (a) Kushmerick, J. G., Lazorcik, J., Patterson, C. H., Shashidhar, R., Seferos, D. S. Bazan, G. C. *Nano Lett.* **2004**, *4*, 639. (b) Wang, W., Lee, T., Kretzschmar, I., Reed, M. A. *Nano Lett.* **2004**, *4*, 643. (c) Yu, L. H., Keane, Z. K., Ciszek, J. W., Cheng, L., Stewart, M. P., Tour, J. M., Natelson, D. *Phys. Rev. Lett.* **2004**, *93*, 266802. (d) Troisi, A., Ratner, M. A., Nitzan, A. *J. Chem. Phys.* **2003**, *118*, 6072. (e) Chen, Y. C., Zwolak, M., Di Ventra, M. *Nano Lett.* **2005**, *5*, 621. (f) Jiang, J., Kula, M., Lu, W., Luo, Y. *Nano Lett.* **2005**, *5*, 1551.
- [2] (a) Mingo, N.; Makoshi, K. *Phys. Rev. Lett.* **2000**, *84*, 3694. (b) Lorente, N.; Persson, M.; Lauhon L.-J.; Ho, W. *Phys. Rev. Lett.* **2001**, *86*, 2593. (c) Troisi, A.; Ratner, M. *Phys. Rev. B* **2005**, *72*, 033408. (d) Paulsson, M.; Frederiksen, T.; Brandbyge, M. *Nano. Lett.* **2006**, *6*, 258. (e) Frederiksen, T.; Paulsson, M.; Brandbyge, M.; Jauho, A. P. *Phys. Rev. B.* **2007**, *75*, 205413. (f) Leng, J. C.; Lin, L. L.; Song, X. N.; Li, Z. L.; Wang, C. K. *J. Phys. Chem. C* **2009**, *113*, 18353. (g) Bocquet, M.-L.; Wang, B. *Progr. Surf. Sci.* **2010**, *85*, 435. (h) Lin, L. L.; Wang C. K.; Luo, Y. *ACS Nano* **2011**, *5*, 2257. (i) Burema, S. R.; Lorente, N.; Bocquet, M.-L. *J. Chem. Phys.* **2012**, *136*, 244507.
- [3] (a) Porezag, D.; Pederson, M. R. *Phys. Rev. B* **1996**, *54*, 7830. (b) Reiher, M.; Liégeois, V.; Ruud, K. *J. Phys Chem. A* **2005**, *109*, 7567. (c) Quinet, O.; Champagne, B.; Van Gisbergen, Stan J. A. *Int. J. Quantum Chem.* **2006**, *106*, 599. (d) Ducasse, L.; Castet, F.; Fritsch, A.; Huc, I.; Buffeteau, T. *J. Phys. Chem. A* **2007**, *111*, 5092. (e) Liégeois, V.; Champagne, B. *J. Phys. Chem. A* **2011**, *115*, 13706. (f) Almeida, A. R.; Calatayud, M.; Tielens, F.; Moulijn, J. A.; Mul, G. J. *Phys. Chem. C* **2011**, *115*, 14164. (g) Bazso, G.; Tarczay, G.; Fogarasi, G.; Szalay, P. G. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6799. (h) Franzen, S.; Brown, D.; Gaff, J.; Delley, B. *J. Phys. Chem. B* **2012**, *116*, 10514. (i) Tetsassi Feugmo C.G.; Champagne, B.; Caudano, Y.; Cecchet, F.; Chabal, Y. J.; Liégeois, V.; *J. Phys.: Cond. Matter* **2012**, *24*, 124111.
- [4] (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R., Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J., Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654-65.
- [5] (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007-23. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358-71.
- [6] (a) Dunning, T. H., Jr.; Hay, P. J. in *Modern Theoretical Chemistry*, Ed. H. F. Schaefer III, Vol. 3 (Plenum, New York, 1976) 1-28. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-83. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284-98. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.
- [7] (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.
- [8] Perdew, J. P. *Phys. Rev B.* **1986**, *33*, 8822.
- [9] Hamprecht, F. A.; Cohen, A. J.; Tozer, D. J.; Handy, N. C. *J. Chem. Phys.* **1998**, *109*, 6264.
- [10] Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129.

- [11] (a) Leininger, T.; Stoll, H.; Werner, H.-J.; Savin, A. *Chem. Phys. Lett.* **1997**, 275, 151. (b) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. *J. Chem. Phys.* **2001**, 115, 3540.
- [12] Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, 393, 51-57.
- [13] Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, 128, 084106.
- [14] (a) Fedorovsky, M. PyVib2, A Program for Analyzing Vibrational Motion and Vibrational Spectra; 2007; <http://pyvib2.sourceforge.net> (b) Fedorovsky, M. *Comput. Lett.* **2006**, 2, 233. (c) Liégeois, V.; Champagne, B. *Theor. Chem. Acc.* **2012**, 131, 1284.
- [15] (a) Halls, M. D.; Schlegel, H. B. *J. Chem. Phys.* **1998**, 109, 10587. (b) Guthmuller, J.; Cecchet, F.; Lis, D.; Caudano, Y.; Mani, A.A.; Thiry, P. A.; Peremans, A.; Champagne, B. *ChemPhysChem* **2009**, 10, 2132. (c) Zvereva E. E.; Shagidullin, A. R. Katsyuba, S. A. *J. Phys. Chem A* **2011**, 115, 63. (d) Cecchet, F.; Lis, D.; Caudano, Y.; Mani, A. A.; Peremans, A.; Champagne, B.; Guthmuller, J. *J. Phys.: Condens. Matter* **2012**, 24, 124110.
- [16] (a) Troisi, A.; Ratner, M. A. *Nano Lett.* **2006**, 6, 1784. (b) Gagliardi, A.; Solomon, G.C.; Pecchia, A.; Frauenheim, T.; Di Carlo, A.; Hush, N.S.; Reimers, J. R. *Phys. Rev. B* **2007**, 75, 174306. (c) Troisi, A.; Beebe, J. M.; Picraux, L. B.; van Zee, R. D.; Stewart, D. R.; Ratner, M. A.; Kushmerick, J. G. *PNAS* **2007**, 104, 14255. (d) Troisi, A. *J. Phys. Condens. Matter* **2008**, 20, 374111. (e) Zou, B.; Li, Z-L.; Song, X-N.; Wang, C-K. *Chin. Phys. Lett.* **2008**, 25, 254.
- [17] (a) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, 100, 16502. (b) Irikura, K.K.; Johnson III, R.D.; Kacker, R.N. *J. Phys. Chem.* **2005**, 109, 8430. (c) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, 111, 11683.
- [18] Herrmann, C.; Solomon, G. C.; Subotnik, J. E.; Mujica, V.; Ratner, M. A. *J. Chem. Phys.* **2010**, 132, 024103.
- [19] Kula, M.; Jiang, J.; Luo, Y. *Nano. Lett.* **2006**, 6, 1693.
- [20] Mietrach, A.; Muesmann, T. W. T.; Christoffers, J.; Wickleder, M. S. *Eur. J. Inorg. Chem.* **2009**, 2009, 5328.
- [21] (a) Bouteiller, Y.; Gillet, J-C.; Grégoire, G.; Schermann, J. P. *J. Phys. Chem A* **2008**, 112, 11656-11660. (b) Bouteiller, Y.; Pouilly, J-C.; Desfrancois, C.; Grégoire, G. *J. Phys. Chem. A* **2009**, 113, 6301-6307.
- [22] (a) Jiménez-Hoyos C. A.; Janesko, B. G. Scuseria, G. E. *Phys. Chem. Chem. Phys.* **2008**, 10, 6621. (b) Laury, M. L.; Boesch, S. E.; Haken, I.; Sinha, P.; Wheeler, R. A.; Wilson, A. K. *J. Comput. Chem.* **2011**, 32, 2339.

Theoretical Insight into the Inelastic Electron Tunneling Spectra of an Anil Derivative

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IV. Theoretical Insight into the Inelastic Electron Tunneling Spectra of an Anil Derivative

IV.A. Introduction

Designing functionalized molecular systems able to mimic the logics of electronic circuits is of major interest in the domains of information transport and storage^[1]. These systems provide solutions in terms of devices miniaturization, processing speed, and memory capacities. Among these, molecular switches are suitable candidates because, upon reversible transformation between two or more states, they can exhibit important contrasts of physicochemical properties, such as optical absorption, fluorescence, nonlinear optical responses and conductivity. A broad range of external stimuli can trigger such commutations of molecular structures and properties, including light, temperature, pressure, redox potential, electrolytes, etc^[2].

Although studies have generally focused on the switching behavior of molecules in gas phase or in solution^[3], switching of molecules adsorbed to surfaces constitutes another challenge towards designing advanced functional materials^[4-6]. Among these molecular switches functionalizing surfaces, azobenzene is known to reversibly commute between an extended *trans* and a shorter *cis* configuration and *vice versa* when irradiated at 360 nm and 480 nm, respectively^[5d]. This leads to a large on/off current ratio after their immobilization on the surface. The change of electron transport properties has also been investigated for other compounds and other switching mechanisms^[5-6], including tautomerism^[5a], which involves an intramolecular proton transfer. The later reaction does not involve large geometric distortions of the molecular backbone and it has therefore the advantage of ensuring a good resistance to fatigue.

In the present study, theoretical approaches are employed to simulate and interpret the Inelastic Electron Tunneling (IET) spectra of two tautomeric forms: enol-imine (**E**) and keto-amine (**K**) of an anil molecule, represented in Fig. (IV.1). This study aims at further understanding and therefore controlling the switching between the **E** and **K** molecular states and thus, it extends recent investigations on the linear and nonlinear optical properties of anils in solutions and in the solid state^[3a,7]. The IET spectra have been simulated following the formalism introduced in Section II.C as implemented in the QCME code^[8,9]. In particular, we analyze the variations of IET responses upon switching between the keto and enol forms. This chapter is organized as follows: Section IV.B summarizes the theoretical and computational aspects, results are presented and discussed in Section IV.C whereas Section IV.D draws conclusions and outlook.

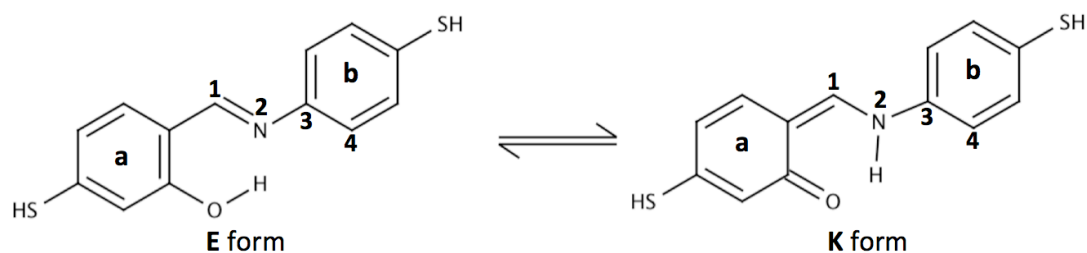


Fig. IV.1. Representation of the enol (**E**) and keto (**K**) tautomeric forms of the anil derivative and labeling of the **a** and **b** rings.

IV.B. Theoretical and computational aspects

Following the model presented in Section II.C.2, each of the two molecular devices is divided into three parts: two electron reservoirs constituted by metallic atoms, called the source (S) and the drain (D), and the molecule connecting them. However, only a small part of the metallic atoms can be considered in the quantum chemistry calculations due to heavy computational costs. This approximation leads to the modeling of an ‘extended molecule’ for representing the scattering region but it has been proved to be sufficient for having an accurate description of the metal-molecule-metal interface interactions because only the metallic atoms that are close to the molecule contribute significantly to the coupling coefficients^[10]. Moreover, we also know that the main contribution to the IET response comes from the molecular part. In our case, the ‘extended molecule’ is composed by the **E** or **K** form of the anil molecule [Fig. (IV.1)] of which the terminal thiol functions are dehydrogenated, sandwiched between two Au(111) surfaces, each containing twelve atoms.

The geometry of the isolated molecule has been optimized and, therefore, the characteristics of the frontier orbitals have been obtained. In a second step, the vibrational frequencies and normal modes of the extended molecule have been calculated together with the $\partial\Psi/\partial Q$ quantities. These calculations have been performed using DFT with the B3LYP exchange-correlation functional. The cc-pVTZ basis set provides a good compromise between accuracy and computational resources for evaluating the IET response^[11] (as proven in Chapter III) and therefore it has been employed for the non metal atoms, while the Au atoms are described with the LANL2DZ pseudo potential basis set. From these molecular properties, the IET spectra are then simulated using the QCME program. The temperature is fixed to 4.2 K and the full width at half maximum (FWHM) to 20 cm^{-1} , although the method is capable of predicting the linewidth. The vibrational frequencies were not scaled by the typical ~ 0.96 factor since we are interested in global trends and since no comparison with experiment is made.

The representation and analysis of the vibrational normal modes were performed using the PyVib2 program^[12]. We focused on the overlap matrices and on the similarities between the normal modes, which are here briefly presented. On a fragment F, the $O_{p'p}^{AB,F}$ overlap between mode p' of molecule A and mode p of molecule B is defined as the square of the scalar product between the two normal modes:

$$O_{p'p}^{AB,F} = \left\langle Q_{p'}^{A,F} \middle| Q_p^{B,F} \right\rangle^2 = \left(\sum_{i\alpha}^F Q_{i\alpha,p'}^A Q_{i\alpha,p}^B \right)^2$$

$Q_{i\alpha,p}^B$ is the mass-weighted Cartesian displacement of atom i in direction α for the p^{th} normal mode of molecule B. Each Q_p is normalized so that $\sum_{i\alpha}^{3N} (Q_{i\alpha,p})^2 = 1$. The similarity $S_{p'p}^{AB,F}$ refers to the resemblance between modes p and p' of molecules A and B and is given by:

$$S_{p'p}^{AB,F} = \frac{O_{p'p}^{AB,F}}{\left\langle Q_{p'}^{A,F} \middle| Q_{p'}^{A,F} \right\rangle \left\langle Q_p^{B,F} \middle| Q_p^{B,F} \right\rangle}$$

The overlap and similarity values are dimensionless and their values range from 0 to 1.

IV.C. Results and discussion

IV.C.1. IET spectra of the isolated anil derivative in its enol and keto forms

The IET spectra of the anil derivative simulated at the B3LYP/cc-pVTZ level of approximation display an obvious dependence on the tautomeric form [Fig. (IV.2)]. Indeed, the IET spectrum of the **E** form is dominated by a single mode (mode **46** at 1114 cm^{-1} or 138 mV) whereas there are three dominant peaks for the **K** form (modes **23**, **43**, and **66**) in addition to mode **1**. The characteristics of the main vibrational transitions of the **E** and **K** forms are respectively listed in Tables (IV.1) and (IV.2), whereas the corresponding atomic displacements of the normal modes are sketched in Fig. (IV.3).

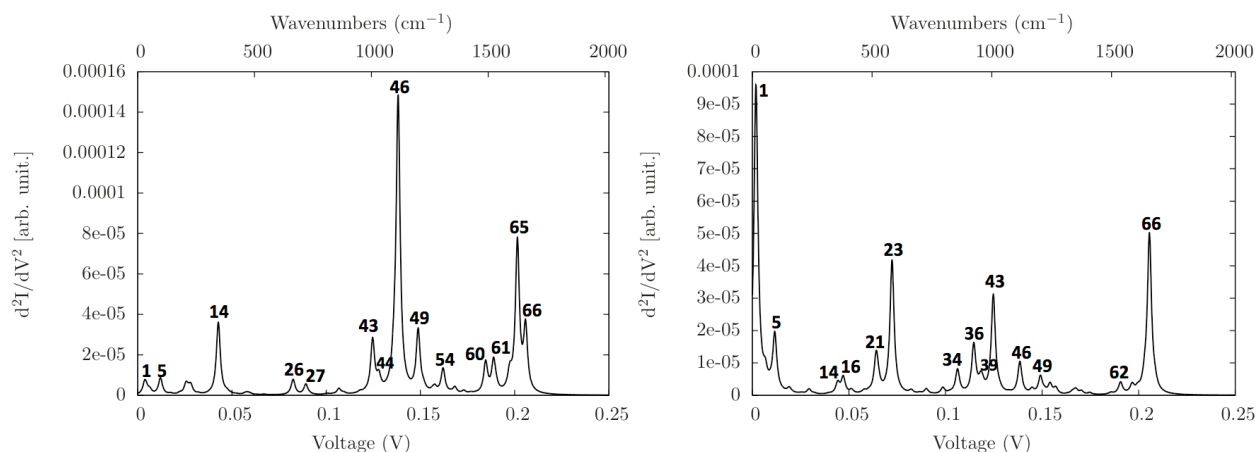


Fig. IV.2. B3LYP/cc-pVTZ IET spectrum of the **E** (left) and **K** (right) forms of the anil derivative. Peaks corresponding to vibrational modes with considerable IET intensity are numbered.

Peak #	Frequency	Potential	Intensity	Relative Intensity
1	30	4	7.69×10^{-6}	0.052
5	97	12	8.72×10^{-6}	0.059
14	345	43	3.61×10^{-5}	0.242
26	665	83	7.91×10^{-6}	0.053
27	719	89	5.69×10^{-6}	0.038
43	1005	125	2.86×10^{-5}	0.192
44	1032	128	1.27×10^{-5}	0.085
46	1114	138	1.49×10^{-4}	1.000
49	1200	149	3.33×10^{-5}	0.223
54	1308	162	1.35×10^{-5}	0.091
60	1489	185	1.75×10^{-5}	0.117
61	1523	189	1.89×10^{-5}	0.127
65	1625	201	7.80×10^{-5}	0.523
66	1660	206	3.75×10^{-5}	0.252

Table IV.1. Frequencies (cm^{-1}), potential (mV) and intensities (arb. units) of the vibrational modes dominating the IET spectrum of the isolated anil molecule in its **E** form, calculated at the B3LYP/cc-pVTZ level of approximation.

Peak #	Frequency	Potential	Intensity	Relative Intensity
1	15	2	9.59×10^{-5}	1.000
5	94	12	1.97×10^{-5}	0.205
14	357	44	4.60×10^{-6}	0.048
16	380	47	6.12×10^{-6}	0.064
21	517	64	1.39×10^{-5}	0.145
23	583	72	4.18×10^{-5}	0.436
34	857	106	8.23×10^{-6}	0.086
36	925	115	1.63×10^{-5}	0.170
39	953	118	7.56×10^{-6}	0.079
43	1006	125	3.12×10^{-5}	0.325
46	1117	139	1.05×10^{-5}	0.109
49	1203	149	6.23×10^{-6}	0.065
62	1538	191	4.19×10^{-6}	0.044
66	1658	206	5.03×10^{-5}	0.525

Table IV.2. Frequencies (cm^{-1}), potential (mV) and intensities (arb. units) of the vibrational modes dominating the IET spectrum of the isolated anil molecule in its **K** form, calculated at the B3LYP/cc-pVTZ level of approximation.

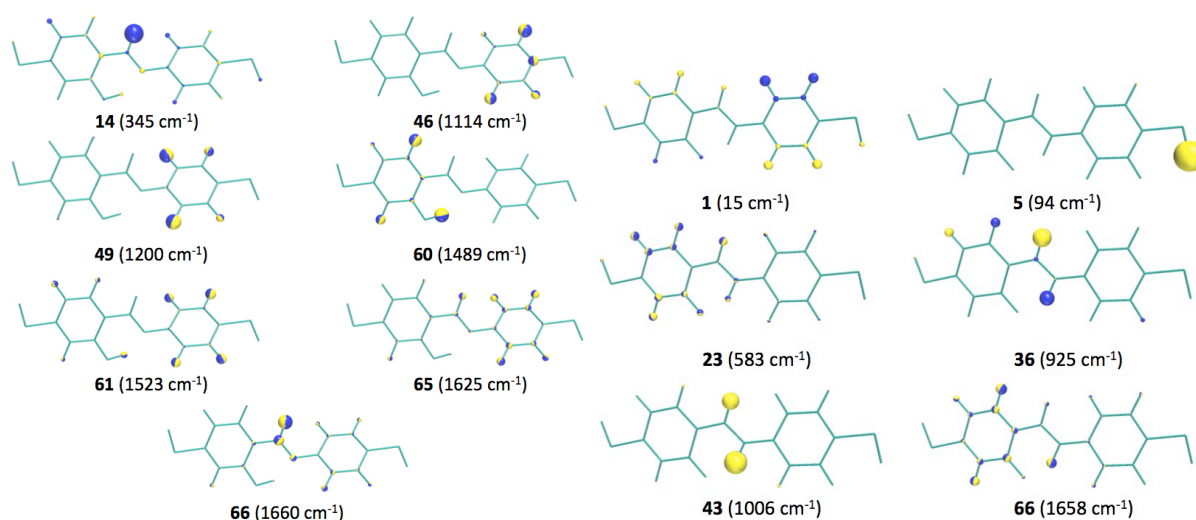


Fig. IV.3. Sketch of the vibrational normal modes corresponding to the dominant peaks of the IET spectrum of the isolated anil derivative in its **E** (left) and **K** (right) forms. The direction of atomic displacements is perpendicular to the junction plane between the two hemispheres of distinct color, and their amplitudes are proportional to the radius of the sphere. The sum of the surfaces of the spheres is always constant.

For the **E** form, the most intense transition (mode **46**) corresponds to in-plane bending motions of the 4 C-H bonds of ring **b** combined with a C-S stretching. This is a typical mode characterized by atomic displacements in the same direction as the tunneling current, which explains its large intensity^[13]. Contrary to mode **46** where the 4 C-H bonds bend in phase, in mode **49** the C-H bendings are out-of-phase and do not mix with C-S stretching. Its intensity is smaller than in mode **46**. Apparently, the large intensity of mode **46** is mostly associated with the C-S stretching motion since mode **61** is also mostly described by in-phase in-plane C-H bendings on the **b** ring but its intensity is small. Modes **60** and **65** also contain C-H bending motions. In mode **60**, these are localized on ring **a** and are combined with a C-O-H bending characteristic of the **E** form. Though these modes are dominated by C-H bending motions, ring distortions are also present, the latter ones are more intense in mode **65**, which describes the aromatic-to-quinoidic transition for **b** ring. Note that mode **65** (201 mV) is the second most intense after mode **46** and before mode **66** (206 mV). Mode **66** is a typical C=N stretching mode combined with N-C-H bending.

For the **K** form, besides mode **1**, the peak with the largest intensity (mode **66**) is also associated with C-H bending motions but on ring **a**. These motions on adjacent C atoms are out-of-phase and are combined with aromatic-to-quinoidic ring distortions. Mode **46** that was intense for the **E** form is now much weaker. The next peak in decreasing order of intensity is mode **23**, which corresponds to in-plane in-phase C-H bendings on ring **a**. Then come modes **43** and **5**, which together with mode **1** correspond to out-of-plane motions of the H atoms on the central C-

N unit, on the terminal S-H, and of the ring, respectively. So, among the dominant peaks, four of them are characteristic of the keto form by involving a bending of the N-H bond: out-of-plane for peaks **36** and **43** and in-plane for peaks **23** and **66**, for which a C=O stretching is also observed.

This analysis evidences that the different moieties of the anil derivative contribute to the main IET peaks and that there are variations of absolute and relative intensities along the **E-to-K** switching. To get more insight, a closer look at similarities and differences between the vibrational normal modes of the two forms is needed and is discussed in the next paragraph.

IV.C.2. Correlations between the vibrational normal modes of the tautomeric forms of the anil

An illustration of the correlation between the atomic displacements of the IET active modes of the two tautomeric forms is shown in Fig. (IV.4) for vibrational frequencies ranging between 835 and 1681 cm^{-1} .

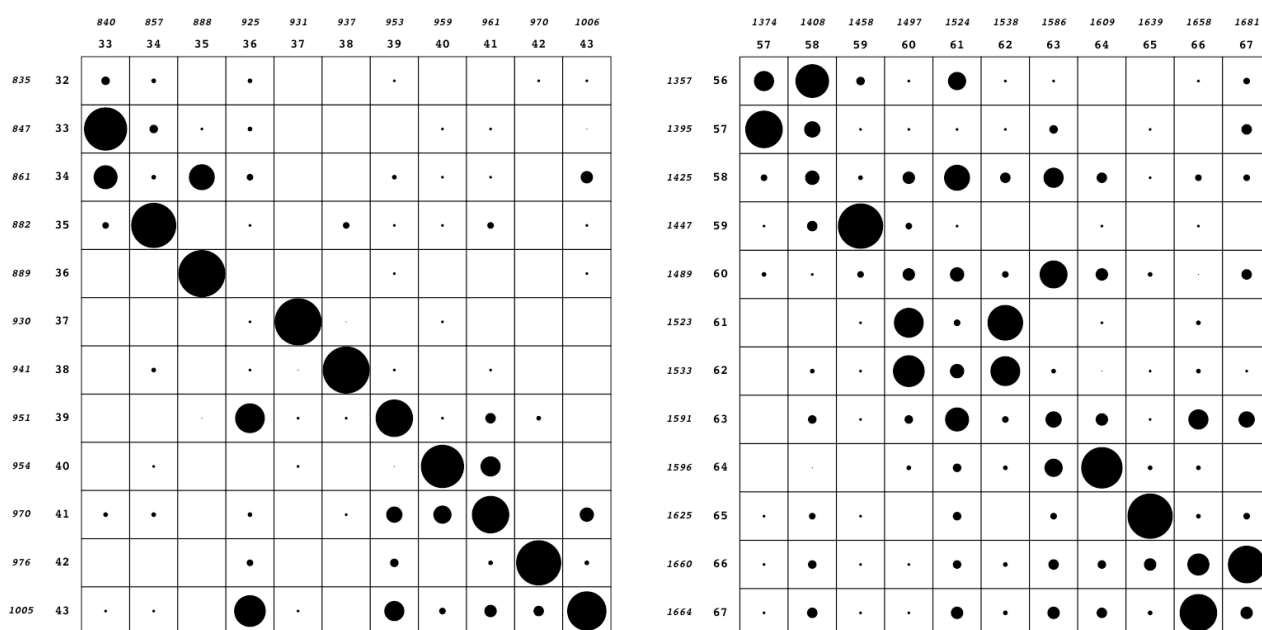


Fig. IV.4. Similarities $S^{AB,F}$ between the normal modes of the **E** and **K** forms. The rows and the columns of the matrix, labelled with normal mode numbers and frequencies, correspond to the **E** and **K** forms, respectively. The surface of the circles is proportional to the overlap between the corresponding pair of p and p' modes. The hydrogen atom migrating during the switching is not considered in the fragment F.

The small number of large circles enables to easily identify the correlations between the modes of each form and to conclude that mode mixings are rather limited. So, to one mode of the **E** form corresponds generally only one mode with substantial overlap of the **K** form, *e.g.* $(p,p') = (33,33), (35, 34), (36, 35), (37, 37), \dots$ On the other hand, for a few modes, more than one overlap

(and similarity) is important. This is typically the case of those modes involving displacements of the O-H of the **E** form and of the N-H of the **K** form. For instance, mode **64** of the enol (in-plane C-O-H bending) presents overlaps with modes **63** and **64** of the keto form. This is further supported by the sketch of the atomic displacements of the corresponding modes in Fig. (IV.5). *Vice versa*, mode **36** of the **K** form, corresponding to out-of-plane C-H and N-H displacements on the bridge between the two rings, presents the largest overlaps/similarities with modes **39** and **43** of the **E** form [Fig. (IV.5)]. We also observe that modes of the **E** form involving delocalized motions on the whole molecule are correlated with modes whose atomic displacements are localized on one of the two rings of the **K** form, as illustrated in Fig. (IV.5) for mode **61**. It can be explained by the geometric distortions induced by the intramolecular migration of the proton notably characterized by a change of torsion angle between the two rings **a** and **b** (see 1-2-3-4 in Fig. (IV.1)) going from 149° to 171° when switching from the **E** to **K** form, respectively. In addition, mode **23** which involves in-plane bending of C-H bonds of ring **a** becomes inactive when going from the **K** to the **E** form. The presence of small out-of-plane displacements of the hydrogen atoms of ring **b** combined with an in-plane C-O-H bending in the **E** form is postulated as an explanation for the inactivity. Thereby, the analysis of the similarity values between the IETS active modes of the **E** and **K** forms [Table (IV.3)] shows that in-plane bending of C-H bonds of ring **b** and out-of-plane bending of the C₁-H bond are the two main vibrational contributions to the activity of IET modes.

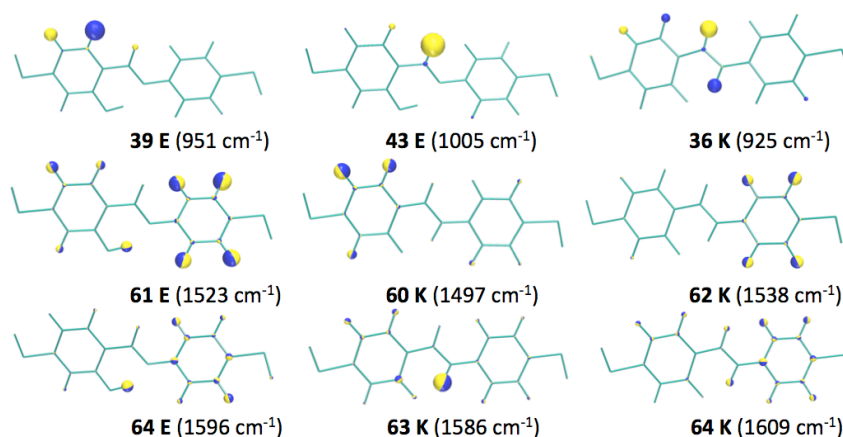


Fig. IV.5. Sketch of the vibrational normal modes correlated to characteristic modes of the **E** (mode **64**, in-plane C-O-H bending) and **K** (mode **36**, out-of-plane motions of the N-H linked C-H bonds) forms.

E form peak (A)		K form peak (B)		K form displacements common to those of the E form	$S^{AB,F}$	$\frac{\partial^2 I / \partial V^2(\mathbf{K})}{\partial^2 I / \partial V^2(\mathbf{E})}$
Mode #	Peak (mV)	Mode #	Peak (mV)			
5	12	5	12	out-of-plane S-H bending	0.893	2.3
14	43	14	44	out-of-plane C-H and S-H bendings of ring b	0.303	0.1
		16	47	out-of-plane C ₁ -H bending	0.473	0.2
23	73	23	72	in-plane C-H bendings of ring a and of C ₁ -H bond	0.929	95.4
39	118	36	115	out-of-plane C-H bendings of ring a and of C ₁ -H bond	0.406	6.0
43	125	36		out-of-plane C ₁ -H bending	0.461	0.6
		43	125	out-of-plane C ₁ -H bending	0.642	1.1
46	138	46	139	in-plane C-H bendings of ring b and C-S stretching	0.977	0.1
49	149	49	149	in-plane C-H bendings of ring b	0.735	0.2
61	189	60	186	in-plane C-H bendings of ring a	0.396	0.1
		62	191	in-plane C-H bendings of ring b	0.529	0.2
65	201	65	203	in-plane C-H bendings of ring b with C=C stretchings	0.867	0.2
66	206	66	206	C=C stretchings of rings a and b	0.219	1.3
		67	208	in-plane C ₁ -H bending	0.602	0.1
67	206	66	206	in-plane distortion motions of ring a	0.587	14.0

Table IV.3. Similarity $S^{AB,F}$ values describing the correlation between the vibrational IET active modes of the **E** (A) and **K** (B) forms of the isolated anil derivative. The modes displayed in red and black color refer to modes with a high and weak IET intensity, respectively. The hydrogen atom migrating during the switching is not considered in the fragment F. The first and third columns display the mode numbers whereas the second and fourth columns the potential at which they appear.

IV.C.3. IET spectra of the anil derivative between Au plates

In a second step, IET spectra of molecular junctions between Au electrodes are simulated. The junctions consist in the anil molecules having dehydrogenated terminal thiol functions sandwiched between Au electrodes. Following the approach adopted in recent investigations^[14] ensuring a good reproducibility of experimental results when using such structure and size of electrodes, each of them is represented by an Au(111) surface containing 12 atoms with interatomic distances of 2.88 Å. It also offers a good compromise between accuracy and computational needs and allows to prevent edge effects. The molecule is oriented such that the S-S axis of the anil forms an angle of 13° with respect to the normal to the electrode planes while the terminal S atoms are in bridge (source) and on-top (drain) positions to the Au (111) surface. The distance between the S atom and the gold electrode was fixed after determining the energy profile of the whole system as a function of the width of the junction. It enables to know from which distance the system becomes steady. The distance between the plates attains typically 20.46 Å, which corresponds to shortest Au-S distances of 3.68 Å (source) and 3.72 Å (drain). The corresponding IET spectra calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation are sketched in Fig. (IV.6). The characteristics of the main vibrational transitions of the **E** and **K** forms of the Au-sandwiched molecules are listed in Tables (IV.4) and (IV.5) and the vibrational modes related to the dominant peaks are illustrated in Fig. (IV.7).

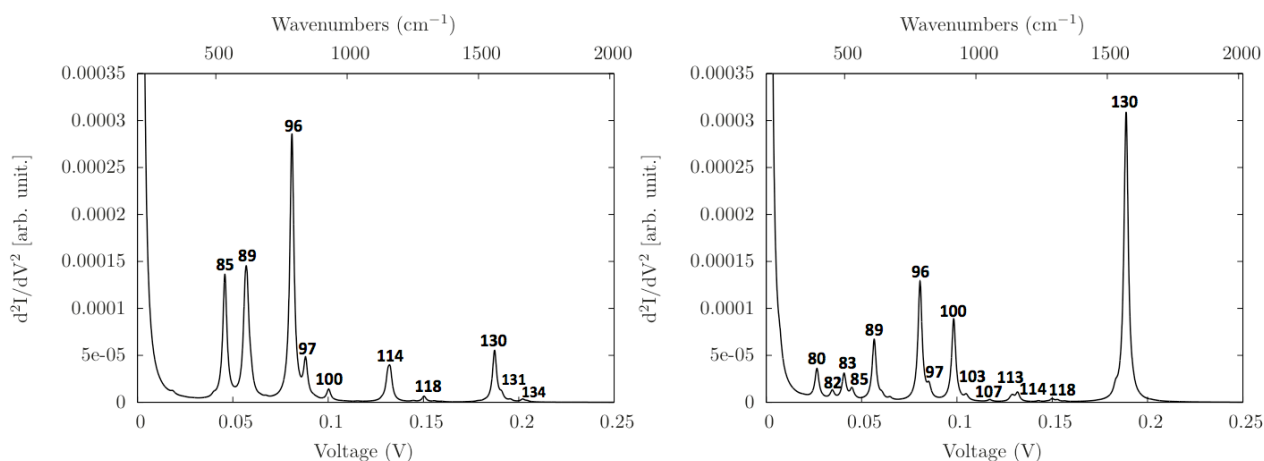


Fig. IV.6. IET spectrum of the **E** (left) and **K** (right) forms of the anil derivative between Au electrodes calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation. Peaks corresponding to vibrational modes with considerable IET intensity are numbered.

Peak #	Frequency	Potential	Intensity	Relative Intensity
85	370	46	1.36×10^{-4}	0.476
89	464	58	1.38×10^{-4}	0.483
96	653	81	2.86×10^{-4}	1.000
97	711	88	4.86×10^{-5}	0.170
100	809	100	1.41×10^{-5}	0.049
114	1069	133	3.83×10^{-5}	0.134
118	1212	150	6.53×10^{-6}	0.023
130	1512	188	5.42×10^{-5}	0.190
131	1540	191	1.24×10^{-5}	0.043
132	1578	196	3.72×10^{-6}	0.013
134	1630	202	3.57×10^{-6}	0.012

Table IV.4. Frequencies (cm^{-1}), potential (mV) and intensities (arb. units) of the vibrational modes dominating the IET spectrum of the **E**-form anil molecule between Au electrodes, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation.

Peak #	Frequency	Potential	Intensity	Relative Intensity
80	214	27	3.62×10^{-5}	0.118
82	279	35	1.34×10^{-5}	0.044
83	329	41	3.12×10^{-5}	0.102
85	363	45	1.59×10^{-5}	0.052
89	457	57	6.72×10^{-5}	0.220
96	651	81	1.29×10^{-4}	0.422
97	689	85	2.20×10^{-5}	0.072
100	793	98	8.89×10^{-5}	0.291
103	846	105	9.18×10^{-6}	0.030
107	946	117	3.02×10^{-6}	0.010
113	1042	129	8.47×10^{-6}	0.028
114	1063	132	1.11×10^{-5}	0.036
118	1209	150	4.00×10^{-6}	0.013
130	1524	189	3.06×10^{-4}	1.000

Table IV.5. Frequencies (cm^{-1}), potential (mV) and intensities (arb. units) of vibrational modes dominating the IET spectrum of the **K**-form anil molecule between Au electrodes, calculated with the B3LYP/cc-pVTZ/LANL2DZ method.

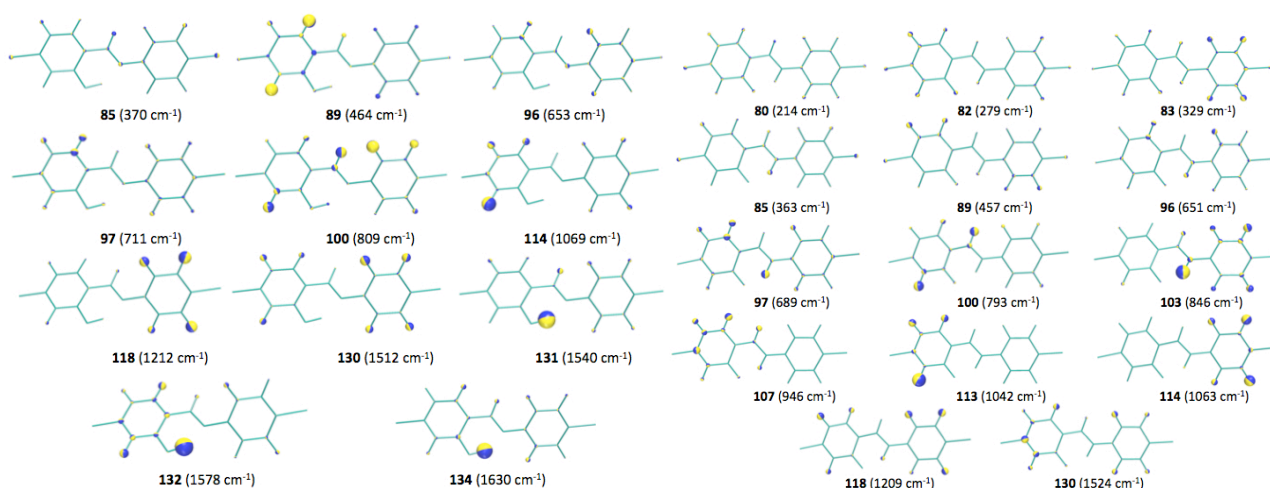


Fig. IV.7. Sketch of the vibrational normal modes corresponding to the dominant peaks of the IET spectrum of the **E**-(left)- and **K**-(right)-form anil derivative between Au electrodes.

The IET spectrum of the anil **E** form is strongly modified when sandwiched between Au electrodes, the electrodes having an impact on both the frequencies and the absolute and relative intensities. Considering the peak with the largest intensity, the presence of the Au plates leads to an intensity increase of 92% (mode **96** versus mode **46**). The IET spectrum is dominated by mode **96** (653 cm⁻¹) with other intense transitions at 370 cm⁻¹ (mode **85**) and 464 cm⁻¹ (mode **89**). Mode **89** corresponds to an out-of-plane distortion of the anil whereas modes **85** and **96** involve in-plane, longitudinal-like atomic motions.

Substantial modifications of the IET spectrum are also observed for the **K** form. Here the dominant peak is associated with mode **130** (1524 cm⁻¹), corresponding to C-H bending displacements on both the **a** and **b** rings. Its intensity is about 6 times larger than that of mode **66** in the isolated species. The next modes in decreasing order of intensities are modes **96**, **100**, and **89**, which all correspond to longitudinal atomic motions and in-plane distortions of the anil derivative.

IV.C.4. Correlations between the vibrational normal modes of the isolated and the Au-sandwiched anil molecules

To analyze the influence of the gold electrodes on the IET response, a correlation between the IET-active vibrational normal modes of the isolated and Au-sandwiched anil molecules was performed. The similarity values for the **E** and **K** forms are reported in Tables (IV.6) and (IV.7), respectively. To focus on the anil core signatures, the Au atoms are not included in the fragment F.

Isolated molecule (A)		Au-sandwiched molecule (B)		isolated molecule displacements common to those of the Au-sandwiched anil molecule	$S^{AB,F}$	$\frac{\partial^2 I / \partial V^2 (A)}{\partial^2 I / \partial V^2 (B)}$
Mode #	Peak (mV)	Mode #	Peak (mV)			
26	83	96	81	in-plane distortions of the anil	0.861	0.0
27	89	97	88	in-plane distortions of the anil	0.654	0.1
43	125	108	122	out-of-plane bending of C ₁ -H bond and of C-H bonds of ring a	0.170	19.3
43		109	124	out-of-plane bending of C ₁ -H bond and of C-H bonds of ring a	0.475	14.9
45	136	114	133	in-plane bending of C-H bonds of ring a and stretching of C-S bond	0.656	1.2
46	138	113	131	in-plane bending of C-H bonds of ring b and stretching of C-S bond	0.323	4.1
		114	133	in-plane bending of C-H bonds of ring b and stretching of C-S bond	0.205	3.9
49	149	117	145	in-plane bendings of C-H bonds of ring b ; stretching of C=N bond	0.600	16.5
50	152	118	150	in plane bending of C ₁ -H bond and of C-H bonds of ring b	0.758	1.3
60	185	128	182	in-plane C-O-H bending and in-plane distortions of ring a	0.479	4.4
		131	191	in-plane C-O-H bending	0.166	1.4
61	189	129	187	in-plane bendings of C-H bonds of rings a and b and of C-O-H group	0.679	0.3
62	190	130	188	in-plane bendings of C-H bonds of rings a and b	0.653	0.2
65	201	131	191	in-plane: C-H bendings of ring b with C=C stretchings and C ₁ -H bending	0.323	6.3
		132	196	in-plane: distortions of rings a and b (C=C stretchings) and C ₁ -H bending	0.268	21.0
66	206	134	202	in-plane: C-H bendings of ring b with C=C stretchings and C ₁ -H bending	0.360	10.5
		135	204	C=N stretching with a N-C-H bending ; in-plane C-H bendings of ring b	0.544	17.4

Table IV.6. Similarity $S^{AB,F}$ values describing the correlation between the vibrational IET active modes of the **E** form of the isolated (A) and Au-sandwiched (B) anil molecules. The modes displayed in red and black color refer to modes with a high and weak IET intensity, respectively. The first and third columns display the mode numbers whereas the second and fourth columns the potential at which they appear.

Isolated molecule (A)		Au-sandwiched molecule (B)		isolated molecule displacements common to those of the Au-sandwiched anil molecule	$S_{AB,F}$	$\frac{\partial^2 I / \partial V^2 (A)}{\partial^2 I / \partial V^2 (B)}$
Mode #	Peak (mV)	Mode #	Peak (mV)			
21	64	92	66	in-plane C ₁ -H bending ; out-of-plane bendings of C-H bonds of ring b	0.863	2.7
23	72	93	71	in-plane C ₁ -H bending ; in-plane distortions of ring a	0.930	11.1
26	82	96	81	in-plane distortions of the anil	0.912	0.0
31	99	100	98	in-plane C ₁ -H bending ; in-plane distortions of ring a	0.932	0.0
34	106	103	105	in-plane N-H and C ₁ -H displacements ; in-plane distortions of ring b	0.948	0.9
36	115	106	115	out-of-plane bendings of the N-H and C ₁ -H bonds	0.786	9.2
39	118	108	122	top of ring a : out-of-plane bending of C-H bonds	0.845	6.1
43	125	111	127	out-of-plane bendings of the N-H and C ₁ -H bonds	0.698	10.1
46	139	114	132	in-plane bending of the 4 C-H bonds of ring b and C-S stretching	0.656	0.9
49	149	117	147	in-plane bendings of C-H bonds of rings a and b ; in-plane N-H bending	0.895	3.6
61	189	130	189	in-plane distortions of ring a with C=C stretchings ; C=O stretching	0.736	0.0
66	206	134	202	in-plane distortions of ring a with C=C stretchings ; C=O stretching	0.759	14.6

Table IV.7. Similarity $S^{AB,F}$ values describing the correlation between the vibrational IET active modes of the **K** form of the isolated (A) and Au-sandwiched (B) anil molecules. The modes displayed in red and black color refer to modes with a high and weak IET intensity, respectively. The first and third columns display the mode numbers whereas the second and fourth columns the potential at which they appear.

For the **E** form, only a few vibrational modes of the isolated molecule present a substantial overlap with single mode of the sandwiched molecule, meaning that the introduction of Au-electrodes lead to significant modifications of the IET response. Such one-to-one relationship notably concerns modes **(26,96)** and **(27,97)**, referring both to in-plane distortions of the anil. In addition to that, an increase of their IET intensity is noticed after the introduction of Au electrodes around the anil molecule [Tables (IV.1) and (IV.4)]. For other modes, more than one similarity index is large. For example, the atomic displacements of mode **65** of the isolated **E**-form, characterized by C-H bending and C=C stretching motions of rings **a** and **b** are observed in modes **132** and **131**, respectively. Similarly, the vibrational motions of mode **66** are shared among two modes of the Au-sandwiched molecule: i) the in-plane bendings of the C-H bonds of ring **b** together with the C=C stretchings match mode **134**, while ii) the stretching of the C=N is recovered in mode **135**. Another example concerns the mode **45 (46)** which is mainly correlated to mode **114 (113)** and presents a small contribution from mode **113 (114)** [Fig. (IV.8)]. The higher IET intensity of mode **114** with respect to mode **113** is attributed to the two C-S stretching motions on both sides of the anil inducing longitudinal motions in the same direction as the tunneling current. For a few modes, the significant change of IET intensity observed when the molecule is placed between Au electrodes is not related to changes of the vibrational motions. This is the case of the pair of modes **(50,118)** [Fig. (IV.8)], having a similarity value 0.758, respectively.

For the **K** form, most of the vibrational modes are also characterized by a large change of the IET activity upon sandwiching between Au plates, even though the vibrational motions remain very similar, as highlighted by similarity values larger than 0.7 for most modes of interest [Table (IV.7)]. This is further illustrated by the sketch of the atomic displacements of the vibrational modes [Fig. (IV.9)]. It means that the IET response strongly depends on the molecular configuration and thereby that the electronic properties are highly affected by the presence of the Au atoms.

For both tautomeric forms, the IET active modes involving out-of-plane bending motions become inactive when the molecule is placed between electrodes. Indeed, the direction of vibrational motions, which is perpendicular to the normal to the electrode planes leads to a small coupling with the metal. For the **E** and **K** forms, this is illustrated with pairs of modes **(43,108)**, **(43,109)** and **(21,92)**, **(36,106)**, **(39,108)**, **(43,111)**, respectively [Fig. (IV.10)].

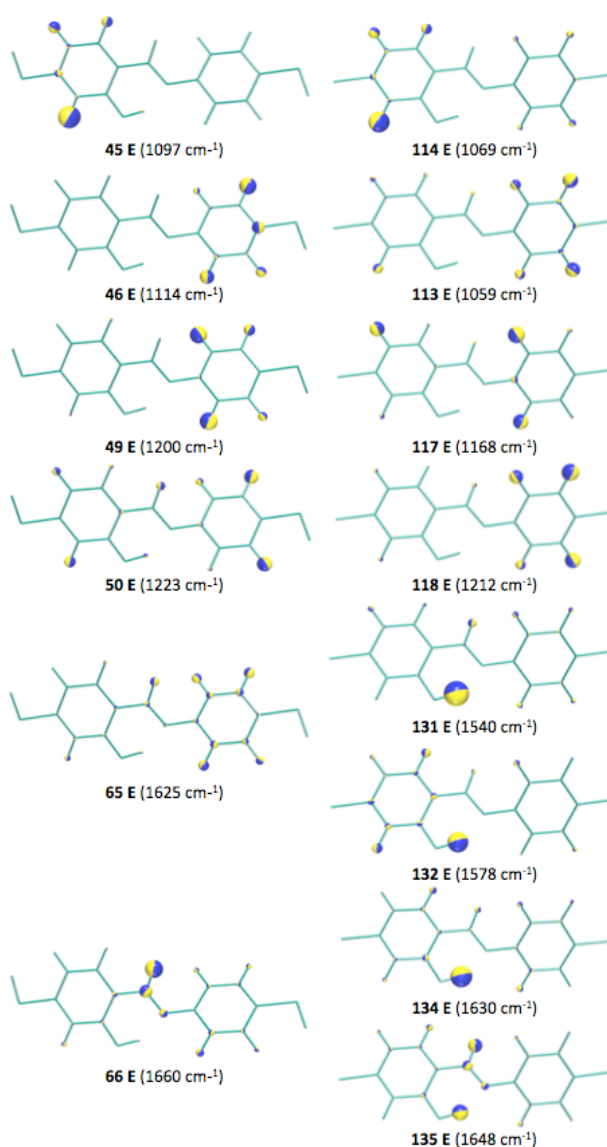


Fig. IV.8. Illustration of the correlation table between the vibrational normal modes of the isolated E anil and of its Au-sandwiched analog.

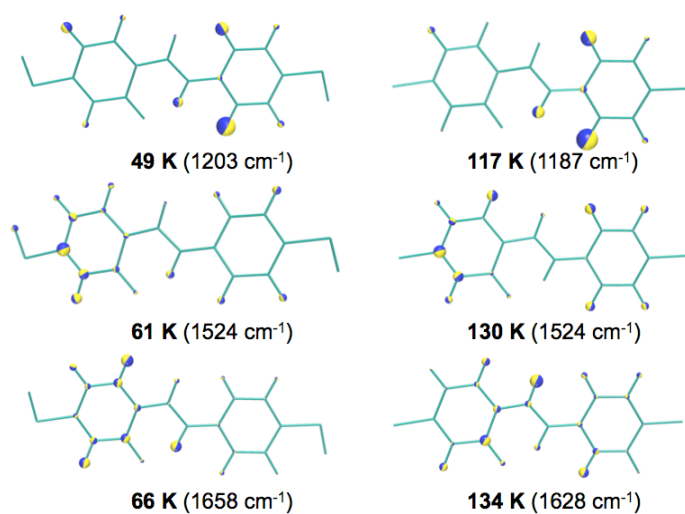


Fig. IV.9. Illustration of the correlation table between the vibrational normal modes of the isolated K anil and of its Au-sandwiched analog.

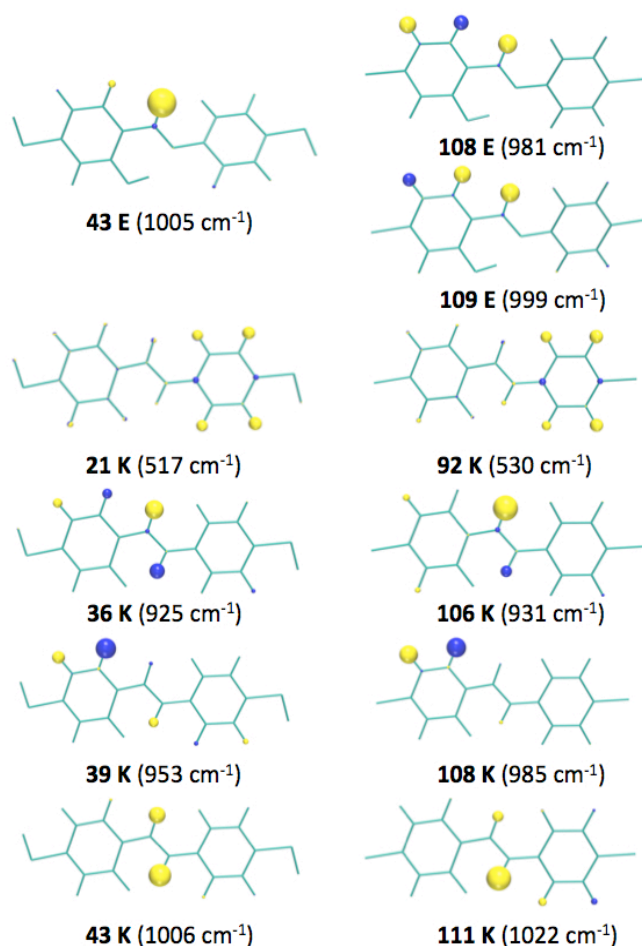


Fig. IV.10. Illustration of the correlation table between the vibrational normal modes involving out-of-plane motions of the isolated anil and of its Au-sandwiched analog.

IV.C.5. Correlations between the vibrational normal modes of the tautomeric forms of the Au-sandwiched anil molecules

Fig. (IV.11) compares the IET spectra of the **E** and **K** forms in both the isolated and intercalated configurations while the **E** versus **K** similarity values are reported in Table (IV.8) for the intercalated structure. For a few IET active modes, to one mode of the **E** form corresponds one mode of the **K** form with a substantial similarity value. In particular, it concerns modes **96**, **97**, and **85** that involve in-plane distortions of the anil and in-plane longitudinal atomic motions, as well as mode **100**. This observation is accompanied by higher intensity values for modes of the **E** form than for the **K** form, except for mode **100**, as illustrated in Fig. (IV.11). Concerning modes **96**, **97** and **85**, this difference of intensity may be explained by the presence of an in-plane bending of the N-H bond observed in the **K** forms [Fig. (IV.7)]. Similarly, if one compares the intensity values of modes **100** in both tautomeric forms the increase of the intensity when going from the **E** to the **K** form is related to the presence of an out-of-plane C-H bendings of ring **b** in the **E** form (the molecule is not planar).

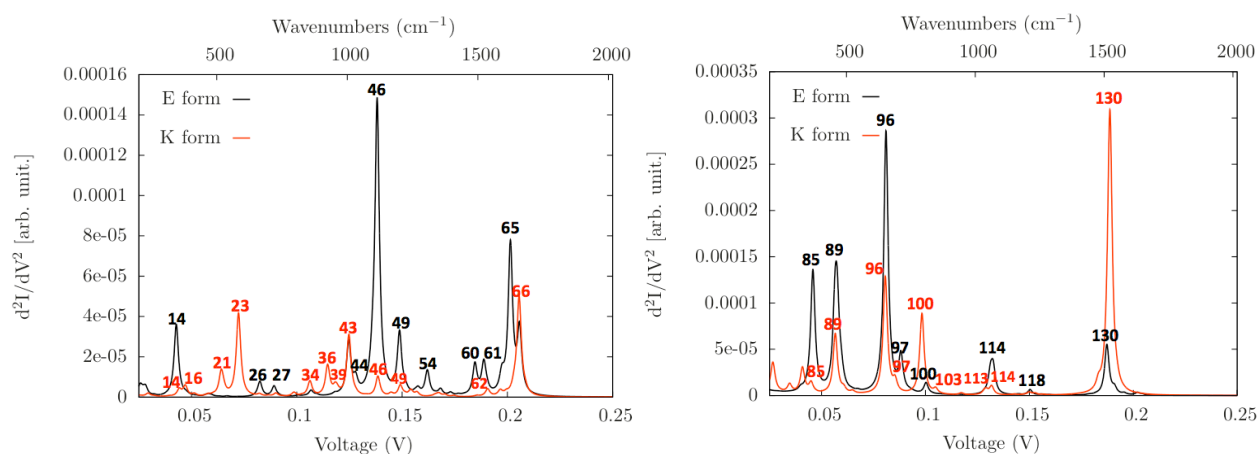


Fig. IV.11. IET spectrum of the **E** and **K** forms of the isolated (left) and sandwiched between Au electrodes anil derivative (right), calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation. Peaks corresponding to vibrational modes with considerable IET intensity are numbered.

For the other IET active modes, more than one similarity index is large. Mode **89** of the **E** form correlated to modes **88** and **89** of the **K** form (with similarity values of 0.475 and 0.465, respectively) illustrates it. The IET activity of mode **89** is therefore attributed to the C-S stretching motions on both sides inducing longitudinal motions in mode **89**, absent in mode **88**. Another example concerns pairs of modes (**118,118**) and (**118,119**) for which the IET activity of modes **118** is related to in-phase bending motions of C-H bonds of the two rings.

As observed for the correlation between the vibrational modes of the tautomeric forms of the isolated species (Section IV.C.2), a few modes of the **E** form characterized by delocalized atomic displacements on the whole molecule are correlated with modes whose atomic motions are localized on one of the two rings of the **K** form. For the **E**-form derivative between Au electrodes, it can be illustrated with mode **114** [Fig. (IV.7)] correlated to modes **113** and **114** of the **K** form with similarity values of 0.720 and 0.240, respectively. Indeed, mode **113** (**K**) involves in-plane C-H bending motions of ring **a** combined with C-S stretching, while mode **114** (**K**) is characterized by the same motions but localized on ring **b**. It concerns also mode **130** of the **E** form correlated to modes **128** and **129** of the **K** form that involve the same atomic motions as mentioned for modes **113** and **114** of form **K**, respectively. The only difference lays in the absence of C-S stretching in modes **128** and **129** of the **K** form, which can be related to the IET-inactivity of these latter modes.

Considering the vibrational modes involving moieties specific to each tautomeric form, the sandwiched configurations also present distinguishable signatures. For example, mode **130** of the **K** form corresponding to in-phase C=O and adjacent C=C stretching motions (in ring **a**) presents the largest intensity of the whole spectrum. On the other hand, the peak associated to mode **130** of

the **E** form appearing at a similar voltage is only six times less intense, what already suggests the potential interest of using the IET technique as a qualitative analysis tool and encourages future experimental measurements on this anil derivative. Note that mode **130** of the **K** form is correlated to several IET active modes of the **E** form, for example the C=C stretching observed in ring **a** is found in mode **132** and the in-plane bendings of ring **b** are observed in mode **130**. For the **E** form, we can also point out the specific modes **131**, **132** and **134** [Fig. (IV.7)] characterized by the in-plane bending motions of the C-O-H groups, while for the **K** form, we can mention specific modes **103** and **107** [Fig. (IV.7)] involving in-plane bending motions of the C-N-H group. Even if these peaks present weaker intensities in comparison to the mode **130** they remain clear signatures of each tautomeric form.

Finally, as in the previous correlations between the vibrational normal modes of the isolated and the Au-sandwiched anil molecule, out-of-plane motions remain unfavorable to the IET activity. It can be illustrated with pairs of modes (**108,106**) and (**108,108**), characterized by out-of-plane motions of the C-H bonds of ring **a**, associated with an out-of plane bending motion of the C₁-H bond [Fig. (IV.10)].

Thereby, for the two studied configurations of the molecule: isolated and sandwiched between Au electrodes, the comparison between the IET responses of the **E** and **K** forms highlights significant changes in the peak intensities, meaning that that this technique strongly depends on the structure and on the molecular conformation. The analysis of the similarity values between the IET active modes of the **E** and **K** forms in these two configurations shows that in-plane longitudinal atomic motions contribute to the IET activity of vibrational modes and are thereby associated to the paths that the electrons follow as they traverse the molecular junctions.

E form (A)		K form (B)		E form displacements common to those of the K form	$S^{AB,F}$	$\frac{\partial^2 I / \partial V^2 (K)}{\partial^2 I / \partial V^2 (E)}$
Mode #	Peak (mV)	Mode #	Peak (mV)			
85	46	85	45	in-plane longitudinal atomic motions	0.920	0.1
88	57	89	57	stretching of the C-S bonds and in-plane C-H bendings of ring b	0.485	0.5
89	58	88	56	out-of-plane bendings of C-H bonds of ring a and of C ₁ -H bond	0.475	0.0
		89	57	stretching of the C-S bonds	0.465	0.5
96	81	96	81	in-plane distortions of the anil	0.923	0.5
97	88	97	85	in-plane distortions of the anil	0.918	0.5
100	100	100	98	in-plane distortions of ring a ; in-plane C ₁ -H bending	0.885	6.3
114	133	113	129	in-plane C-H bendings of ring a with a C-S stretching	0.720	0.2
		114	132	in-plane C-H bendings of ring b with C-S stretchings	0.240	0.3
118	150	118	150	in-plane C-H bendings of ring b	0.671	0.6
		119	153	in-plane C-H bendings of ring b	0.260	0.5
128	182	130	189	in-plane distortions of ring a with C=C stretchings	0.237	76.1
130	188	128	183	in-plane C-H bendings of ring a	0.194	0.5
		129	188	in-plane C-H bendings of ring b	0.494	2.0
		130	189	in-phase C-H bending displacements on both a and b rings	0.218	5.6
132	196	130	189	in-plane distortions of ring a with C=C stretchings	0.225	82.3

Table IV.8. Similarity $S^{AB,F}$ values describing the correlation between the vibrational IET active modes of the **E** (A) and **K** (B) forms of the Au-sandwiched anil molecules. The modes displayed in red and black color refer to modes with a high and weak IET intensity, respectively. The hydrogen atom migrating during the switching is not considered in the fragment F. The first and third columns display the mode numbers whereas the second and fourth columns the potential at which they appear. The last column contains the intensity ratios.

IV.D. Conclusions

The IET spectra of the enol and keto forms of an anil molecular switch have been simulated from first principles calculations and analyzed with respect to the character of the vibrational normal modes. When the molecules are sandwiched between Au plates, the dominant IET signatures appear at very similar voltages for both forms but their intensities are clearly different (intensity ratios going from 0.1 for mode **85** and 0.5 for modes **96** and **97** to 6.3 for mode **100**), which makes IET an efficient technique to probe the molecular state of switches. Most of these IET-active modes consist of in-plane molecular motions, C-C and ring stretching as well as C-H bending motions, and there are little differences between the two forms. Moreover, the IET activity of vibrational modes involving bending motions of the C-O-H and C-N-H groups, respectively specific to the enol and keto forms, shows that IET spectroscopy is an efficient technique to characterize the molecular states of switches. Theoretical calculations have also shown that the enol form adopts a less planar structure than the keto form.

In addition to be sensitive to the molecular configuration, simulations of IET spectra highlight the impact of the gold electrodes on the positions and intensities of the vibrational signatures.

IV.E. References.

- [1] (a) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777; (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685; (c) Bouas-Laurent, H.; Durr, H. *Pure Appl. Chem.* **2001**, *73*, 639 (d) Feringa, B. L. *Molecular Switches*, Wiley-VCH, Weinheim, 2001; (e) Raymo, F.; Tomasulo, M. *Chem. Eur. J.* **2006**, *12*, 3186; (f) Gust, D.; Moore, T.A.; Moore, A. L. *Chem. Commun.* **2006**, 1169; (g) de Silva, A.P.; Vance, T.P.; West, M. E. S.; Wright, G. D. *Org. Biomol. Chem.* **2008**, *6*, 2468.
- [2] (a) Coe, B. J. *Chem. Eur. J.* **1999**, *5* (9), 2464; (b) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817; (c) Antonov, L.; Fabian, W.M.F.; Taylor, P. J. *J. Phys. Org. Chem.* **2005**, *18*, 1169; (d) Sanguinet, L.; Pozzo, J. L.; Rodriguez, V.; Adamietz, F.; Castet, F.; Ducasse, L.; Champagne, B. *J. Phys. Chem. B* **2005**, *109*, 11139; (e) Boggio-Pasqua, M.; Bearpark, M. J.; Ogliaro, F.; Robb, M.A. *J. Am. Chem. Soc.* **2006**, *128*, 10533; (f) Zakharova, M.I.; Coudret, C.; Pimienta, V.; Micheau, J. C.; Delbaere, S.; Vermeersch, G.; Metelitsa, A.V.; Voloshin, N.; Minkin, V. I. *Photochem. Photobiol. Sci.* **2010**, *9*, 199; (g) Broman, S.L.; Petersen, M. Å.; Tortzen, C.G.; Kadziola, A.; Kilså, K.; Nielsen, M. B. *J. Am. Chem. Soc.* **2010**, *132*, 9165.
- [3] (a) Sliwa, M.; Létard, S.; Malfant, I.; Nierlich, M.; Lacroix, P.G.; Asahi, T.; Masuhara, H.; Yu, P.; Nakatani, K. *Chem. Mater.* **2005**, *17*, 4727; (b) Aubert, V.; Guerschais, V.; Ishow, E.; Hoang-Thi, K.; Ledoux, I.; Nakatani, K.; Le Bozec, H. *Angew. Chem. Int. Ed.*, **2008**, *47*, 577; (c) Boubekeur-Lecaque, L.; Coe, B.J.; Clays, K.; Foerier, S.; Verbiest, Th.; Asselberghs, I. *J. Am. Chem. Soc.*, **2008**, *130*, 3286; (d) Mançois, F.; Pozzo, J. L.; Pan, J.; Adamietz, F.; Rodriguez, V.; Ducasse, L.; Castet, F.; Plaquet, A.; Champagne, B. *Chem. Eur. J.* **2009**, *15*, 2560; (e) Gauthier, N.; Argouarch, G.; Paul, F.; Toupet, L.; Ladjarafi, A.; Costuas, K.; Halet, J. F.; Samoc, M.; Cifuentes, M. P.; Corkery, T. C.; Humphrey, M. G. *Chem. Eur. J* **2011**, *17*, 5561; (f) Liu, C. G.; Guan, X. H.; Su, Z. M. *J. Phys. Chem. C* **2011**, *115*, 6024.
- [4] van der Molen, S.J.; Liljeroth, P. *J. Phys.: Condens. Mater.* **2010**, *22*, 133001.
- [5] (a) Liljeroth, P.; Repp, J.; Meyer, G. *Science* **2007**, *317*, 1203; (b) Huang, J.; Li, Q.; Ren, H.; Su, H.; Shi Q. W.; Yang J. *J. Chem. Phys.* **2007**, *127*, 094705; (c) Piantek, M.; Schulze, G.; Koch, M.; Franke, K. J.; Leyssner F.; Krüger A.; Navio, C.; Miguel, J.; Bernien M.; Wolf M.; Kuch W.; Tegeder P.; Pascual, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 12729; (d) Karpe S.; Oçafrain, M.; Smaali, K.; Lenfant, S.; Vuillaume, D.; Blanchard, P.; Roncali, J. *Chem Commun.* **2010**, *46*, 3657.
- [6] (a) Frederich, N.; Nysten, B.; Muls, B.; Hofkens, J.; Habib Jiwan, J. L.; Jonas, A. M. *Photochem. Photobiol. Sci.* **2008**, *7*, 460; (b) Simao, C.; Mas-Torrent, M.; Casado-Montenegro, J.; Oton, F.; Veciana, J.; Rovira, C. A. *J. Am. Chem. Soc.* **2011**, *133*, 13256.
- [7] (a) Sliwa, M.; Mouton, N.; Ruckebusch, C.; Aloïse, S.; Poizat, O.; Buntinx, G.; Métivier, R.; Nakatani, K.; Masuhara, H.; Asahi, T. *J. Phys. Chem. C* **2009**, *113*, 11959; (b) Bogdan, E.; Plaquet, A.; Antonov, L.; Rodriguez, V.; Ducasse, L.; Champagne, B.; Castet, F. *J. Phys. Chem. C* **2010**, *114*, 12760; (c) Ségerie, A.; Castet, F.; Kanoun, M. B.; Plaquet, A.; Liégeois, V.; Champagne, B. *Chem. Mater.* **2011**, *23*, 3993.
- [8] Jiang, J.; Wang, C. K.; Luo, Y. 2006, *Quantum Chemistry for Molecular Electronics* (QCME-V1.1), Royal Institute of Technology, Sweden.
- [9] (a) Economou, E. N. *Green's Functions in Quantum Physics*, Springer, Berlin, 1990 ; (b) Taylor J. R. *Scattering Theory*, Wiley, New York, 1972 (c) Mujica, V.; Kemp, M.; Ratner, M. A. *J. Chem. Phys.* **1994**, *101*, 6849 (d) Jiang, J.; Kula, M.; Luo, Y. *J. Chem. Phys.* **2006**, *124*, 034708.

- [10] (a) Li, Z. L.; Zou, B.; Wang, C. K.; Luo, Y. *Phys. Rev. B* **2006**, 73, 075326 (b) Evers, F.; Weigend, F.; Koentopp, M. *Phys. Rev. B* **2004**, 69, 235411.
- [11] Ségerie, A.; Lin, L-L.; Liégeois, V.; Luo, Y.; Champagne, B. *Spectrochim. Acta Part A: Mol. and Biomol. Spectrosc.* **2014**, 119, 34-41.
- [12] (a) Fedorovsky, M. PyVib2, A Program for Analyzing Vibrational Motion and Vibrational Spectra; 2007; <http://pyvib2.sourceforge.net>. (b) Fedorovsky, M. *Comput. Lett.* **2006**, 2, 233. (c) Liégeois, V.; Champagne, B. *Theor. Chem. Acc.* **2012**, 131, 1284.
- [13] (a) Kushmerick, J. G.; Lazorcik, J.; Patterson, C. H.; Shashidhar, R.; Seferos, D. S. Bazan, G. C. *Nano Lett.* **2004**, 4, 639. (b) Zou, B.; Li, Z-L.; Song, X-N.; Wang C-K. *Chin. Phys. Lett.* **2008**, 25, 254.
- [14] Lin, L. L.; Wang C. K.; Luo, Y. *ACS Nano* **2011**, 5, 2257.

Influence of the contact configuration on the IET signature of molecular junctions based on hydrocarbon molecules

Ségerie, A.; Liégeois, V.; Champagne, B. (in preparation)

V. Influence of the contact configuration on the IET signature of molecular junctions based on hydrocarbon molecules

V.A. Introduction.

The ultimate goal of molecular electronics consists in reducing the size of electronic circuits to the molecular scale. Considering each individual molecule as a potential independent electronic component, the characterization of its intrinsic transport properties is essential for the understanding of charge transport mechanisms to be involved in nanotechnology applications.

A typical unimolecular electronic device is characterized by a molecular junction constituted by a single molecule embedded between metallic electrodes. Such junction can be conceptually partitioned into three distinct parts: the molecular core itself and two molecule-metal contacts, which are respectively situated on each end-side of the core. Note that the characteristics of these contacts depend on the nature of both the metallic electrodes and the chemical function connecting the molecular core to the electrodes. These characteristics have a direct impact on the amount of mixing between the discrete molecular orbitals of the core and the continuum of electronic states associated to the metal band structure. Therefore, the influence of the molecule-metal contacts on the current-voltage characteristics is as important as the influence of the molecular core itself.

So, the I-V characteristics have been proven to depend on several junction parameters including the intrinsic properties of the molecule such as the molecular length^[1], the π -conjugated structure^[2], the molecular conformation^[3], but also the orientation of the molecule with respect to the electrodes and the electrode-molecule distance^[4], the contact bonding nature^[5] and, indirectly, on the precise experimental setup used to obtain the studied junction^[6].

Experimentally, the fabrication of unimolecular devices faces two challenges: i) the functional target molecule is not always easy to synthesize, and ii) the fabricated junction must be reliable, stable and reproducible. Regarding the additional difficulty of embedding one single molecule in a junction, some groups proposed to use self-assembled conjugated oligomers as functional electronic components^[7], and more particularly monolayers formed by the molecular self-assembly technique^[8]. Such self-assembled monolayers (SAMs) have already been exploited in various areas, finding applications in the fields of nanoelectronics, biosensing, and surface engineering^[9].

Among the large variety of SAMs, the ones using alkanethiol structures present several advantages for applications in molecular electronics using gold atoms: i) their structures and properties are well-known ; ii) they can form strong SAMs on gold surfaces^[9a], acting as an inert protecting layer against any source of alteration or contamination, even under ambient conditions ; iii) devices using alkanethiol SAMs as a tunneling barrier present stable electron transport properties over a long period of time (more than several months)^[10]. Many studies of alkanethiol SAMs surface properties have been carried, using various techniques such as IR^[11], Raman^[12], Sum Frequency Generation (SFG)^[13] or STM^[14]. Kushmerick et al. have proposed the first study using the IETS technique^[15] by setting a crossed-wire junction experiment. Practically, two 10 μm diameter gold wires (one of them modified with a SAM of the molecule of interest) are connected to the terminals of a DC generator, placed in an external magnetic field and positioned in a crossed geometry so that one of the wires is perpendicular to the applied field. The adjustment of the small current passing through the wire allows to control the distance between the two wires because of variations of the Lorentz force deflecting the system^[16]. By bringing the two wires together, this setup allows to produce the conditions where electrons can tunnel from one gold wire to the other via the SAM tunneling channel.

In this chapter, we focus on the impact of the molecule-metal bonding on the IET response by analyzing the variation of IET signatures upon modification of the shape and size of the electrodes in single-molecule junctions using hydrocarbons of interest for molecular electronics. More precisely, we considered a single 1-undecanethiol molecule (C11) sandwiched between two gold electrodes, and two π -conjugated molecular junctions based on oligo(phenylene ethynylene) (OPE) and oligo(phenylene vinylene) (OPV), which have been intensively studied in the literature^[17]. In particular, the IET spectra of these three molecules have been measured by Kushmerick et al.^[15] by using a crossed-wire tunnel junction.

V.B. Computational aspects

In this study, the optimizations of the geometrical structures, the vibrational frequencies as well as the first-order derivatives of the wavefunction with respect to the normal mode coordinates have been performed using DFT with the B3LYP XC functional. Based on the observations presented in Chapter III^[18], we have shown that the cc-pVTZ basis offers a good compromise between accuracy and computational needs, justifying its use to describe the non metal atoms while the Au atoms are described with the LANL2DZ pseudo potential basis set. Then the IET spectra have been simulated by using the QCME code. In order to compare our theoretical

simulations to the experimental measurements performed by Kushmerick et al.^[15] shown in Fig. (V.1) the temperature has been fixed to 4.2K. The results presented in this work have been obtained for different molecule-metal orientations and are complementary to those obtained by Kula et al.^[19] who consider more simple gold structures to model the electrodes.

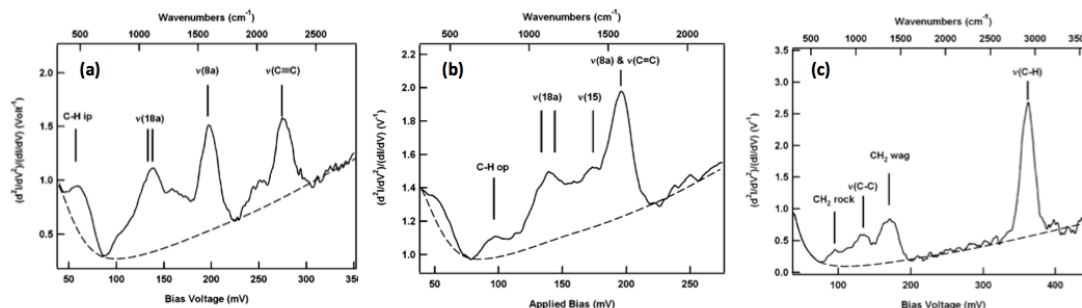


Fig. V.1. Sketch of the experimental IET spectra of the OPE (a), OPV (b) and C_{11} - (c) based junctions, taken from Ref. [15].

V.C. Effect of junction parameters on the IET response

V.C.1. Investigation of C_{11} -based junctions

Concerning the C_{11} junction, the experimental IET spectrum sketched in Fig. (V.1) is dominated by an intense peak at 362 mV (2920 cm^{-1}) associated to the C-H stretchings of the terminal CH_3 group, and is also characterized by three other contributions appearing at 95 mV (766 cm^{-1}), 134 mV (1081 cm^{-1}), and 170 mV (1371 cm^{-1}) corresponding respectively to CH_2 rocking (assigned as “ CH_2 rock”), C-C stretching (“ $\nu(\text{C-C})$ ”), and CH_2 wagging motions (“ CH_2 wag”). Relying on the conclusion drawn by Kula et al.^[19], *i.e.* the C_{11} molecule is chemically bonded to only one of the electrodes, we have simulated three different adsorption configurations represented in Fig. (V.2).

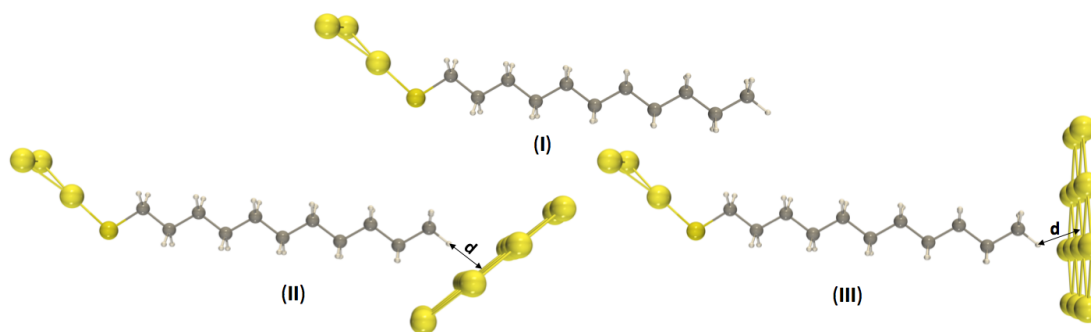


Fig. V.2. Representation of the three C_{11} -based junctions labelled I, II and III where the C_{11} molecule is chemically bonded to the source reservoir.

Configuration I corresponds to the optimized C₁₁ structure chemically linked to three gold atoms representing the source reservoir where the sulfur forms a covalent bond with the gold atom of 2.28 Å, while for configurations II and III an Au(111) surface containing 12 atoms with interatomic distances of 2.88 Å is added with two different tilting angle values with respect to the molecule to describe the drain reservoir. In the case of the contact configuration II the C-H bond of the terminal methyl group closest to the drain reservoir is set parallel to the normal of the gold surface, while for configuration III the normal to the gold surface is set parallel to the average direction of the longitudinal carbon chain. Since experimental results performed on a series of hexadecanethiol molecular junctions have shown that the hollow-type bonding is the most probable^[20], we have imposed in each case the carbon atom of terminal methyl group to be in hollow position to the Au(111) surface. As we know that the molecule-electrode distance has an impact on the IET response, we have considered different molecule-drain distances (labeled d in Fig. (V.2)) which have been defined as the distance between the hydrogen atom of the methyl group closest to the drain reservoir and the hollow position of the Au(111) surface for consistency reasons. The peak positions (expressed in mV and cm⁻¹), intensities (given in arbitrary units) and descriptions of the IET active modes calculated at the B3LYP/cc-pVTZ level of approximation for the three contact configurations I, II and III are reported in Table (V.1).

Concerning the contact configuration I where the methyl group is coupled to a fictive drain electrode (*i.e.* the coupling between the molecule and the drain is defined as a constant parameter set to 0.05 eV), the IET spectrum [Fig. (V.3)] is characterized by three main bands at 90 mV (724 cm⁻¹), 151 mV (1249 cm⁻¹) and 184 mV (1481 cm⁻¹) that are respectively associated to C-S stretching, CH₂ wagging, and CH₂ scissoring motions. The latter corresponds to the major signature, which is consistent with previous works dedicated to alkanethiols^[19,20].

Contact configuration		Peak position mV cm ⁻¹		Intensity (arb. units)	mode description
I		90	724	4.26×10 ⁻¹¹	ν(C-S)
		151	1249	3.74×10 ⁻¹¹	CH ₂ wag
		184	1481	5.29×10 ⁻¹¹	CH ₂ scis
II	d=(1.3Å)	122	980	2.06×10 ⁻¹⁰	ν(C-C)
		170	1373	6.64×10 ⁻¹⁰	CH ₂ wag
		361-376	2909-3035	8.80×10 ⁻¹⁰ -1.12×10 ⁻⁰⁹	ν(C-H)
	d=(1.4Å)	107	864	1.48×10 ⁻¹⁰	C-H bending
		170	1372	8.85×10 ⁻¹⁰	CH ₂ wag
		365-377	2943-3039	3.70×10 ⁻¹⁰ -4.91×10 ⁻¹⁰	ν(C-H)
	d=(1.5Å)	108	870	2.09×10 ⁻¹⁰	C-H bending
		170	1372	9.58×10 ⁻¹⁰	CH ₂ wag
		367-377	2964-3044	2.78×10 ⁻¹⁰ -2.31×10 ⁻¹⁰	ν(C-H)
	d=(1.7Å)	90	724	9.35×10 ⁻¹³	ν(C-S)
		167	1347	3.54×10 ⁻¹²	CH ₂ wag
	d=(1.9Å)	90	724	5.50×10 ⁻¹³	ν(C-S)
		159	1282	1.63×10 ⁻¹²	CH ₂ wag
		184	1481	4.09×10 ⁻¹²	CH ₂ scis
III	d=(1.3Å)	134	1082	5.73×10 ⁻⁰⁸	ν(C-C)
		168	1359	4.59×10 ⁻⁰⁸	CH ₂ wag
		345	2782	2.82×10 ⁻⁰⁹	ν(C-H)
	d=(1.4Å)	135	1090	2.19×10 ⁻⁰⁸	ν(C-C)
		168	1356	2.50×10 ⁻⁰⁸	CH ₂ wag
		356	2869	7.64×10 ⁻⁰⁹	ν(C-H)
	d=(1.7Å)	117	940	1.19×10 ⁻⁰⁹	C-H bending
		136	1094	1.29×10 ⁻⁰⁹	ν(C-C)
		172	1384	1.27×10 ⁻⁰⁹	CH ₂ wag
		368-377	2967-3039	3.24×10 ⁻¹⁰ -2.99×10 ⁻¹⁰	ν(C-H)
	d=(1.9Å)	90	724	8.01×10 ⁻¹³	ν(C-S)
		155	1250	2.27×10 ⁻¹²	CH ₂ wag
		184	1481	3.06×10 ⁻¹²	CH ₂ scis

Table V.1. Peak positions (mV and cm⁻¹), intensities (arb. units) and description of the IET active modes of the C₁₁-based junctions calculated at the B3LYP/cc-pVTZ level of approximation for the three contact configurations I, II and III.

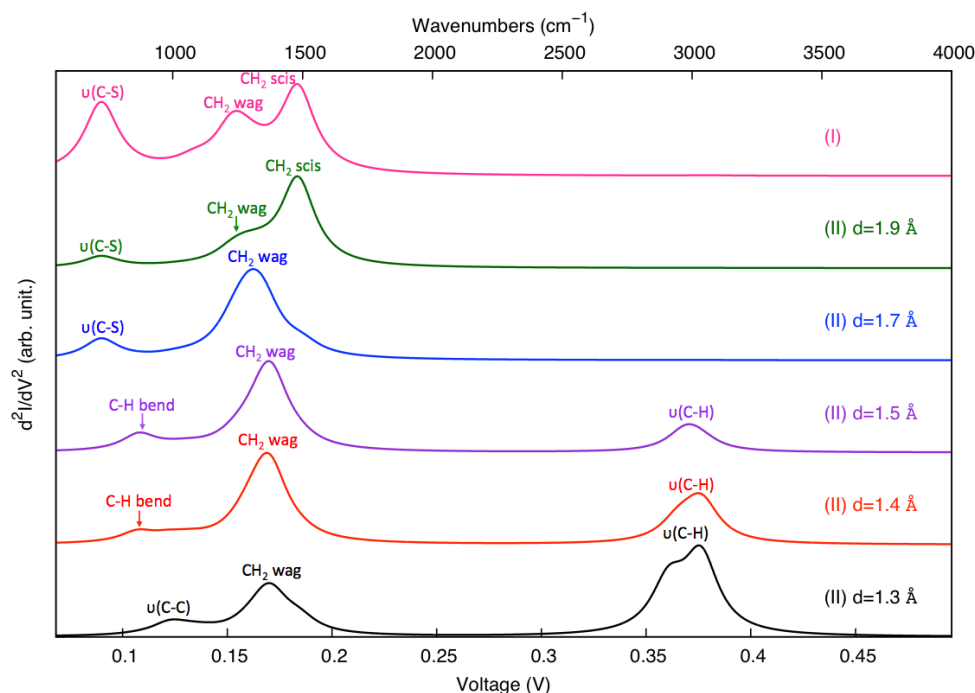


Fig. V.3. IET spectra associated to the contact configuration **II** of the C_{11} -based junctions for various molecule-drain distances with respect to the configuration **I**. The spectra are calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation. The full width at half maximum (FWHM) is set to 20 mV.

Concerning the adsorption configuration **II**, for the smallest molecule-drain distance $d=1.3\text{\AA}$ we can observe two dominant contributions at 361 mV (2909 cm^{-1}) and 376 mV (3035 cm^{-1}), which are associated to the C-H stretchings of the terminal methyl group, and two other bands are found at 122 mV (980 cm^{-1}) and 170 mV (1373 cm^{-1}) related to C-C stretching and CH_2 wagging motions, as illustrated in Fig. (V.4). When considering a distance $d=1.4\text{ \AA}$ ($d=1.5\text{ \AA}$) a band appears at 107 mV (108 mV) and is associated to C-H bending motions as sketched in Fig. (V.5). We can also observe an increase of the intensity of the band corresponding to the CH_2 wagging motions and a decrease of the one associated to the C-H stretchings of the terminal methyl group. The intensity variation observed for the band associated to the CH_2 wagging motions can not be explained by a change of the mode nature since the overlap value between the pairs of wagging vibrational modes obtained for $d=1.3\text{ \AA}$ and $d=1.5\text{ \AA}$ is equal to 0.997, while the ones associated to the two modes corresponding to C-H stretchings motions observed respectively at 361 mV (367 mV) and 376 mV (377 mV) for $d=1.3\text{ \AA}$ ($d=1.5\text{ \AA}$) are equal to 0.968 and 0.969. For each of these latter modes, the decrease of intensity is related to a smaller amplitude of the corresponding major stretching motion, as represented in Fig. (V.6).

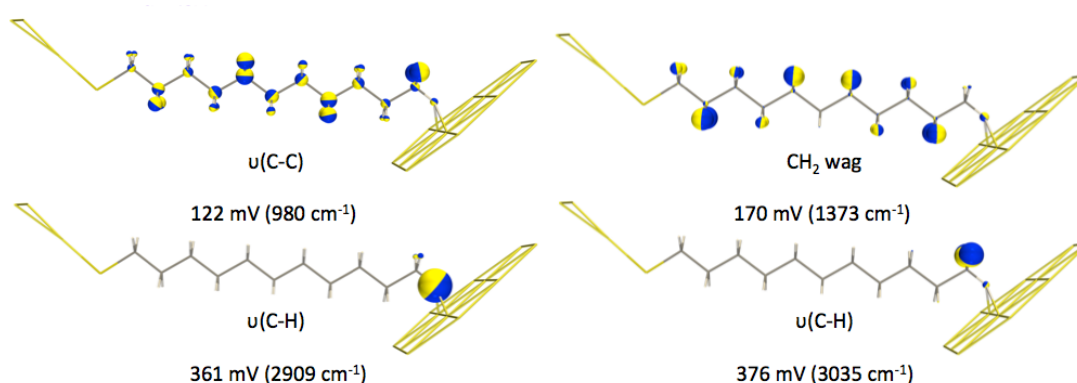


Fig. V.4. Sketch of the IET active modes of configuration II of the C₁₁-based junction with $d=1.3$ Å, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation. In this representation, the direction of atomic displacements is perpendicular to the junction plane between the two hemispheres of distinct color, and their amplitudes are proportional to the radius of the sphere. The sum of the surfaces of the spheres is always constant.

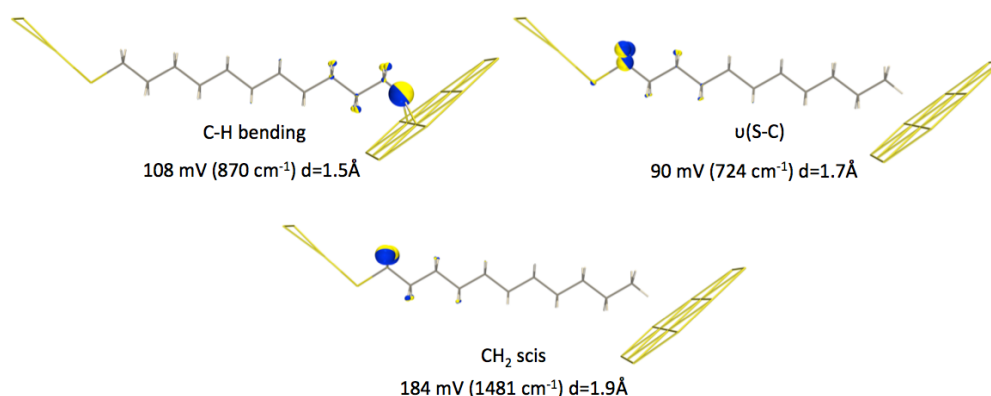


Fig. V.5. Representation of the C-H bending motions (108 mV/870 cm^{-1}) when considering configuration II of the C₁₁-based junction with $d=1.5$ Å, C-S stretching motions (90 mV/724 cm^{-1}) for $d=1.7$ Å, and CH₂ scissoring motions for $d=1.9$ Å (184 mV/1481 cm^{-1}). These results have been obtained at the B3LYP/cc-pVTZ/LANL2DZ level of approximation.

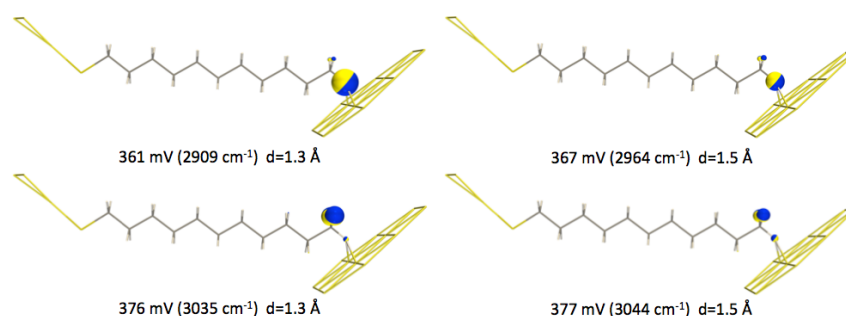


Fig. V.6. Sketch of the C-H stretching motions of contact configuration II of the C₁₁-based junction calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation with $d=1.3$ Å and $d=1.5$ Å. The overlap value between the pairs of modes (361 mV/367 mV) and (376 mV/377 mV) are equal to 0.968 and 0.969, respectively.

When increasing the molecule-drain distance to $d=1.7$ Å and $d=1.9$ Å, a small band at 90 mV (724 cm^{-1}) associated to C-S stretching motions appears [Fig. (V.5)], while the band associated to C-H stretchings of the terminal methyl group disappears. Note that, for $d=1.9$ Å, the IET active modes are similar to the ones observed for the contact configuration I, each spectrum being dominated by a band at 184 mV (1481 cm^{-1}) associated to CH_2 scissoring motions, as sketched in Fig. (V.5), while the intensity ordering for the two other contributions (*i.e.* C-S stretching and CH_2 wagging motions) is different.

On the basis of these various IET results [Fig. (V.3)], we have highlighted the influence of the distance between the terminal methyl group and the drain on the IET response, what has also been reported in a study performed by Luo's group^[4c] dealing with a decanethiol molecule sandwiched between Au(111) surfaces. Moreover, the signatures observed for the contact configuration II with the smallest molecule-drain distance ($d=1.3$ Å) present a very good agreement with the experimental data. This is even more remarkable knowing that many theoretical calculations have failed in reproducing the dominant signature associated to the C-H stretching motions of the methyl group^[21].

When comparing the IET spectra of configuration III [Fig. (V.7)] to those of configuration II [Fig. (V.3)] for a molecule-drain distance $d=1.3$ Å, different IET signatures are observed since the dominant band is no longer associated to C-H stretchings of the terminal methyl group as its intensity strongly drops, but rather corresponds to the peak appearing at 134 mV (1082 cm^{-1}) associated to C-H bendings localized around the terminal methyl group together with C-C stretching motions, as sketched in Fig. (V.8). A deeper analysis of the intensities of the peaks associated to the C-H stretchings of contact configuration III reveals that only the mode associated to the stretching of the C-H bond closer to the drain is always active. Indeed, the mode associated to the stretchings of the two other C-H bonds of the terminal methyl group only emerges for $d=1.7$ Å with an intensity similar to the former one. This inability to get a consistent information on the C-H stretching signature in configuration III proves the strong influence of the orientation of the molecule with respect to the gold plane on the IET response, as it has already been stressed in a previous study performed on a series of hexadecanethiol molecular junctions^[20].

When going from $d=1.3$ Å to $d=1.4$ Å one observes a diminution of the intensity of the band associated to the C-H bendings localized around the terminal methyl group together with C-C stretching motions. This is attributed to a smaller amplitude of the bending motions, as illustrated in Fig. (V.8). This intensity variation is characterized by an overlap value equal to 0.891.

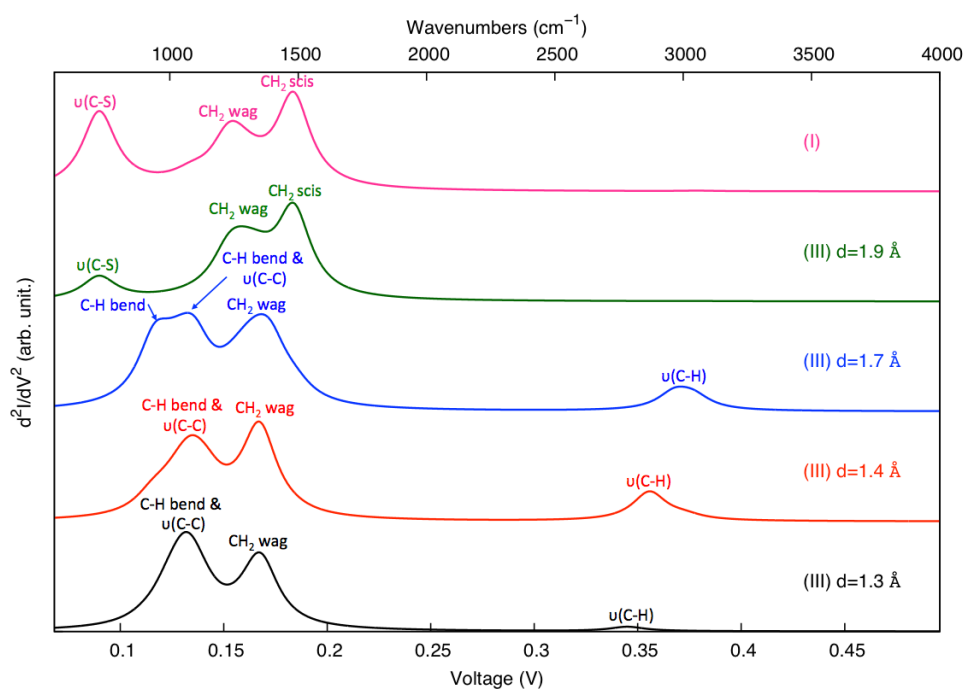


Fig. V.7. IET spectra associated to the contact configuration configuration **III** of the C_{11} -based junctions for various molecule-drain distances with respect to the configuration **I**. The spectra are calculated at the B3LYP/cc-pVTZ/LANL2DZ level. The full width at half maximum (FWHM) is set to 20 mV.

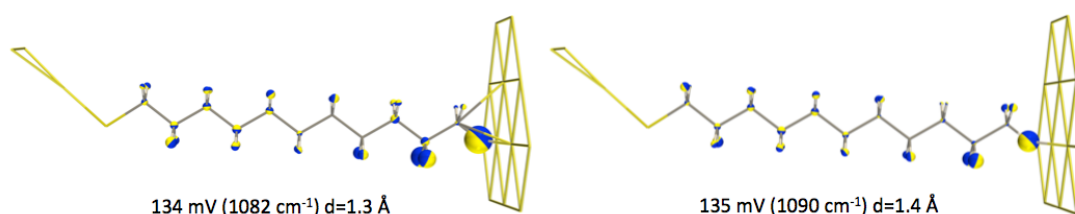


Fig. V.8. Sketch of the atomic displacements of the modes combining bending motions of the C-H bonds of the terminal methyl with C-C stretching motions, as calculated for $d=1.3$ Å and $d=1.4$ Å at the B3LYP/cc-pVTZ level of calculation for the contact configuration **III** of the C_{11} -based junction. The overlap value between the pair of modes (1.3 Å / 1.4 Å) is equal to 0.891.

The comparison of the IET spectra obtained for configurations **II** and **III** with $d=1.9$ Å shows similar IET signatures, close to the case of configuration **I**, thereby highlighting the smaller influence of the orientation of the molecule with respect to the gold plane on the IET response for large molecule-drain distances.

V.C.2. Investigation of OPE-based junctions

The experimental spectrum of an OPE-based junction measured by Kushmerick et al. [Fig. (V.1)] shows three prominent peaks at 138 mV (1114 cm^{-1}), 196 mV (1582 cm^{-1}) and 274 mV (2211 cm^{-1}), which are assigned as the $\nu(18a)$, $\nu(8a)$ ring modes and stretching motions of the $C\equiv C$

bonds, respectively. At 57 mV (463 cm^{-1}) the IET activity of a vibrational mode associated to in-plane bending motion is also suggested. Following the same procedure as for the C_{11} molecule, different contact configurations have been studied in order to evaluate the impact of the bonding configuration at the molecule-electrode interface on the IET response. The four contact configurations illustrated in Fig. (V.9) were first considered. They represent the contact of an OPE structure terminated by thiol (S-H) groups with various shapes of the source electrode. Configuration I corresponds to the isolated molecule for which we consider a coupling constant between the molecule and the fictive source electrode equal to 0.05 eV. The B3LYP/cc-PVTZ/LANL2DZ optimized structure of the OPE molecule chemically linked to 3 gold atoms used to mimic the shape of a STM tip defines configuration II, where the sulfur forms a covalent bond with the gold atom of 2.29 Å. Configuration III involves an optimized cluster of 13 gold atoms. An Au(111) surface containing 12 atoms with interatomic distances of 2.88 Å which offers a good compromise between accuracy with experimental results and computational needs^[4a], is used to model the source reservoir in configuration IV. In the contact configurations III and IV, the sulfur atom is positioned in a hollow position, and the distances between the hollow site and the sulfur atoms have been fixed to 1.5 Å (configuration III) and 3.4 Å (configuration IV) after determining the energetic profile of the molecular system (*i.e.* we have selected the configuration presenting the lowest energy with respect to variations of the molecule-electrode distances). More precisely, in the case of configuration III the sulfur atom binds covalently to the closest gold atom with a distance of 2.50 Å, while the distance between the sulfur atom and the closest gold atom is equal to 3.75 Å when considering the configuration IV.

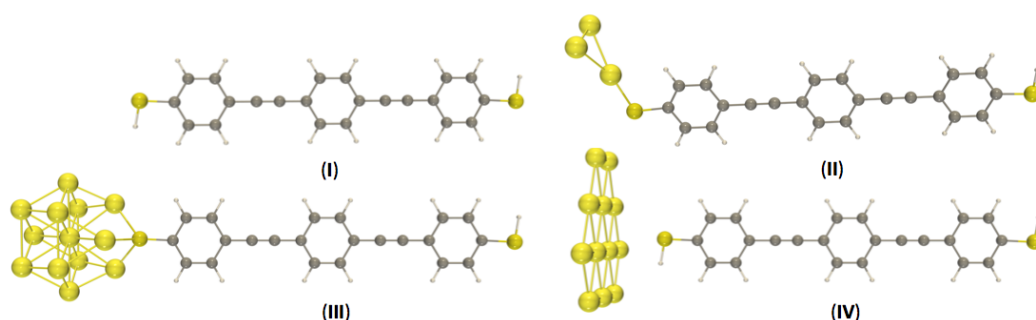


Fig. V.9. Structures of contact configurations I, II, III and IV of the OPE-based junctions.

The IET signatures obtained for these molecular systems [Fig. (V.10)] are characterized by three contributions associated to the $\nu(18a)$ ring mode together with a stretching of the C-S bonds, a $\nu(8a)$ ring mode and the stretching (symmetric and antisymmetric) motions of the $C\equiv C$ bonds. The corresponding peak positions and intensities are reported in Table (V.2), and the IET active modes calculated for the isolated molecule are represented in Fig. (V.11). Comparing these

results with the experimental spectrum in [Fig. (V.1)] leads to a contrasted analysis because theory correctly predicts which are the IET active but not their relative intensities. Indeed, the peak intensity of the C $\equiv$ C stretching mode is overestimated. This observation has also been reported in experimental measurements performed by Yoon et al.^[22] Note that for the specific case of configuration **III** additional bands emerge in the 65-105 mV range and are associated to out-of-plane C-H bending motions. In a second step, the drain electrode was included, under the form of an Au(111) surface constituted by twelve gold atoms [Fig. (V.12)]. Their IET signatures are compared to those of drain-less structures [Fig. (V.13)], while the corresponding peak positions and intensities are reported in Table (V.3). After determining the energetic profiles of molecular systems **V** and **VI** as a function of the molecule-drain distance, the distance between the sulfur and the hollow site was fixed to 3.80 Å in both cases, corresponding more precisely to a distance between the sulfur atom and the closest gold atom of 4.07 Å.

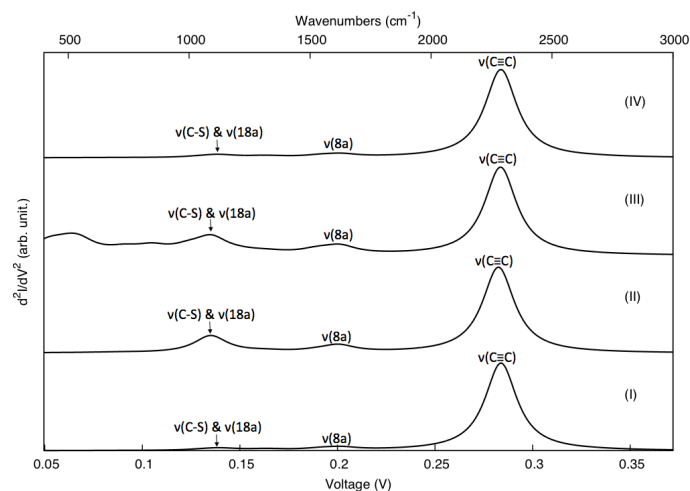


Fig. V.10. IET spectra of configuration **I** calculated at the B3LYP/cc-pVTZ level, and of the configurations **II**, **III** and **IV** of the OPE-based junctions evaluated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation. The FWHM is set to 20 mV.

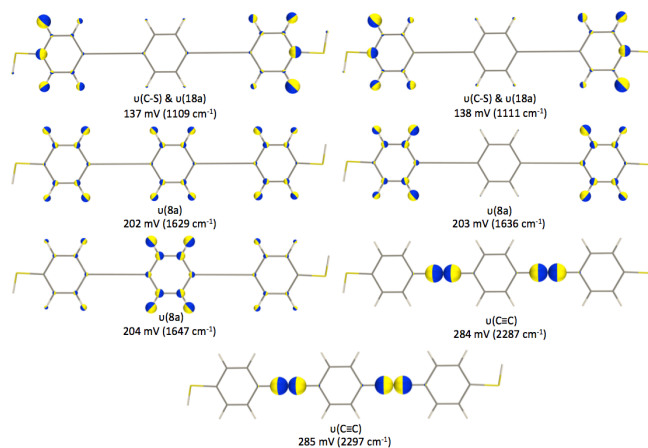


Fig. V.11. Sketch of the IET active modes of the configuration **I** associated to the isolated OPE molecule, calculated at the B3LYP/cc-pVTZ level of calculation.

Contact configuration	Peak position mV cm ⁻¹		Intensity (arb. units)	mode description
I	137	1109	1.39×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1111	1.40×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	202	1629	2.01×10^{-13}	$\nu(8\text{a})$
	203	1636	1.99×10^{-13}	$\nu(8\text{a})$
	204	1647	1.93×10^{-13}	$\nu(8\text{a})$
	284	2287	3.85×10^{-12}	sym $\nu(\text{C}\equiv\text{C})$
	285	2297	3.82×10^{-12}	antisym $\nu(\text{C}\equiv\text{C})$
II	135	1089	3.41×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1110	3.22×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	201	1618	1.75×10^{-13}	$\nu(8\text{a})$
	202	1633	1.69×10^{-13}	$\nu(8\text{a})$
	204	1646	1.59×10^{-13}	$\nu(8\text{a})$
	282	2277	1.65×10^{-12}	sym $\nu(\text{C}\equiv\text{C})$
	284	2294	1.59×10^{-12}	antisym $\nu(\text{C}\equiv\text{C})$
III	66	536	6.70×10^{-16}	out-of-plane C-H bendings
	69	556	6.20×10^{-16}	out-of-plane C-H bendings
	91	734	3.57×10^{-16}	out-of-plane C-H bendings
	135	1091	6.39×10^{-16}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1110	6.04×10^{-16}	$\nu(\text{C-S}) + \nu(18\text{a})$
	201	1623	3.51×10^{-16}	$\nu(8\text{a})$
	202	1633	3.42×10^{-16}	$\nu(8\text{a})$
	204	1646	3.22×10^{-16}	$\nu(8\text{a})$
	283	2285	2.71×10^{-15}	sym $\nu(\text{C}\equiv\text{C})$
	285	2297	2.67×10^{-15}	antisym $\nu(\text{C}\equiv\text{C})$
IV	137	1108	1.15×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1110	1.15×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	202	1628	1.51×10^{-13}	$\nu(8\text{a})$
	203	1635	1.50×10^{-13}	$\nu(8\text{a})$
	204	1647	1.45×10^{-13}	$\nu(8\text{a})$
	284	2287	2.75×10^{-12}	sym $\nu(\text{C}\equiv\text{C})$
	285	2297	2.72×10^{-12}	antisym $\nu(\text{C}\equiv\text{C})$

Table V.2. Peak positions (mV and cm⁻¹), intensities (arb. units) and descriptions of the IET active modes of contact configurations I, II, III, and IV of the OPE-based junctions.

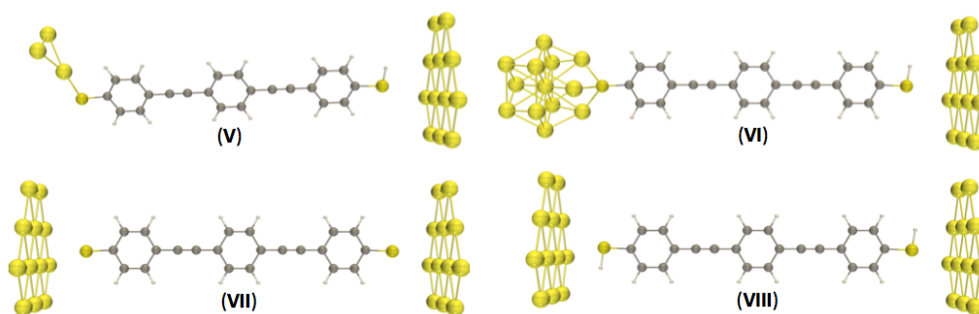


Fig. V.12. Structures of contact configurations V, VI, VII and VIII of the OPE-based junctions.

Contact configuration	Peak position mV cm ⁻¹		Intensity (arb. units)	mode description
V	60	485	9.78×10 ⁻¹¹	ν(Au-S) & long. motions
	75	607	1.94×10 ⁻¹⁰	ν(C-S) & long. motions
	87	701	2.22×10 ⁻¹⁰	ν(C-S) & ring distortions
	95	763	1.60×10 ⁻¹⁰	ν(C-S) & ring distortions
	135	1089	2.30×10 ⁻¹¹	ν(C-S)+ ν(18a)
	137	1109	2.15×10 ⁻¹¹	ν(C-S)+ ν(18a)
	188	1515	5.82×10 ⁻¹²	C-H bendings & ν(C-S)
	189	1526	5.76×10 ⁻¹²	C-H bendings & ν(C-S)
VI	60	486	4.17×10 ⁻¹⁵	ν(Au-S) & long. motions
	75	606	3.23×10 ⁻¹⁵	ν(C-S) & long. motions
	87	700	1.80×10 ⁻¹⁵	ν(C-S) & ring distortions
	95	763	1.33×10 ⁻¹⁵	ν(C-S) & ring distortions
	135	1091	1.24×10 ⁻¹⁵	ν(C-S)+ ν(18a)
	137	1109	1.28×10 ⁻¹⁵	ν(C-S)+ ν(18a)
	188	1518	8.84×10 ⁻¹⁵	C-H bendings & ν(C-S)
	189	1527	8.98×10 ⁻¹⁵	C-H bendings & ν(C-S)
	201	1623	5.53×10 ⁻¹⁵	ν(8a)
	202	1632	5.20×10 ⁻¹⁵	ν(8a)
	204	1646	4.66×10 ⁻¹⁵	ν(8a)
VII	58	469	7.97×10 ⁻¹³	ν(Au-S) & long. motions
	74	597	1.12×10 ⁻¹²	ν(C-S) & long. motions
	86	691	9.11×10 ⁻¹³	ν(C-S) & ring distortions
	131	1058	1.20×10 ⁻¹²	ν(C-S)+ ν(18a)
	132	1061	1.20×10 ⁻¹²	ν(C-S)+ ν(18a)
	187	1510	3.96×10 ⁻¹³	C-H bendings & ν(C-S)
	188	1513	3.96×10 ⁻¹³	C-H bendings & ν(C-S)
VIII	75	605	1.48×10 ⁻¹²	ν(C-S) & long. motions
	87	700	2.19×10 ⁻¹²	ν(C-S) & ring distortions
	95	763	1.78×10 ⁻¹²	ν(C-S) & ring distortions
	128	1035	2.11×10 ⁻¹²	C-C-C & C-H bendings
	137	1108	3.26×10 ⁻¹²	ν(C-S)+ ν(18a)
	137	1109	3.26×10 ⁻¹²	ν(C-S)+ ν(18a)
	189	1521	5.89×10 ⁻¹²	C-H bendings & ν(C-S)
	190	1529	5.99×10 ⁻¹²	C-H bendings & ν(C-S)
	202	1628	3.98×10 ⁻¹²	ν(8a)
	203	1635	3.81×10 ⁻¹²	ν(8a)

Table V.3. Peak positions (mV and cm⁻¹), intensities (arb. units) and descriptions of the IET active modes of the OPE-based junctions for contact configurations **V**, **VI**, **VII**, and **VIII**.

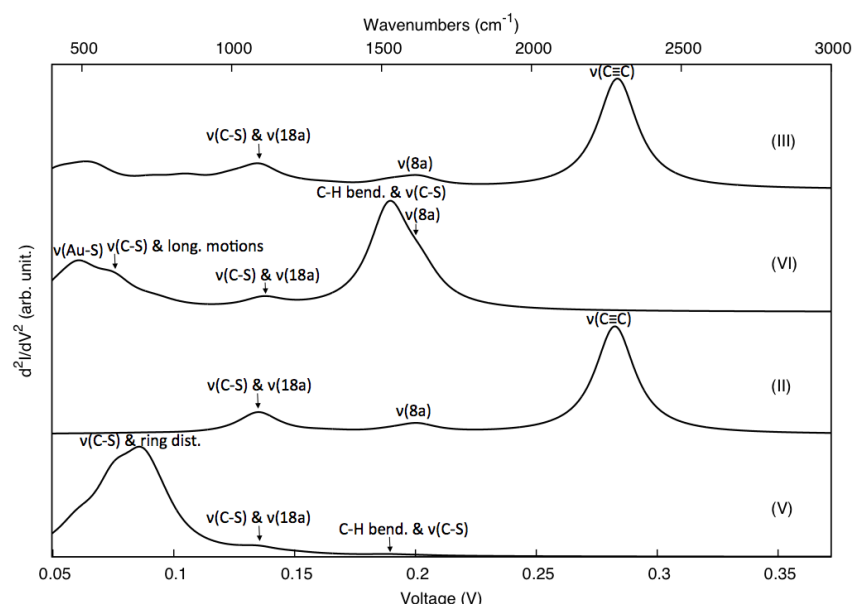


Fig. V.13. IET spectra of configurations **II**, **V**, **III** and **VI** of the OPE-based junctions calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation. The FWHM is set to 20 mV.

The analysis of the IET spectra of configurations **II** and **V** shows that the addition of the drain electrode modifies significantly the IET response. Indeed, only the modes associated to the stretching of the C-S bond together with the $\nu(18a)$ ring motion are found for both systems, emerging at 135 mV and 138 mV (configuration **II**) and at 135 mV and 137 mV (configuration **V**). Then, the dominant band associated to the $C\equiv C$ bonds disappears when adding the Au(111) surface to define the drain, while intense bands appear in the 60-95 mV range, the most intense observed at 87 mV (701 cm^{-1}) is associated to C-S stretching motions together with ring distortions [Fig. (V.14)].

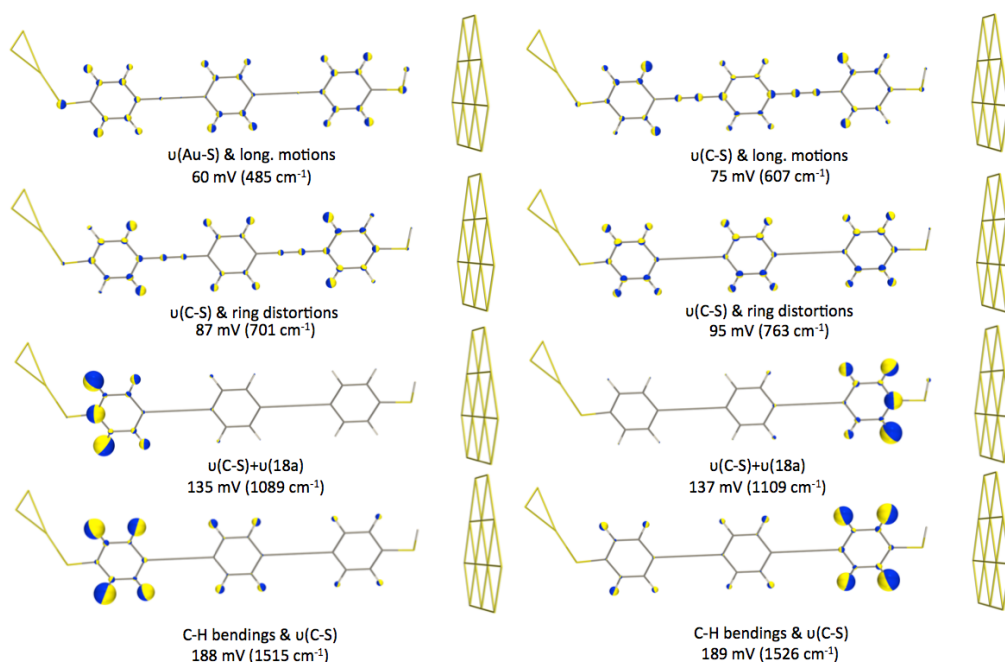


Fig. V.14. Sketch of the IET active modes of the contact configuration **V** of the OPE-based junction, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation.

Similar observations can be made when comparing configuration **VI** with configuration **III**. Adding the drain electrode leads to the apparition of prominent bands associated to C-S stretching motions together with C-H bendings at 188 mV (1518 cm^{-1}) and 189 mV (1527 cm^{-1}), as illustrated in Fig. (V.15), as well as an increase of the intensity of the bands related to the $\nu(8a)$ ring mode emerging at 201 mV (1623 cm^{-1}), 202 mV (1633 cm^{-1}) and 204 mV (1646 cm^{-1}). For the latter case, the intensity variation is not attributed to changes of the vibrational normal modes since the overlap values between the different pairs of modes are larger than 0.998. These observations are consistent with simulations of Kula et al.^[19] considering two different contact configurations of OPE-, OPV- and C_{11} -based junctions: the first one is characterized by a sulfur atom binding over the middle of a triangular gold trimer (representing a bond over the hollow site of an Au(111) surface), while in the second case the sulfur atom is bonded to the outermost Au atom of a linear gold trimer (representing an ideal gold wire). They have stressed the absence of contribution of the $\nu(C\equiv C)$ mode, as well as the observation of $\nu(Au-S)$ at low voltages and the significant contribution of $\nu(C-S)$ which is also predicted by the theoretical investigation of Paulsson et al.^[21c]

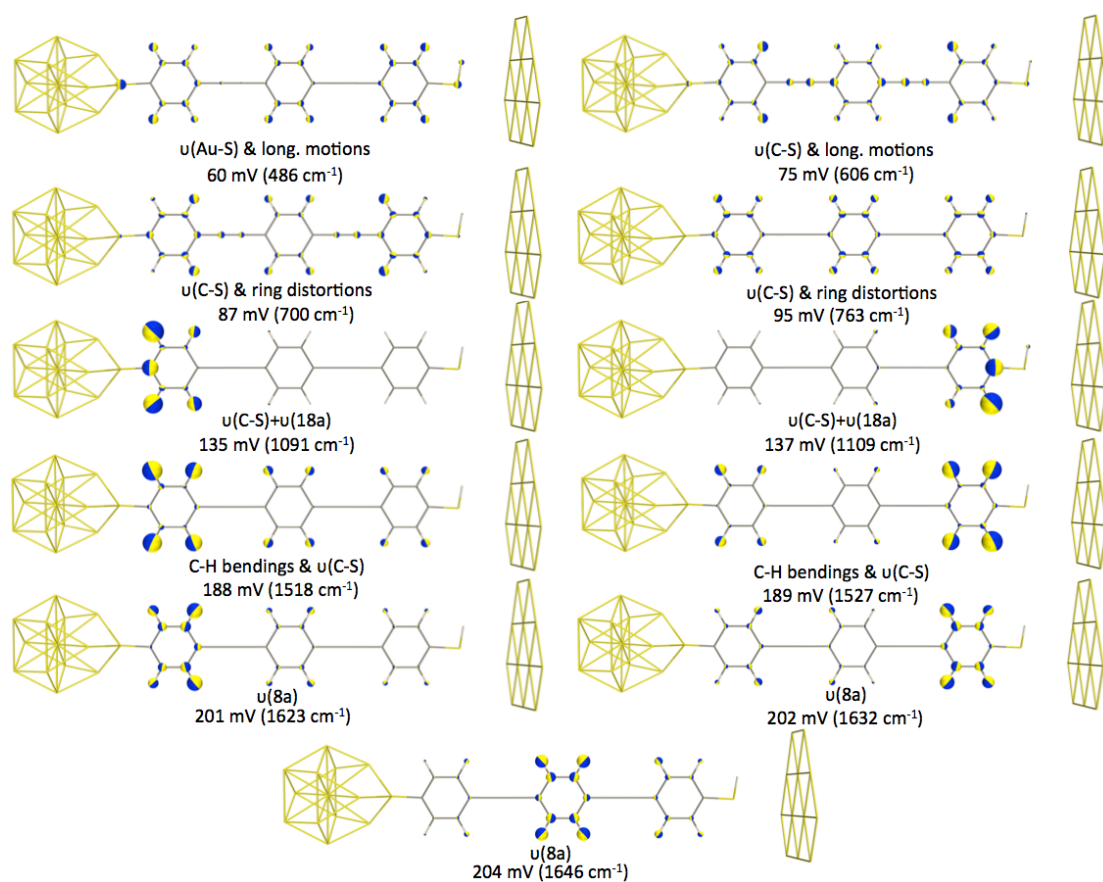


Fig. V.15. Sketch of the IET active modes of the contact configuration **VI** of the OPE-based junction, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

Theoretical and experimental investigations have proven that when embedding a sulfur terminated molecule between two gold electrodes, gold-thiol and gold-thiolate interfaces can potentially coexist. Indeed, the energy of these two kinds of systems are very similar, and the S-H bond can remain reasonably strong even if the sulfur is involved in a S-Au bond^[23]. The IETS technique can be useful to distinguish the thiol and thiolate forms by identifying features specific to the thiol hydrogen atom. We have therefore considered the two contact configurations **VII** and **VIII** represented in Fig. (V.12) where the sulfur atoms are anchored in hollow position, the distance between the hollow site and each sulfur atom being fixed to 3.4 Å, corresponding more precisely to a distance between the sulfur atom and the closest gold atom of 3.72 Å.

The IET spectrum of configuration **VII** involving the molecule terminated by a thiolate group [Fig. (V.16)] is characterized by five intense IET active modes: the most intense being associated to stretching of the C-S bond together with $\nu(18a)$ ring motions appear at 131 mV (1058 cm^{-1}) and 132 mV (1061 cm^{-1}), followed by peaks appearing at 74 mV (597 cm^{-1}) associated to $\nu(\text{C-S})$ and longitudinal motions, the peak observed at 86 mV (691 cm^{-1}) being associated to $\nu(\text{C-S})$ and ring distortions, and the one found at 58 mV (469 cm^{-1}) related to $\nu(\text{Au-S})$ and longitudinal motions. The smallest contributions appearing at 187 mV (1510 cm^{-1}) and 188 mV (1513 cm^{-1}) correspond to C-H bending motions together with C-S stretchings. The corresponding modes can be visualized in Fig. (V.17).

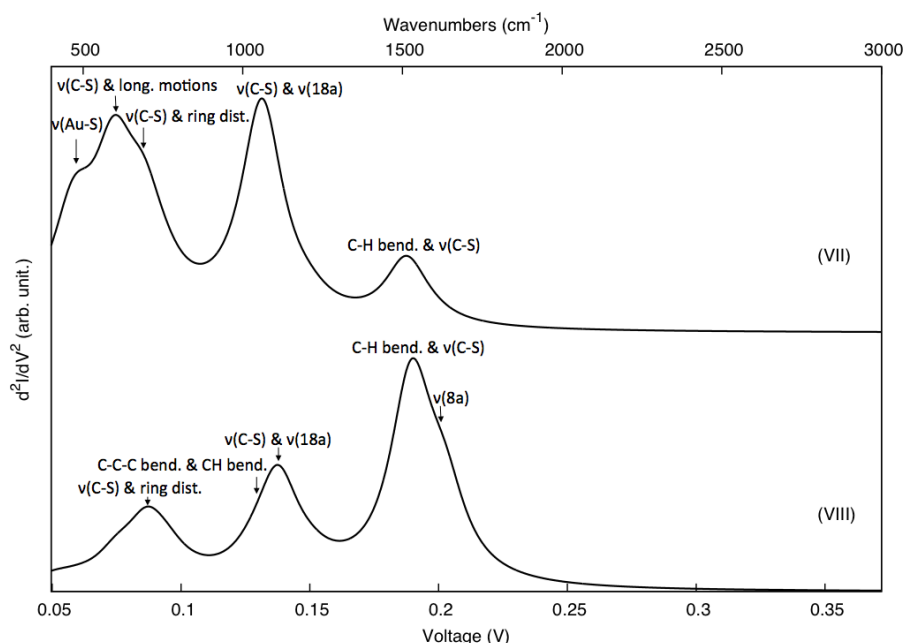


Fig. V.16. IET spectra of the contact configurations **VII** and **VIII** of the OPE-based junctions, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation. The FWHM is set to 20 mV.

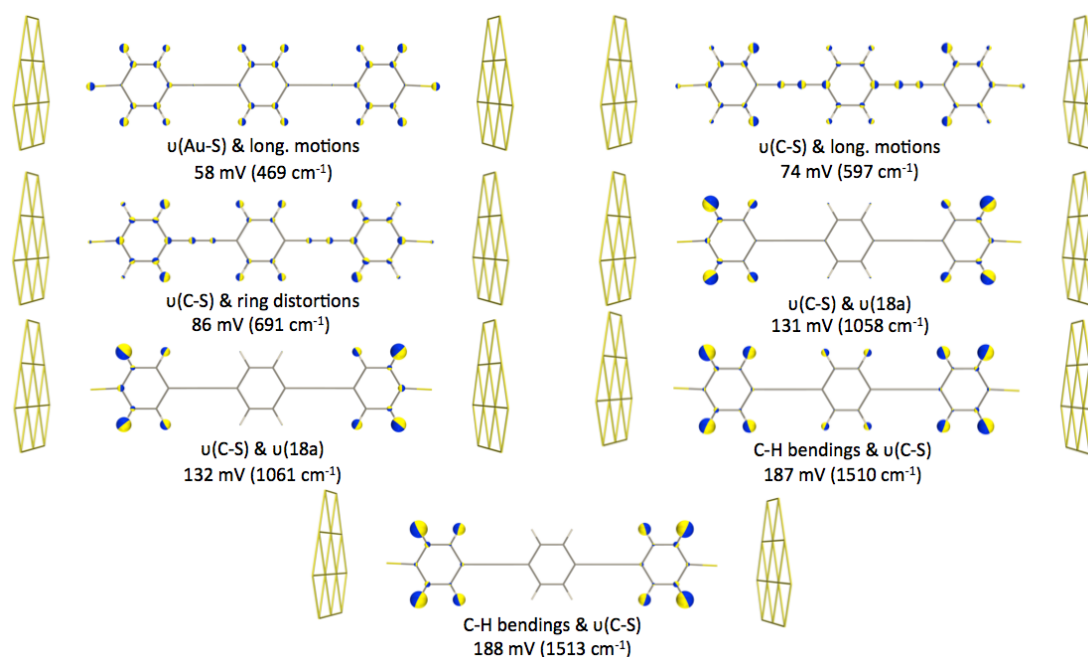


Fig. V.17. Sketch of the IET active modes of the contact configuration **VII** of the OPE-based junction, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

By analyzing the IET spectrum of contact configuration **VIII** involving the molecule terminated by thiol functions, we can observe similar signatures to the case of configuration **VII** in terms of nature of the IET active modes [Fig. V.18], but the relative intensities are different: e.g. the mode associated to C-S bond together with $\nu(18a)$ ring motions dominates the spectrum relative to configuration **VII**, while the major contribution to the spectrum of configuration **VIII** is associated to C-H bending motions together with C-S stretchings. These important variations can be explained by considering the distortion of the conjugated path due to the vibrational motions. Taking the example of the modes appearing at 131 mV (configuration **VII**) and 137 mV (configuration **VIII**) whose intensity decrease when removing the thiol hydrogen (*i.e.* it is the major contribution for the configuration **VII**), we can observe a variation of the nature of the vibrational modes characterized by an overlap value equal to 0.547 [Fig. V.19]. This small value can be attributed to the change in the deformation of the conjugated path: i) the stretching motions of the carbons in position **3** and **5** (on both sides of the molecule) follow the direction of C=C bonds (and therefore of the conjugation path) in configuration **VII**, while they follow the direction of C-H bonds in configuration **VIII**; ii) the elongation of the C₄-C₇-C₈-C₉ bridge between these terminal and central phenyl rings is stronger in the case of configuration **VIII**. These two contributions lead to a greater deformation of the conjugated path in the case of configuration **VIII**, what could explain the decrease of the relative intensity of the peak associated to this mode. However, in the case of the ones observed in the 58-87 mV range, the decrease of their relative intensities can not

be explained in terms of changes of the vibrational normal modes since the overlap values between the **VII/VIII** pairs of modes (74 mV/75 mV) and (86 mV/87 mV) are higher than 0.99.

We can finally notice the apparition of two new bands associated to C-C-C bendings and C-H bending motions (128 mV) and to the $\nu(8a)$ ring motions (202 mV and 203 mV), as sketched in Fig. (V.18). These results highlight the impact of the thiol hydrogen on the IET signatures, what is consistent with the previous work of Demir et al.^[24]. A way to improve the accuracy of the calculated relative intensities would be to take into account the deformation of the molecular structure in experimental conditions, for example when making the molecule-electrodes contact. Therefore we could consider more than one conformation for each studied contact configuration, following the same approach as the one adopted by Das^[25] in a recent theoretical study dealing with OPE and OPV molecules.

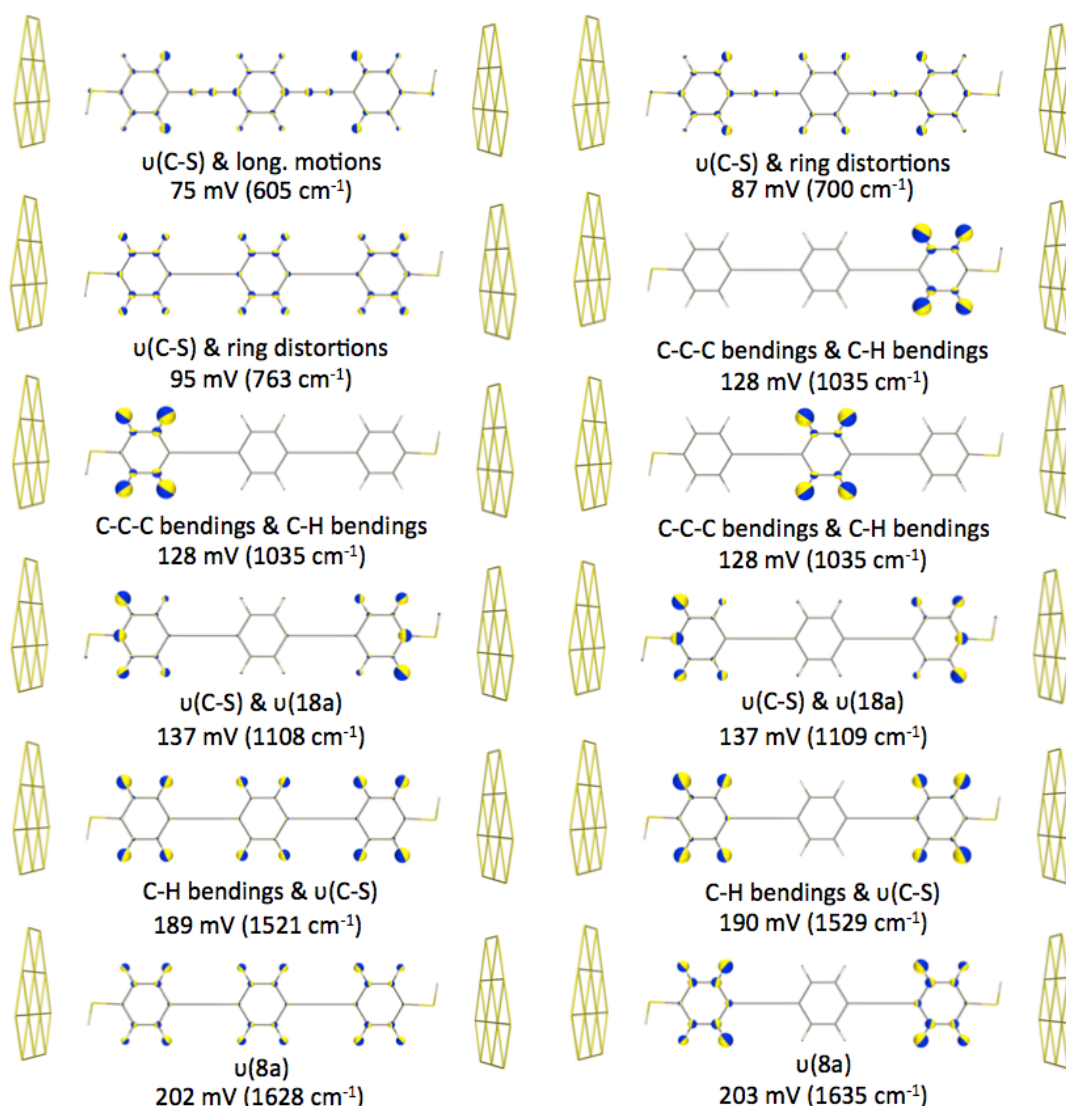


Fig. V.18. Sketch of the IET active modes of the contact configuration **VIII** of the OPE-based junction, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

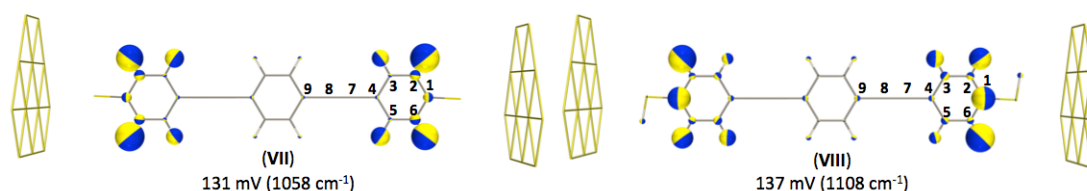


Fig. V.19. Illustration of the B3LYP/cc-pVTZ/LANL2DZ bending motions of the C-H bonds associated with C-S stretching motions of contact configurations **VII** and **VIII** of the OPE-based junctions observed at 131 mV (1058 cm^{-1}) and at 137 mV (1108 cm^{-1}), respectively. The overlap value between the pair of modes is equal to 0.547.

As an intermediate conclusion, we can mention that the dominant signatures found for each contact configuration are consistent with the IET theory^[26], vibrational motions parallel to the direction of the conjugated path have larger IET intensities. Indeed, the $\nu(\text{C}\equiv\text{C})$ mode is associated to the dominant signature for the drain-less configurations **I**, **II**, **III** and **IV**, while for configurations **V**, **VI**, **VII** and **VIII** C-S stretching motions provide the most intense IET bands.

V.C.3. Investigation of OPV-based junctions

The experimental spectrum of the OPV molecule shown in Fig. (V.1) is characterized by two major bands attributed to the $\nu(18a)$ ring motion (134 and 144 mV) and to the $\nu(8a)$ ring motion together with C=C stretchings (195 mV). Weaker C-H out-of-plane bending motions and $\nu(15)$ stretchings of the phenyl rings are also observed at 96 mV and at 174 mV, respectively. Consistently with the investigation of OPE-based junctions, we have first considered four drain-less contact configurations [Fig. (V.20)]. The B3LYP/cc-pVTZ/LANL2DZ optimized structure of the OPV molecule chemically linked to 3 gold atoms used to mimic the shape of a STM tip defines configuration **II**, where the sulfur forms a covalent bond with the gold atom of $2.29\text{ \AA}$. In the contact configurations **III** and **IV**, the sulfur atom is positioned in a hollow position, and the distances between the hollow site and the sulfur atoms have been fixed to $1.5\text{ \AA}$ (configuration **III**) and $3.4\text{ \AA}$ (configuration **IV**) after determining the energetic profile of the molecular system. More precisely, in the case of configuration **III** the sulfur atom binds covalently to the closest gold atom with a distance of $2.37\text{ \AA}$, while the distance between the sulfur atom and the closest gold atom is equal to $3.65\text{ \AA}$ when considering the configuration **IV**. The corresponding IET spectra are shown in Fig. (V.21), and the peak positions and intensities are reported in Table (V.4). Two systematic signatures are observed [Fig. (V.22)]: the most intense is associated to $\nu(8a)$ ring motions together with C=C stretchings and emerges around 209 mV, and the second associated to C-H bending motions appear around 169 mV. Configuration **II** is however the only one to exhibit a band associated to $\nu(18a)$ ring motions associated with C-S stretchings. Such decrease can be attributed

to the smaller amplitude of the longitudinal motion associated to the C-S stretchings [Fig. (V.23)], which plays a major role in the coupling between the source reservoir and the molecule and thereby modulates the IET intensity. The comparison of the IET spectra with the experimental measurements shows that contact configuration **II** provides the best agreement in terms of reproducibility of both the IET active modes and their relative intensities.

Contact configuration	Peak position		Intensity (arb. units)	mode description
	mV	cm ⁻¹		
I	138	1115	1.72×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1115	1.72×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	149	1198	2.37×10^{-13}	C-H bendings & $\nu(\text{C-C})$
	169	1361	3.17×10^{-13}	C-H bendings
	201	1624	1.21×10^{-12}	$\nu(8\text{a}) + \nu(\text{C=C})$
	209	1683	1.51×10^{-12}	$\nu(8\text{a}) + \nu(\text{C=C})$
	209	1683	1.51×10^{-12}	$\nu(8\text{a}) + \nu(\text{C=C})$
II	136	1092	2.19×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1115	2.12×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	148	1196	1.48×10^{-13}	C-H bendings & $\nu(\text{C-C})$
	168	1356	1.45×10^{-13}	C-H bendings
	199	1608	2.73×10^{-13}	$\nu(8\text{a}) + \nu(\text{C=C})$
	208	1674	1.95×10^{-13}	$\nu(8\text{a}) + \nu(\text{C=C})$
	208	1681	1.85×10^{-13}	$\nu(8\text{a}) + \nu(\text{C=C})$
III	136	1095	1.89×10^{-14}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1114	2.06×10^{-14}	$\nu(\text{C-S}) + \nu(18\text{a})$
	149	1198	2.55×10^{-14}	C-H bendings & $\nu(\text{C-C})$
	169	1362	3.34×10^{-14}	C-H bendings
	201	1618	8.03×10^{-14}	$\nu(8\text{a}) + \nu(\text{C=C})$
	209	1682	9.56×10^{-14}	$\nu(8\text{a}) + \nu(\text{C=C})$
	209	1683	9.53×10^{-14}	$\nu(8\text{a}) + \nu(\text{C=C})$
IV	138	1113	1.30×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	138	1115	1.30×10^{-13}	$\nu(\text{C-S}) + \nu(18\text{a})$
	149	1198	1.68×10^{-13}	C-H bendings & $\nu(\text{C-C})$
	169	1361	2.11×10^{-13}	C-H bendings
	201	1623	6.67×10^{-13}	$\nu(8\text{a}) + \nu(\text{C=C})$
	209	1683	7.75×10^{-13}	$\nu(8\text{a}) + \nu(\text{C=C})$
	209	1683	7.75×10^{-13}	$\nu(8\text{a}) + \nu(\text{C=C})$

Table V.4. Peak positions (mV and cm⁻¹), intensities (arb. units) and descriptions of the IET active modes of the OPV-based junctions for the four contact configurations **I**, **II**, **III**, and **IV**.

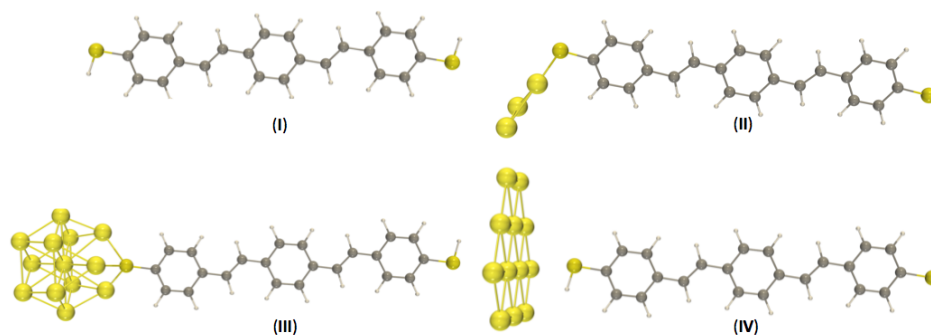


Fig. V.20. Illustration of contact configurations I, II, III and IV of the OPV-based junctions.

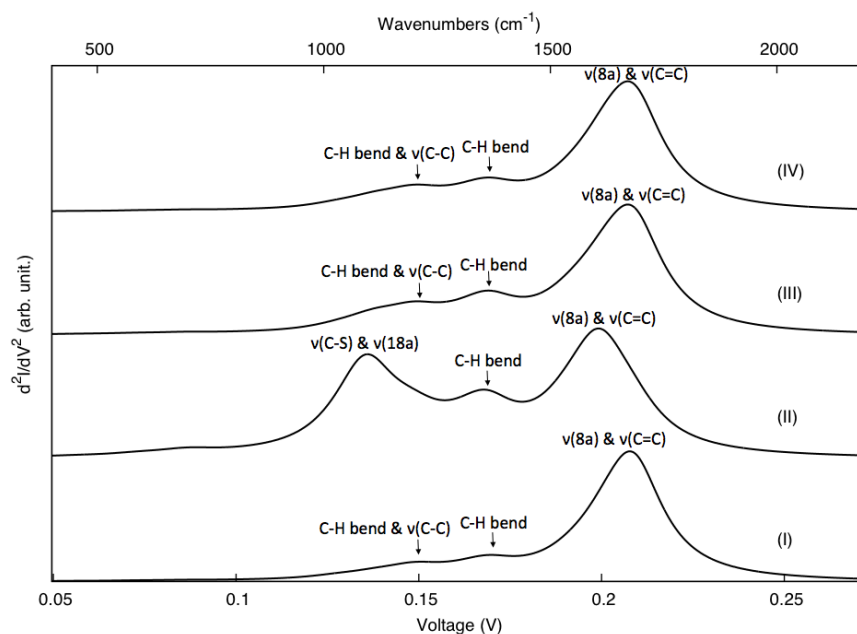


Fig. V.21. IET spectra of the configuration I calculated at the B3LYP/cc-pVTZ level and of the configurations II, III and IV of the OPV-based junctions evaluated at the B3LYP-cc-pVTZ/LANL2DZ level of calculation. The FWHM is set to 20 mV.

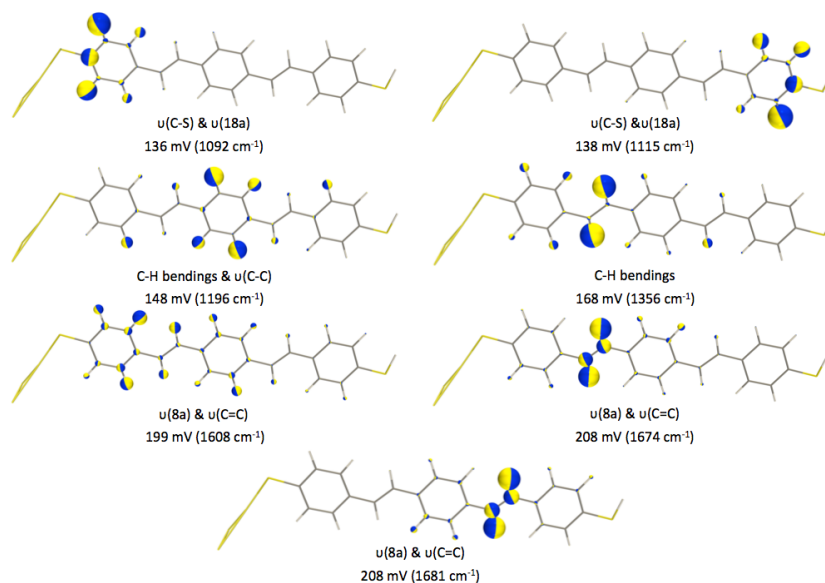


Fig. V.22. Sketch of the IET active modes of the configuration II of the OPV-based junction, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of approximation.

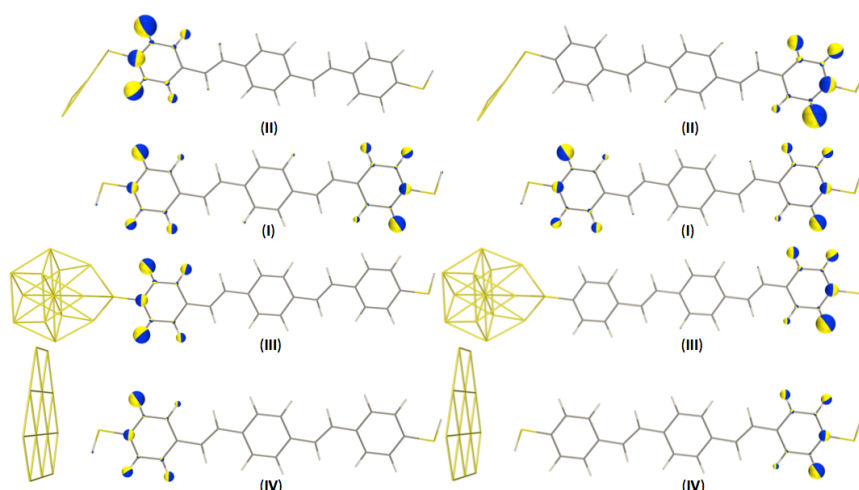


Fig. V.23. Illustration of the $\nu(18a)$ ring motions together with C-S stretchings obtained for the configurations I, II, III and IV of the OPV-based junctions.

As observed in the case of the OPE-based junctions, the addition of the Au(111) surface to represent the drain reservoir [Fig. (V.24)] leads to significant variations of the IET response [Fig. (V.25)], and their corresponding peak positions and intensities are reported in Table (V.5). Let us first consider the molecular systems **V** and **VI**, for which the distance between the sulfur and the closest gold atom is 4 Å on the basis of energetic profiles studies. The major signature associated to $\nu(8a)$ ring motions together with C=C stretchings and the band associated to C-H bending motions become inactive with respect to configuration **II** and **III**, while C-S stretchings and ring distortions observed at 85 mV (sketched in Fig. (V.26) and Fig. (V.27)) dominate the spectrum. In addition, the comparison of the IET responses of configurations **II** and **V** shows a decrease of the relative intensity of the band associated to $\nu(18a)$ ring motions together with C-S stretchings which is not related to a change of the nature of the vibrational modes since the correlation between the **II/V** modes provides overlap values equal to 1. Finally, we note that the high similarity between the IET spectra of configurations **V** and **VI** suggests that, in this case, the shape of the source electrode (triangular gold trimer vs. cluster of 13 gold atoms) does not affect the IET response.

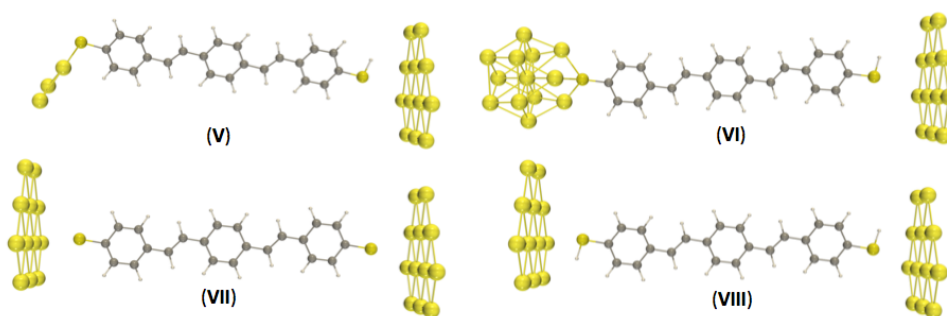


Fig. V.24. IET spectra of the contact configurations **V**, **VI**, **VII** and **VIII** of the OPV-based junctions, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

Contact configuration	Peak position mV cm ⁻¹		Intensity (arb. units)	mode description
V	73	590	1.60×10 ⁻¹⁰	ν(C-S) & long. motions
	85	685	3.19×10 ⁻¹⁰	ν(C-S) & ring distortions
	88	709	3.10×10 ⁻¹⁰	ν(C-S) & ring distortions
	135	1092	2.32×10 ⁻¹¹	ν(C-S)+ ν(18a)
	138	1114	2.13×10 ⁻¹¹	ν(C-S)+ ν(18a)
VI	73	589	8.28×10 ⁻¹²	ν(C-S) & long. motions
	85	683	1.65×10 ⁻¹¹	ν(C-S) & ring distortions
	88	708	1.59×10 ⁻¹¹	ν(C-S) & ring distortions
	136	1095	1.01×10 ⁻¹²	ν(C-S)+ ν(18a)
	138	1114	9.54×10 ⁻¹³	ν(C-S)+ ν(18a)
VII	54	436	4.33×10 ⁻¹³	ν(Au-S) & long. motions
	72	580	6.53×10 ⁻¹³	ν(C-S) & long. motions
	83	673	1.03×10 ⁻¹²	ν(C-S) & ring distortions
	87	698	9.73×10 ⁻¹³	ν(C-S) & ring distortions
	131	1059	9.62×10 ⁻¹³	ν(C-S)+ ν(18a)
	132	1064	9.61×10 ⁻¹³	ν(C-S)+ ν(18a)
	188	1516	2.69×10 ⁻¹³	C-H bendings & ν(C-S)
	188	1519	2.69×10 ⁻¹³	C-H bendings & ν(C-S)
VIII	85	683	6.32×10 ⁻¹²	ν(C-S) & ring distortions
	88	708	6.22×10 ⁻¹²	ν(C-S) & ring distortions
	128	1032	4.60×10 ⁻¹²	C-C-C & C-H bendings
	138	1113	3.17×10 ⁻¹²	ν(C-S)+ ν(18a)
	138	1113	3.17×10 ⁻¹²	ν(C-S)+ ν(18a)
	190	1530	6.82×10 ⁻¹²	C-H bendings & ν(C-S)
	190	1531	6.82×10 ⁻¹²	C-H bendings & ν(C-S)
	202	1633	4.10×10 ⁻¹²	ν(8a)
	204	1645	3.76×10 ⁻¹²	ν(8a)

Table V.5. Peak positions (mV and cm⁻¹), intensities (arb. units) and descriptions of the IET active modes of the OPV-based junctions for the four contact configurations **V**, **VI**, **VII**, and **VIII**.

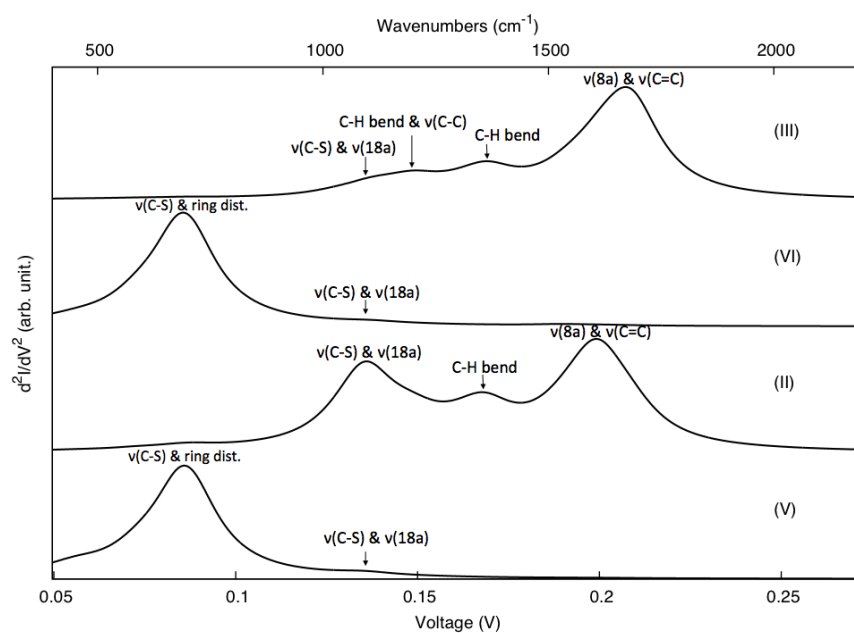


Fig. V.25. IET spectra of the configurations **V**, **II**, **VI** and **III** of the OPV-based junctions calculated at the B3LYP-cc-pVTZ/LANL2DZ level of calculation. The FWHM is set to 20 mV.

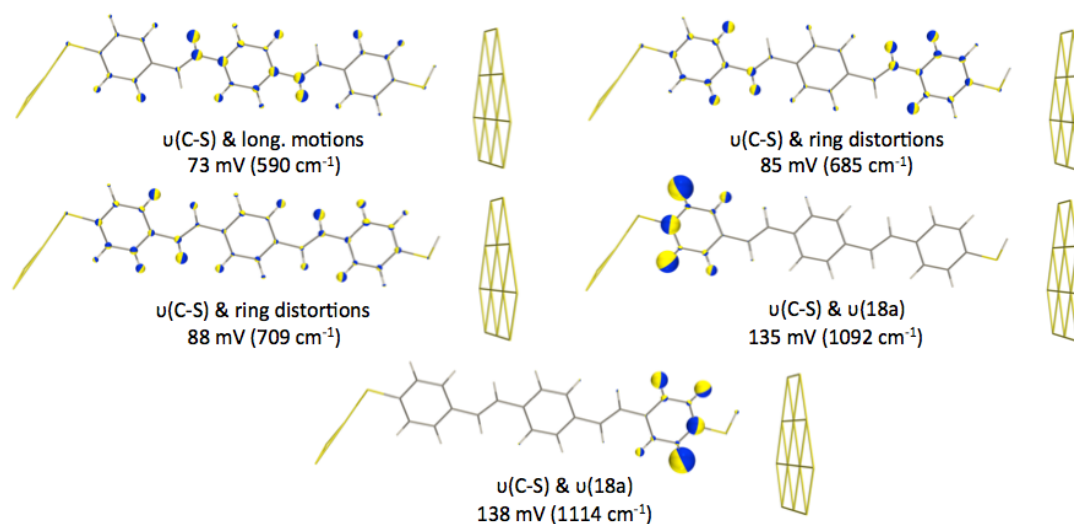


Fig. V.26. Sketch of the IET active modes of the configuration **V** of the OPV-based junction evaluated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

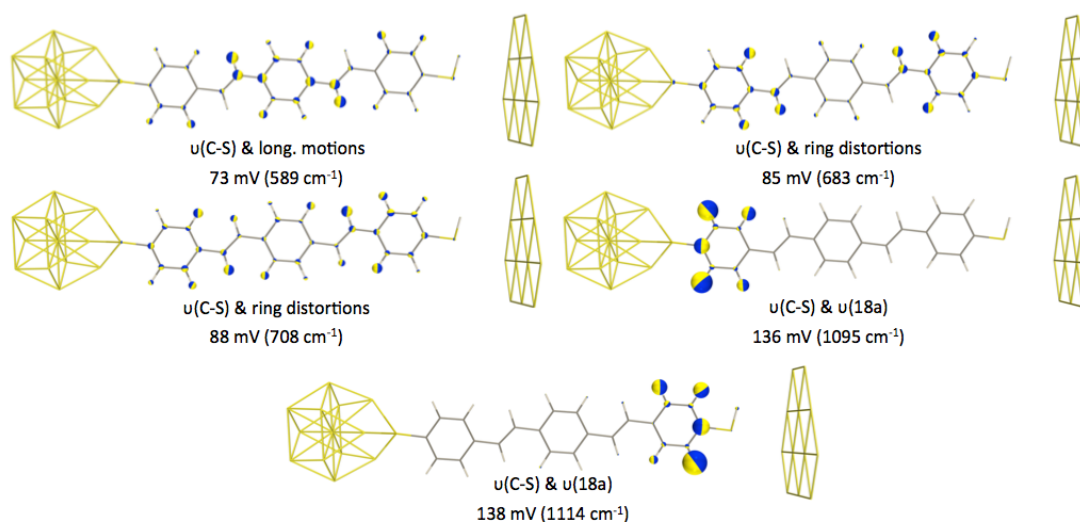


Fig. V.27. Illustration of the IET active modes of the configuration **VI** of the OPV-based junction calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

In addition to these calculations, we have evaluated the effect of the thiol hydrogen on the IET signatures by comparing the responses of molecular systems **VII** and **VIII** represented in Fig. (V.24), for which the sulfur atoms are anchored in hollow position (the distance between the sulfur atom and the closest gold atom being equal to 3.5 Å). As observed in the case of the OPE-based junctions, the IET spectroscopy can be useful for identifying the presence of the hydrogen characteristic of the terminal thiol groups anchored to the gold surfaces. Indeed, even if both spectra are dominated by C-S stretchings and ring distortions (respectively found at 83 mV and 85 mV for configurations **VII** and **VIII**), differences in the IET signatures may be observed [Fig. (V.28)]. The IET active modes of these configurations are presented in Figs. (V.29) and (V.30). In the case of configuration **VIII** characterized by a thiol-terminated OPV structure two IET active modes emerge. They correspond to C-C-C- and C-H bending motions (128 mV) and to $\nu(8a)$ ring motions (202 and 204 mV) [Fig. (V.30)]. We can notice that such variation already occurred in the case of the analog OPE-based junction (configuration **VIII**). Among the common IET active modes, we can make similar observations with respect to the case of OPE-based junctions. Indeed, the relative intensity of the band associated to C-S stretchings together with $\nu(18a)$ ring motions (observed at 132 mV **VII** and 138 mV **VIII**) decrease for configuration **VIII** characterized by thiol-terminated structures, what can again be rationalized by the larger deformation of the conjugated path in this case [Fig. (V.31)]. On the other hand, the relative intensity of the band corresponding to C-H bendings together with C-S stretchings (observed at 188 mV (**VII**) and 190 mV (**VIII**)) increase for configuration **VIII**, and is associated to a larger amplitude of the motion of carbon atoms in the direction of the conjugated path [Fig. (V.31)]. The distinction of the thiol- and thiolate structures on the basis of their IET signatures is therefore straightforward.

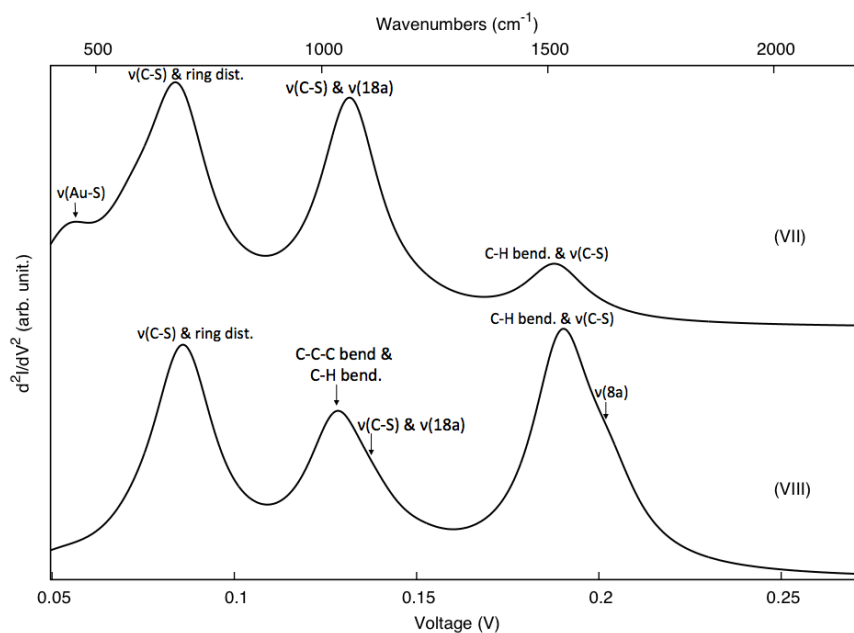


Fig. V.28. IET spectra of the contact configuration **VII** and **VIII** of the OPV-based junctions, calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

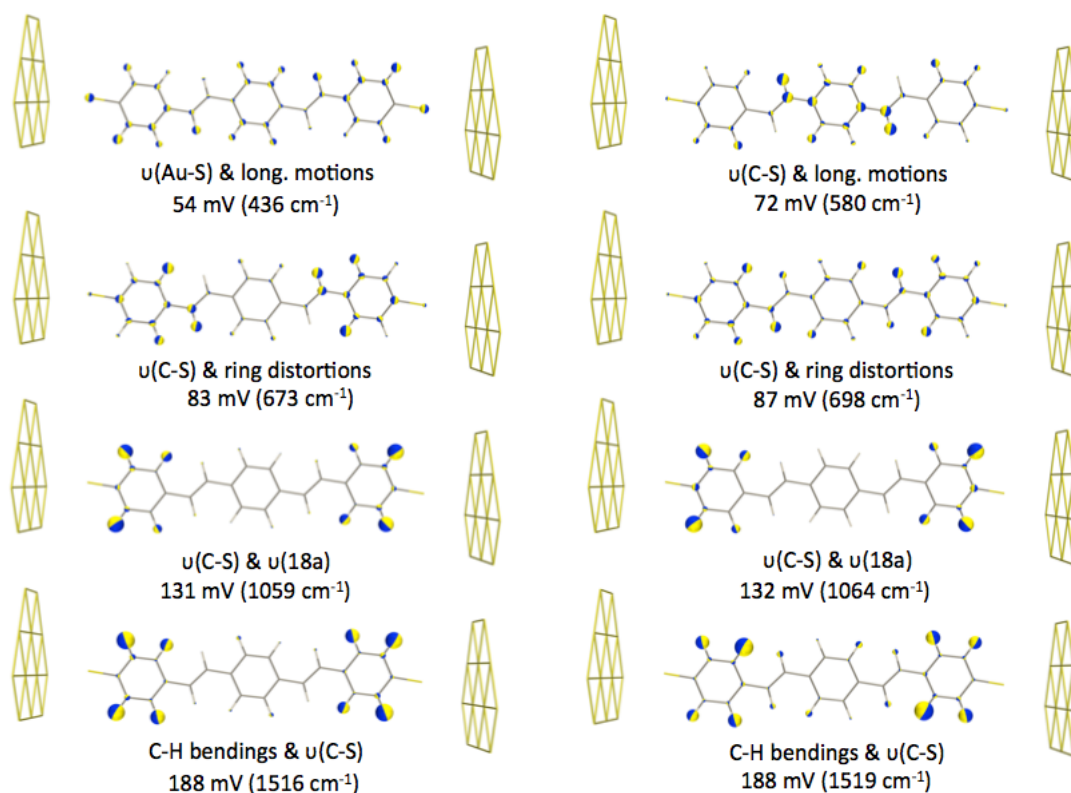


Fig. V.29. Illustration of the IET active modes of the configuration **VII** of the OPV-based junction calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

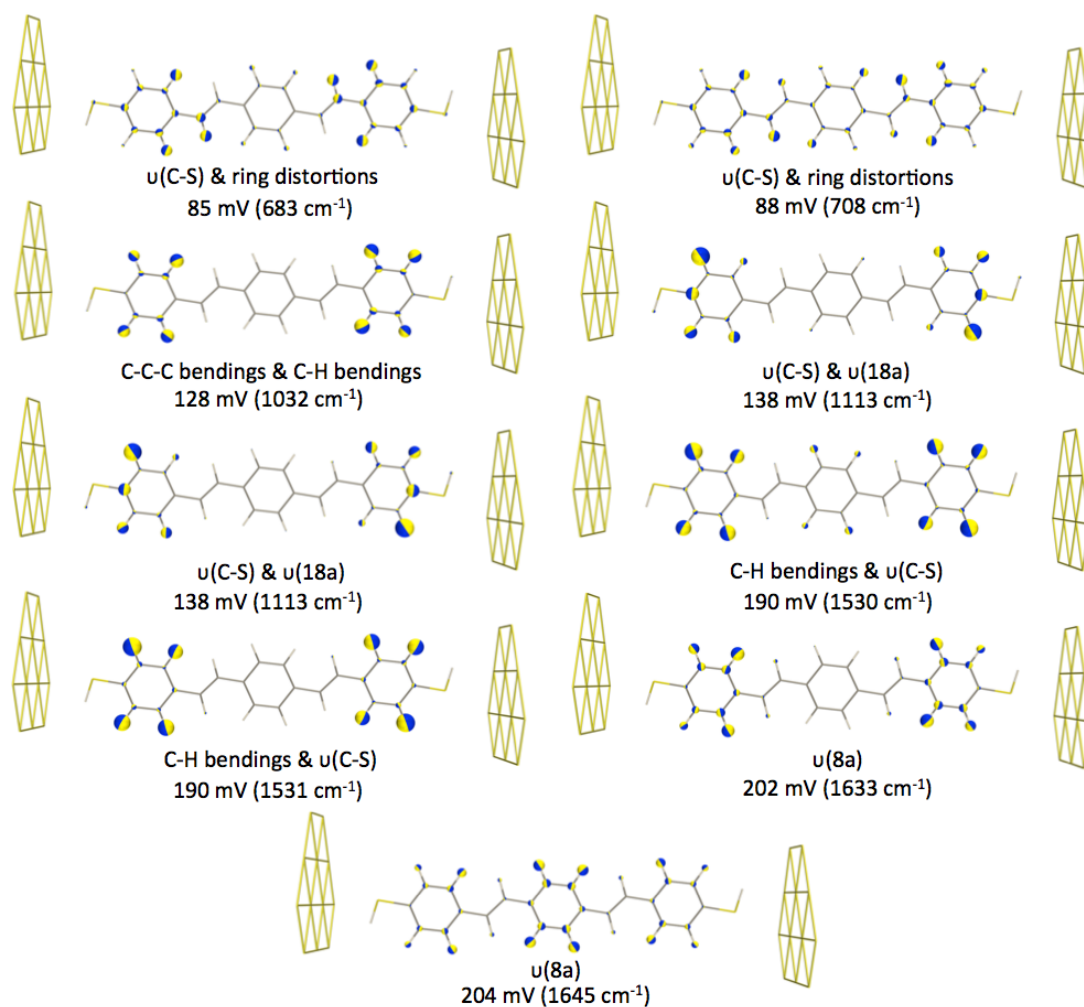


Fig. V.30. Illustration of the IET active modes of the configuration **VIII** of the OPV-based junction calculated at the B3LYP/cc-pVTZ/LANL2DZ level of calculation.

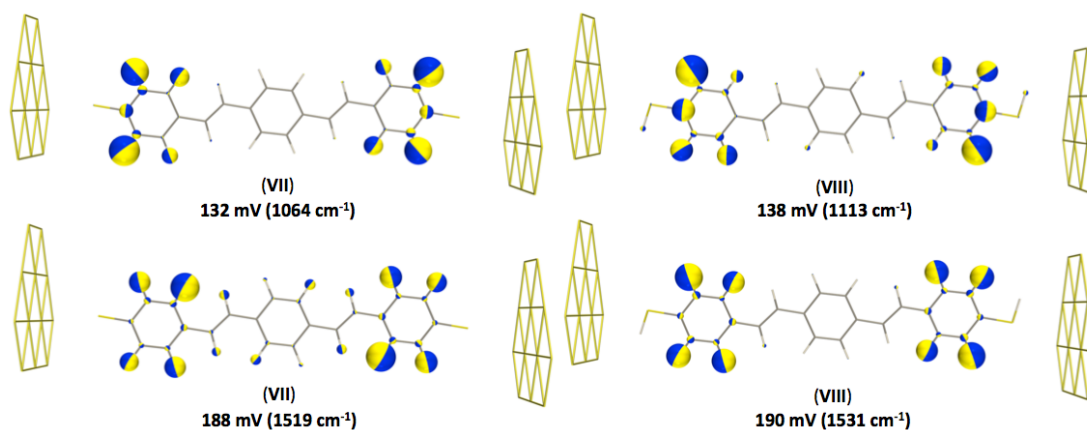


Fig. V.31. Illustration of i) the B3LYP/cc-pVTZ/LANL2DZ $\nu(18a)$ ring motions associated with C-S stretchings of contact configurations **VII** and **VIII** of the OPV-based junctions observed at 132 mV (1064 cm^{-1}) and at 138 mV (1113 cm^{-1}), respectively ; ii) the B3LYP/cc-pVTZ/LANL2DZ C-H bending motions associated with C-S stretchings observed at 188 mV (1519 cm^{-1}) for configuration **VII** and at 190 mV (1531 cm^{-1}) for configuration **VIII** of the OPV-based junctions. The overlap values between the **VII/VIII** pair of modes are equal to i) 0.750 and ii) 0.779.

V.D. Conclusions

On the basis of these results, we can draw some conclusions. In the case of a C₁₁-based junction we showed that two factors can have a significant impact on the IET response: i) the orientation of the molecule with respect to the electrode planes, and ii) the molecule-drain distance. We also showed that the differences in IET signature tend to vanish when increasing the molecule-electrode distance, independently of the molecular orientation. Among the set of studied configurations, we found that configuration **II** with $d=1.3$ Å provides the best agreement with experimental measurements. This observation is of great interest to propose which configuration may better correspond to the experimental setup, since we know that the IET spectroscopy is sensitive to the junction configuration and previous investigations on other geometries have often shown a neat underestimation of the peak corresponding to C-H stretchings of the terminal methyl group. Our results on the configuration consisting of a gold-trimer source electrode are consistent with the investigation of Kula et al., who already observed that the C₁₁ molecule is chemically bonded via the anchoring thiol group to a gold trimer electrode.

Considering conjugated molecular cores, e.g. the OPE and OPV structures, we observed via the investigation of drain-less configurations that the shape of the source reservoir does not affect much the IET response, except in the case of the OPV configuration **II** for which we notice a greater contribution of the mode associated to C-S stretchings and $\nu(18a)$ ring motions. This specific feature originates from the larger amplitude of the longitudinal C-S stretching motion involved in the molecule-metal coupling. Moreover, this configuration leads to the best agreement with experiment.

The study of drain-including configurations has shown that the explicit description of the drain electrode affects significantly the IET responses. Indeed, only the bands relative to C-S stretchings together with $\nu(18a)$ ring modes are active for all the contact configurations. Upon the addition of the drain reservoir, longitudinal C-S stretching motions are involved in all the modes presenting the major contribution to each IET spectrum. Note that, in the case of the OPE-based junction, none of the studied configurations can be associated to the experimental response. However, the latter can be viewed as an intermediate situation between the signatures obtained for configurations **IV** and **VIII** (i.e. the drain-less and drain-including structures for which every electrode is represented by Au(111) surfaces). It could therefore be interesting to investigate further the influence of the junction asymmetry on this response by varying the molecule-drain

distance, in order to verify if such an intermediate configuration matching the experimental spectrum can be identified.

The IET spectroscopy can be useful to determine the experimental structure involved in the molecule-metal junction, *i.e.* it allows to differentiate thiol- and thiolate-terminated molecules. The comparisons of the IET signatures of configurations **VII** and **VIII** for both systems present several similarities: indeed, some modes (all involving C-S stretching motions) are common to all the configurations even if they present different relative intensities, while two bands involving CCC bendings together with C-H bending motions and $\nu(8a)$ specifically emerge for thiol-terminated configurations **VIII**. We also suggested that the intensity variations of the common modes can be rationalized considering the propensity of the atomic motions involved in each vibrational mode to follow the direction of the conjugated path or to deform it.

V.E. References.

- [1] Moreno-Garcia, P.; Gulcur, M.; Manrique, D. Z.; Pope, T.; Hong, W.; Kaliginedi, V.; Huang, C.; Batsanov, A. S.; Bryce, M. R.; Lambert, C.; Wandlowski, T. *J. Am. Chem. Soc.* **2013**, *135*, 12228-12240.
- [2] (a) Kushmerick, J. G.; Holt, D. B.; Pollack, S. K.; Ratner, M. A.; Yang, J. C.; Schull, T. L.; Naciri, J.; Moore, M. H.; Shashidhar, R. *J. Am. Chem. Soc.* **2002**, *124*, 10654-10655. (b) Dadosh, T.; Gordin, Y.; Krahne, R.; Khivrich, I.; Mahalu, D.; Frydman, V.; Sperling, J.; Yacoby, A.; Bar-Joseph, I. *Nature*, **2005**, *436*, 677-680.
- [3] (a) Seminario, J. M.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 12418-12419. (b) Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nature* **2006**, *442*, 904-907. (c) Chen, I-W. P.; Fu, M-D.; Tseng, W-H.; Chen, C-H.; Choub, C-M.; Luh, T-Y. *Chem. Comm.* **2007**, 3074-3076.
- [4] (a) Lin, L. L.; Wang C. K.; Luo, Y. *ACS Nano* **2011**, *5*, 2257-2263; (b) Troisi, A.; Ratner, M. A. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2421-2427. (c) Leng, J. C.; Lin, L. L.; Song, X. N.; Li, Z. L.; Wang, C. K. *J. Phys. Chem. C* **2009**, *113*, 18353-18357.
- [5] (a) Chen, F.; Li, X.; Hihath, J.; Huang, Z.; Tao, N. *J. Am. Chem. Soc.* **2006**, *128*, 15874-15881. (b) Seminario, J. M.; De La Cruz, C. E.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 5616-5617. (c) Hipps, K. W. *Science* **2001**, *294*, 536-537. (d) Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571-574.
- [6] (a) Salomon, A.; Cahen, D.; Lindsay, S.; Tomfohr, J.; Engelkes, V. B.; Frisbie, C. D. *Adv. Mater.* **2003**, *15*, 1881-1890. (b) Akkerman, H. B.; de Boer, B. J. *Phys.: Condens. Matter* **2008**, *20*, 013001.
- [7] Czerwinski, W.; Linden, L. A.; Rabek, J. F. *J. Mater. Sci.* **2000**, *35*, 455-463.
- [8] Aviram, A.; Ratner, M. A. Eds. *Molecular Electronics: Science and Technology*, The annals of the New York Academy of Sciences, Vol 852, The New York Academy of Sciences, New York, 1998.
- [9] (a) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to self-assembly*, Academic Press, Boston, 1991. (b) Wink, Th. van Zuilen, S. J.; Bult, A.; van Bennekom, W. P. *Analyst.* **1997**, *122*, 43R-50R. (c) Chaki, N. K.; Vijayamohan, K. *Biosens. Bioelectron.* **2002**, *17*, 1-12. (d) Miozzo, L.; Yassar, A.; Horowitz, G. *J. Mater. Chem.* **2010**, *20*, 2513-2538.
- [10] Akkerman, H. B.; Blom, P. W. M.; de Leuw, D; M.; de Boer, B. *Nature* **2006**, *441*, 69-72.
- [11] (a) Chang, S. C.; Chao, I.; Tao, Y. T. *J. Am. Chem. Soc.* **1994**, *116*, 6792-6805. (b) Arnold, R.; Terfort, A.; Wöll, C. *Langmuir*, **2001**, *17*, 4980-4989.
- [12] (a) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.*, **1991**, *113*, 8284-8293. (b) Bensebaa, F.; Zhou, Y.; Brolo, A. G.; Irish, D. E.; Deslandes, Y.; Kruus, E.; Ellis, T. H. *Spectrochim. Acta Mol. Biomol. Spectros.* **1999**, *55*, 1229-1236.
- [13] (a) Lis, D.; Peremans, A.; Sartenaer, Y.; Caudano, Y.; Mani, A. A.; Dreesen, L.; Thiry, P. A.; Guthmuller, J.; Champagne, B.; Cecchet, F. *J. Phys. Chem. C* **2009**, *113*, 9857-9864. (b) Cecchet, F.;

Lis, D.; Guthmuller, J.; Champagne, B.; Caudano, Y.; Silien, C.; Mani, A. A.; Thiry, P. A.; Peremans, A. *ChemPhysChem* **2010**, *11*, 607-615. (c) Cecchet, F.; Lis, D.; Caudano, Y.; Mani, A. A.; Peremans, A.; Champagne, B.; Guthmuller, J. *J. Phys.: Condens. Matter*. **2012**, *24*, 124110.

[14] Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117-1127.

[15] Kushmerick, J. G.; Lazorcik, J.; Patterson, C. H.; Shashidhar, R.; Seferos, D. S.; Bazan, G. C. *Nano Lett.* **2004**, *4*, 639-642.

[16] (a) Gregory, S. *Phys. Rev. Lett.* **1990**, *64*, 689-692. (b) Kushmerick, J.G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. *Phys. Rev. Lett.* **2002**, *89*, 086802.

[17] (a) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705-1707. (b) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, *119*, 10563-10564. (c) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721-2732. (d) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. *Nature* **1998**, *396*, 60-63. (e) Creager, S.; Yu, C. J.; Bamdad, C.; O'Sonnor, S.; MacLean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059-1064. (f) Sikes, H. D.; Smalley, J.F.; Dudek, S. P.; Cook, A. R.; Newton, M. D.; Chidsey, C. E. D.; Feldberg, S. W. *Science* **2001**, *291*, 1519-1523.

[18] Ségerie, A.; Lin, L-L.; Liégeois, V.; Luo, Y.; Champagne, B. *Spectrochim. Acta Part A: Mol. and Biomol. Spectrosc.* **2014**, *119*, 34-41.

[19] Kula, M.; Jiang, J.; Luo, Y. *Nano Lett.* **2006**, *6*, 1693-1698.

[20] Lin, L-L. ; Zou, B. ; Wang, C-K.; Luo, Y. *J. Phys. Chem. C* **2011**, *115*, 20301-20306.

[21] (a) Chen, Y-C.; Zwolak, M.; Di Ventra, M. *Nano Lett.* **2005**, *5*, 621-624. (b) Troisi, A.; Ratner, M. A. *Phys. Rev. B* **2005**, *72*, 033408. (c) Paulsson, M.; Frederiksen, T.; Brandbyge, M. *Nano Lett.* **2006**, *6*, 258-262. (d) Okabayashi, N.; Paulsson, M.; Ueba, H.; Konda, Y.; Komeda, T. *Nano Lett.* **2010**, *10*, 2950-2955.

[22] Yoon, H. P.; Maitani, M. M.; Cabarcos, O. M.; Cai, L.; Mayer, T. S.; Allara, D. L. *Nano Lett.* **2010**, *10*, 2897-2902.

[23] (a) Grönbeck, H.; Curioni, A.; Andreoni, W. *J. Am. Chem. Soc.* **2000**, *122*, 3839-3842. (b) Basch, H.; Ratner, M. A. *J. Chem. Phys.* **2004**, *120*, 5771-5780. (c) Strange, M.; Rostgaard, C.; Häkkinen, H.; Thygesen, K. S. *Phys. Rev. B* **2011**, *83*, 115108(1)-115108(12).

[24] Demir, F.; Kirczenow, G. J. *Chem. Phys.* **2012**, *136*, 014703-014713

[25] Das, B. *Nanotechnology* **2010**, *21*, 395201.

[26] *Tunneling Spectroscopy: Capabilities, Applications, and new Techniques*, ed. Hansma, P. K., Plenum, New York, 1982.

Inelastic Electron Tunneling of C_{60} on gold surfaces from first principles calculations

Ségerie, A.; Liégeois, V.; Champagne, B. (to be submitted)

VI. Inelastic Electron Tunneling of C₆₀ on gold surfaces from first principles calculations

VI.A. Introduction

Among promising candidates for the development of new functional materials, fullerene-based nanojunctions^[1] have been intensively investigated over the last decade due to their interesting properties, such as a high symmetry^[2] which defines a large number of degenerate electronic and vibrational levels, an efficient charge conduction,^[3] etc... The interest of using fullerene-based devices as functional units in electronic circuits, *e.g.* electrical amplifiers,^[4] single transistors,^[5] molecular switches,^[6] or sensors^[7] has been proved in the literature, and thereby encourages the development of future nanodevices.

The design of such systems is however hindered by practical difficulties related to the control of the contact between the functional molecule and the metallic electrodes, as it greatly affects the transport properties^[8]. In order to get an accurate description of the molecular junctions at the atomic scale, different experimental techniques and theoretical methods have been developed^[9] to study the relationships between the interactions at the interface, the tunneling charge carriers, the vibrational signatures, and the charge transport characteristics.

Scanning Tunneling Microscopy (STM) has appeared as a powerful analysis tool since the first studies on the electrical contact of a single-C₆₀ molecule adsorbed on a Au(110) surface because it provides information about the molecular orientations and electronic properties^[10]. Moreover, it has evidenced the ability of C₆₀ to act as an efficient electromechanical amplifier under the mechanical deformation exercised by the metallic tip^[4b]. Studies based on STM measurements are however limited by the asymmetric contacts and the difficulties to maintain a stable chemical bond between the molecule and the metallic tip when working at room temperature. The experimental conditions can be improved by the introduction of the Mechanically Controllable Break Junction (MCBJ) technique,^[11] which offers a huge control and tunability of the contact size, and enhances the reproducibility and mechanical stability of a single contact configuration, allowing to carry multiple measurements over several hours and thereby to provide highly reliable conductance results.

The Inelastic Electron Tunneling Spectroscopy (IETS) technique^[12] introduced in Chapter I probes the molecular structure of the junction by detecting the inelastic interactions between the tunneling electrons and the vibrational modes of the molecule, and emerged as a powerful tool to

identify and characterize vibrational signatures of single-molecular contacts. Its high sensitivity to the contact geometry and to the molecular orientation with respect to the metallic electrodes can provide structural information on the molecular junction,^[13] and enables to ascertain that the molecule is inside the junction and participates to the conduction process. Studies based on the combination of the IET spectroscopy with the MCBJ technique have shown the possibility to get specific fingerprint information of a controlled contact geometry.^[14]

Here, we report theoretical simulations of the IET spectra of a single C₆₀ molecule embedded between two gold electrodes. In particular, we focus on the effects i) of the molecular orientation of the C₆₀ molecule on the gold electrode plane and ii) of the molecule-electrode distance on the IET response. These results are compared to recent experimental measurements using a MCBJ device.^[15]

VI.B. Theoretical and Computational aspects

In our calculations, the scattering region (*i.e.* the extended molecule) is represented by a single C₆₀ molecule sandwiched between two gold electrodes. Each of them is described as an Au(111) surface containing 12 atoms with interatomic distances of 2.88 Å. This size of electrodes has been proved to reproduce correctly experimental results^[16], and provides a good compromise between accuracy and computational needs. Geometry optimizations, vibrational frequencies as well as the first-order derivatives of the wavefunction with respect to the normal coordinates were performed at the density functional theory (DFT) level. In a recent investigation^[17] (reported in Section III) we have shown the adequacy of using a double- ζ (cc-pVDZ) basis set with respect to more extended basis sets like the triple- ζ cc-pVTZ to describe the vibrational modes of the organic junction. This was combined with the LANL2DZ pseudo potential basis set for describing the gold atoms. The effect of adding dispersion corrections to the XC functionals, recommended for applications where non-covalent interactions are expected to be significant, has been analyzed by comparing the IET responses obtained with the traditional B3LYP XC functional and with B3LYP including Grimme's D3 atom-atom dispersion corrections with Becke-Johnson damping^[18]. Following the molecular properties calculation, the density current through the molecular junction is obtained by using the QCME code. In the IET simulation, the temperature is fixed to 10K and the full width at half maximum (FWHM) of the IET spectra to 20 cm⁻¹.

The analysis of the modifications of IET active vibrational modes observed by changing the molecule-electrode distances (dispersion corrections in the B3LYP XC functional) was performed

by using the PyVib2 program,^[19] which determines the mode overlaps. So, for a fragment F, the $O_{p'p}^{AB,F}$ overlap between mode p' of molecular junction A (XC functional A) and mode p of molecular junction B (XC functional B) is defined as the square of the scalar product between the two normal modes:

$$O_{p'p}^{AB,F} = \left\langle Q_{p'}^{A,F} \left| Q_p^{B,F} \right. \right\rangle^2 = \left(\sum_{i\alpha}^F Q_{i\alpha,p'}^A Q_{i\alpha,p}^B \right)^2$$

$Q_{i\alpha,p}$ is the mass-weighted Cartesian displacement of atom i in direction α for the p^{th} normal mode. Each Q_p is normalized so that $\sum_{i\alpha}^{3N} (Q_{i\alpha,p})^2 = 1$. The overlaps are dimensionless and their values range from 0 to 1.

VI.C. Results and discussion

Two major junction parameters modulating the IET intensity have been analyzed: i) the orientation of the C_{60} molecule on the gold electrode plane and ii) the molecule-electrode distance. Concerning the first, Wang et al.^[20] have evidenced by performing DFT calculations that the energetically preferred adsorption configuration corresponds to a hexagon of C_{60} aligned parallel to the Au(111) surface and centered on an hcp site. In this study, to highlight the sensitivity of IETS to the adsorption configurations, four different orientations of the C_{60} molecule are tackled and they correspond to i) two hexagons (on both sides) of C_{60} aligned parallel to the surface and centered on an hcp site ii) two pentagons of C_{60} aligned parallel to the surface and centered on an hcp site iii) two 6:6 ring bonds (hexagon:hexagon) parallel to the surface and centered on an hcp site, and iv) two 6:5 ring bonds (hexagon:pentagon bond) parallel to the surface and centered on an hcp site. Figure (VI.1) displays these four orientations, which are respectively labeled **H**, **P**, **H-H** and **H-P**. The forthcoming analysis starts with the IET responses for the **H** adsorption configuration and the study of (i) the influence of the molecule-electrode distance on the IET response, and (ii) the impact of adding dispersion corrections in the XC functional. Then, the effect of the orientation of the molecule on the gold electrode is addressed by analyzing the IET spectra obtained for the **P**, **H-H**, and **H-P** adsorption configurations with different molecule-electrode distances.

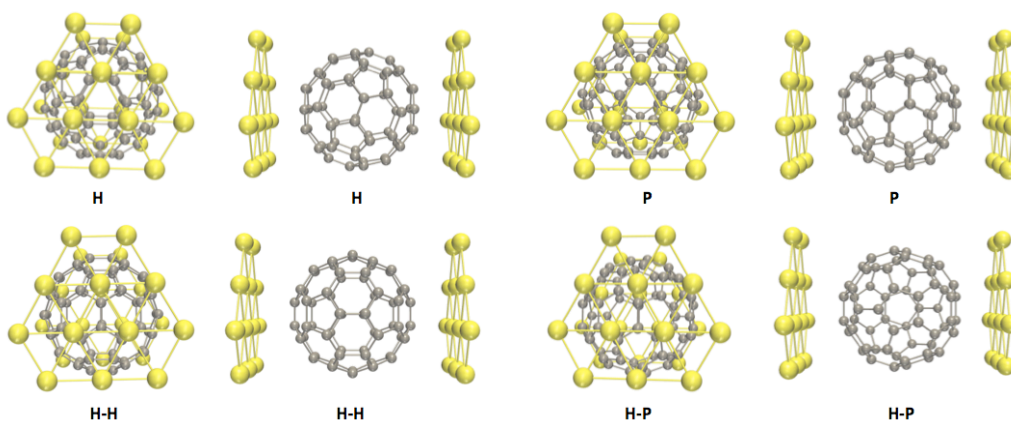


Fig. VI.1. Representation of the top and side views of the different adsorption configurations (**H**, **P**, **H-H** and **H-P**) of the C_{60} molecule between Au electrodes.

VI.C.1. Analysis of the IET response in the H adsorption configuration by varying the molecule-electrode distance.

First the *equilibrium* distance between the C_{60} molecule and the Au electrodes has to be determined. This is achieved by evaluating the energy profile as a function of the C_{60} molecule-electrode distance. In the **H** adsorption configuration this is the distance between the center of the hexagon (aligned parallel to the Au(111) surface) and the hcp site of the Au(111) surface. It is observed that the molecular junction becomes stable when the C_{60} molecule-electrode distance is 2.8 Å when using B3LYP(D) (3.2 Å with B3LYP). These observations are in good agreement with experimental and theoretical studies that have evidenced that C_{60} is tightly held on gold by van der Waals interactions with an equilibrium distance from the center of the C_{60} molecule to the gold surface of about 6.2 Å.^[21] The distance between the C_{60} center and any hexagon center amounts to 3.3 Å. However, it is expected that this distance varies in real devices as a function of the *surrounding* effects, which implies a study of the influence of the molecule-electrode distance on the IET response. So, IET spectra calculated at the B3LYP/cc-pVDZ/LANL2DZ level are represented in Fig. (VI.2) for C_{60} molecule-electrode distances ranging from 2.0 Å to 4.0 Å. The vibrational frequencies (cm^{-1}) and corresponding transition potentials (mV), and the IET intensities (arb. units) of the dominant vibrational modes are reported in Tables (VI.1-7). Note that modes which are not labeled in our tables are not correlated with the modes found for the equilibrium distance $d=2.8$ Å we have considered as references.

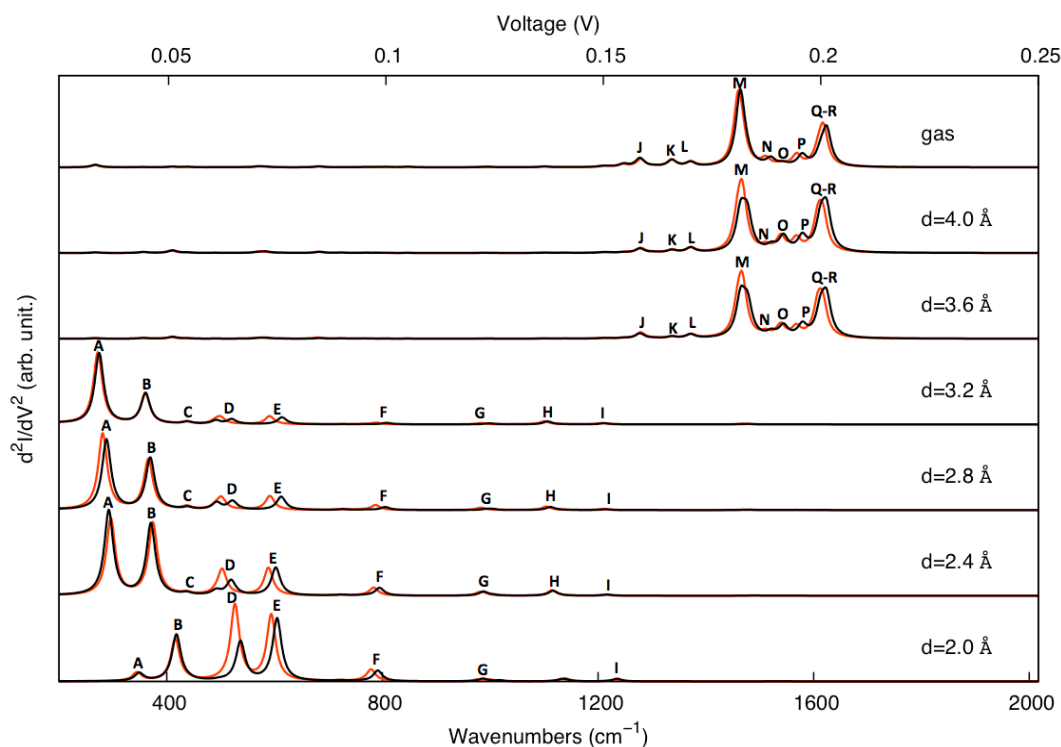


Fig. VI.2. IET spectra of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ (red line) and B3LYP(D)/cc-pVDZ/LANL2DZ (black line) levels of approximation by considering molecule-electrode distance values ranging from 2.0 Å to 4.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	344	43	5.45×10^{-8}	0.122
B	416	52	2.48×10^{-7}	0.554
D	526	65	4.48×10^{-7}	1.000
E	594	74	3.90×10^{-7}	0.871
F	779	97	7.04×10^{-8}	0.157
G	999	124	1.25×10^{-8}	0.028
-	1139	141	1.84×10^{-8}	0.041
I	1233	153	1.08×10^{-8}	0.024

Table VI.1. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.0 Å. Note that modes which are not labeled in our tables are not correlated with the modes found for the equilibrium distance d=2.8 Å we have considered as references.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	296	37	6.59×10 ⁻¹⁰	1.000
B	374	46	6.22×10 ⁻¹⁰	0.944
C	437	54	4.28×10 ⁻¹¹	0.065
D	503	62	2.30×10 ⁻¹⁰	0.349
E	589	73	2.39×10 ⁻¹⁰	0.363
F	784	97	6.93×10 ⁻¹¹	0.105
G	989	123	3.29×10 ⁻¹¹	0.050
H	1114	138	4.67×10 ⁻¹¹	0.071
I	1214	151	9.44×10 ⁻¹²	0.014

Table VI.2. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.4 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	281	35	1.97×10 ⁻¹²	1.000
B	366	45	1.32×10 ⁻¹²	0.670
C	437	54	1.26×10 ⁻¹³	0.064
D	501	62	3.53×10 ⁻¹³	0.179
E	591	73	3.66×10 ⁻¹³	0.186
F	787	98	1.31×10 ⁻¹³	0.066
G	985	122	6.00×10 ⁻¹⁴	0.030
H	1104	137	9.15×10 ⁻¹⁴	0.046
I	1208	150	2.84×10 ⁻¹⁴	0.014

Table VI.3. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.8 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	272	34	3.20×10 ⁻¹⁵	1.000
B	360	45	1.39×10 ⁻¹⁵	0.434
C	437	54	1.51×10 ⁻¹⁶	0.047
D	500	62	3.65×10 ⁻¹⁶	0.114
E	591	73	3.71×10 ⁻¹⁶	0.116
F	788	98	8.11×10 ⁻¹⁷	0.025
G	983	122	5.67×10 ⁻¹⁷	0.018
H	1101	137	1.43×10 ⁻¹⁶	0.045
I	1207	150	6.40×10 ⁻¹⁷	0.020

Table VI.4. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=3.2 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
J	1279	159	1.04×10 ⁻¹³	0.098
K	1337	166	4.59×10 ⁻¹⁴	0.043
L	1372	170	8.18×10 ⁻¹⁴	0.077
M	1468	182	1.06×10 ⁻¹²	1.000
N	1511	187	1.62×10 ⁻¹³	0.153
O	1539	191	2.61×10 ⁻¹³	0.246
P	1568	194	2.39×10 ⁻¹³	0.225
Q	1608	199	7.60×10 ⁻¹³	0.717
R	1617	200	7.78×10 ⁻¹³	0.734

Table VI.5. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=3.6 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
J	1279	159	1.11×10 ⁻¹⁴	0.073
K	1337	166	8.10×10 ⁻¹⁵	0.053
L	1372	170	1.26×10 ⁻¹⁴	0.083
M	1468	182	1.52×10 ⁻¹³	1.000
N	1511	187	2.31×10 ⁻¹⁴	0.152
O	1539	191	3.93×10 ⁻¹⁴	0.259
P	1568	194	3.67×10 ⁻¹⁴	0.241
Q	1608	199	1.02×10 ⁻¹³	0.671
R	1617	200	1.08×10 ⁻¹³	0.711

Table VI.6. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=4.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
J	1279 (1277)	159 (158)	5.18×10 ⁻¹⁴ (5.89×10 ⁻¹⁴)	0.110 (0.124)
K	1337 (1336)	166 (166)	4.99×10 ⁻¹⁴ (4.77×10 ⁻¹⁴)	0.106 (0.100)
L	1372 (1372)	170 (170)	3.90×10 ⁻¹⁴ (3.77×10 ⁻¹⁴)	0.083 (0.079)
M	1467 (1475)	182 (183)	4.70×10 ⁻¹³ (4.75×10 ⁻¹³)	1.000 (1.000)
N	1511 (1520)	187 (188)	7.09×10 ⁻¹⁴ (6.72×10 ⁻¹⁴)	0.151 (0.141)
O	1539 (1544)	191 (191)	4.00×10 ⁻¹⁴ (3.84×10 ⁻¹⁴)	0.085 (0.081)
P	1568 (1579)	194 (196)	8.83×10 ⁻¹⁴ (8.80×10 ⁻¹⁴)	0.188 (0.185)
Q	1608 (1613)	199 (200)	2.06×10 ⁻¹³ (1.77×10 ⁻¹³)	0.438 (0.373)
R	1618 (1624)	201 (201)	2.72×10 ⁻¹³ (2.56×10 ⁻¹³)	0.579 (0.539)

Table VI.7. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ (B3LYP(D)/cc-pVDZ/LANL2DZ) level of approximation, considering the 'gas model'.

For a molecule-electrode distance of 2.8 Å, the IET spectrum is composed of four major vibrational signatures described in Table (VI.8). The most intense peak (labeled **A**) appearing at 281 cm⁻¹ (35 mV) corresponds to the lowest-energy excitation mode, where the molecule oscillates between a spherical and a prolate shape [Fig. (VI.3)]. Among the three other dominant signatures, peak **B** at 366 cm⁻¹ (45 mV) involves longitudinal motions of the two hexagons moving from one electrode to the other. The peaks **A** and **B** correspond to symmetric and anti-symmetric displacements of the adsorbed hexagon rings with respect to the electrodes. Peaks **D** and **E** are associated to the C₆₀ breathing mode (modification of the radius of the sphere), and to distortions of the two hexagons of the C₆₀ molecule swaying between the two electrodes, respectively.

Peak label	B3LYP		B3LYP(D)		Mode description
	Freq (cm ⁻¹)	Potential (mV)	Freq (cm ⁻¹)	Potential (mV)	
A	281	35	288	36	spherical-to-prolate distortion corresponding to symmetric displacements of the adsorbed hexagon rings with respect to the electrodes
B	366	45	369	46	anti-symmetric displacements of the adsorbed hexagon rings with respect to the electrodes
C	437	54	438	54	distortions of the C ₆₀ molecule: out-of-plane motions of carbon atoms
D	501	62	522	65	C ₆₀ breathing mode
E	591	73	612	76	distortions of the adsorbed hexagons swaying between the electrodes
F	787	98	805	100	distortions motions mainly localized on the carbon atoms closest of each electrodes
G	985	122	1004	124	distortions of the C ₆₀ molecule: C-C stretchings
H	1104	137	1112	138	C-C stretchings of the adsorbed hexagons
I	1208	150	1215	151	C-C stretchings of the adsorbed hexagons

Table VI.8. Label, frequency (cm⁻¹), potential (mV), and description of the vibrational normal modes dominating the IET spectrum of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ and B3LYP(D)/cc-pVDZ/LANL2DZ levels of approximation for d=2.8 Å, represented in Fig. (VI.3).

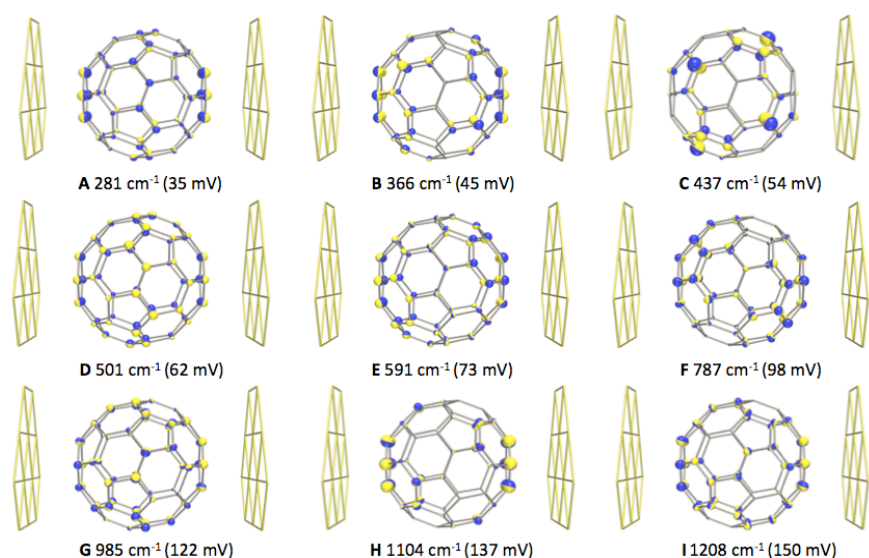


Fig. VI.3. Sketch of the IET active modes (for $d=2.8$ Å) of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation. The direction of atomic displacements is perpendicular to the junction plane between the two hemispheres of distinct color, and their amplitudes are proportional to the radius of the sphere. The sum of the surfaces of the spheres is always constant.

In order to evaluate the effect of the molecule-electrode distance on the IET spectra, we focus on three specific features: the frequency shifts, the relative IET intensities, and the evolution of nature of the vibrational modes given by the overlaps. As displayed in Fig. (VI.2), the same IET signatures are observed for distances ranging from 2.4 Å to 3.2 Å. The frequency shifts observed upon increasing the molecule-electrode distance are the largest for vibrational modes involving atomic motions that are mainly localized on the pair of hexagons parallel to the gold electrodes: e.g. modes **A** and **B** described hereabove and mode **H** involving C-C stretchings in these two hexagons. Their frequencies respectively decrease by 24 cm^{-1} , 14 cm^{-1} , and 13 cm^{-1} when going from a molecule-electrode distance $d=2.4$ Å to $d=3.2$ Å. For the other IET active modes the frequency variations are smaller than 7 cm^{-1} .

When the molecule-electrode distance increases the IET intensities decrease, which is obviously explained by the fact that the energy coupling between the molecule and the electrode decreases. For a molecule-electrode distance ranging from $d=2.4$ Å to $d=3.2$ Å, the relative intensity of peak **B** with respect to the dominant peak **A** presents the largest intensity variation. Based on the mode overlaps reported in Table (VI.9), one observes a perfect correlation between the vibrational modes at 2.8 Å and at 2.4 Å and 3.2 Å. Indeed, among the dominant peaks (*i.e.* **A**, **B**, **D** and **E**), all the overlaps are very close to one.

Peak label	d=2.0Å	d=2.4Å	d=3.2Å
A	0.668	0.995	0.997
B	0.923	0.996	0.993
C	-	0.762	0.851
D	0.783	0.991	0.990
E	0.837	0.854	0.987
F	0.625	0.653	0.694
G	0.978	0.992	0.991
H	-	0.980	0.998
I	0.875	0.479	0.995

Table VI.9. Overlap values between the IET active vibrational modes of the **H** junction obtained for different molecule-electrode distance values, taking as reference the results with $d=2.8\text{\AA}$, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

Then, going to even smaller molecule-electrode distance *i.e.* $2.0\text{\AA}$, the IET spectrum is again characterized by the same peaks though the frequency shifts are larger and the relative intensities change a lot. The largest frequency variations appear for peaks **A** and **B**, with frequencies increasing by 72 cm^{-1} and 56 cm^{-1} , respectively. The peak **A** is no longer dominant but the breathing mode (peak **D**) presents the largest IET intensity followed by peak **E**. The analysis of the nature of the vibrational modes shows that, in mode **A**, the atomic displacements localized on the adsorbed hexagons get smaller [Fig. (VI.4)] with respect to the corresponding ones observed for $d=2.8\text{\AA}$. This explains the significant decrease of the IET relative intensity of this peak upon reducing the C_{60} /electrode distance. On the other hand, modes **D** and **E** involve larger motions localized on the hexagons parallel to the Au(111) surface. This brings additional evidence that the motions localized on the hexagons centered on a hcp site strongly modulate the coupling between the molecule and the electrodes, thereby having a direct impact on the IET intensities.

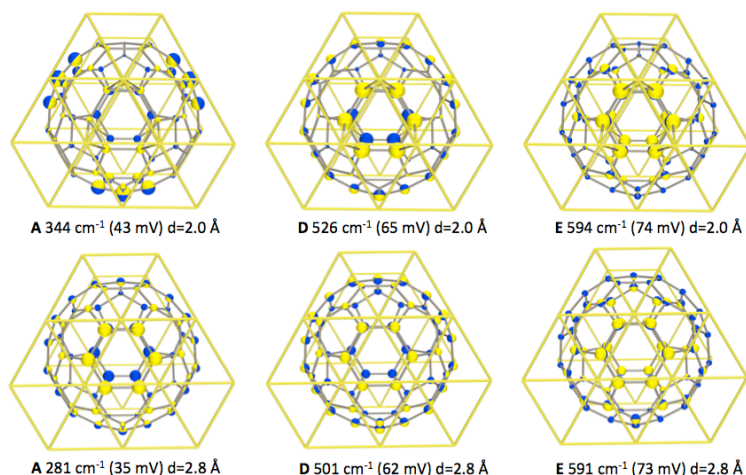


Fig. VI.4. Sketch of modes **A**, **D** and **E** of the **H** junction characterized by significant intensity variations when going from $d=2.0\text{\AA}$ to $d=2.8\text{\AA}$, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of

approximation. The overlap values between the pairs of modes **A**, **D** and **E** are equal to 0.668, 0.783 and 0.837, respectively.

On the other hand, going towards larger distances, from $d=3.6 \text{ \AA}$ to ∞ – which corresponds to the *gas* model where the molecule is isolated and only implicitly coupled to fictive electrodes, *i.e.* the molecule/electrode coupling is set to a constant parameter of 0.05 eV – the major IET signatures described in Table (VI.10) are different than those observed with shorter molecule-electrode distances and they appear at larger frequencies. A similar phenomenon has been observed in a study by Luo et al.^[16] on the evolution of the IET signatures of a gold-benzenedithiol-gold junction as a function of molecule-electrode distance. The IET spectra are now dominated by three peaks **M**, **Q** and **R**, respectively observed at 1468 cm^{-1} , 1608 cm^{-1} , and 1617 cm^{-1} for $d=3.6$ - $4.0 \text{ \AA}$ and at 1467 cm^{-1} , 1608 cm^{-1} , and 1618 cm^{-1} for the *gas* model, respectively. These peaks are associated to C-C stretchings mainly localized on the two adsorbed hexagons of the C_{60} molecule and are illustrated in Fig. (VI.5). When the molecule-electrode distance goes from $d=3.6 \text{ \AA}$ to $4.0 \text{ \AA}$, their frequency variations are negligible while their relative IET intensities are similar. On the other hand, in absolute value, the intensities decrease. The overlap values [Table (VI.11)] highlight a high degree of correlation between the vibrational modes calculated for $d=3.6 \text{ \AA}$, $d=4.0 \text{ \AA}$ and with the *gas* model.

Peak label	B3LYP		B3LYP(D)		Mode description
	Freq (cm^{-1})	Potential (mV)	Freq (cm^{-1})	Potential (mV)	
J	1279	159	1278	158	6:5 bond stretchings
K	1337	166	1337	166	6:5 bond stretchings
L	1372	170	1372	170	6:5 bond stretchings
M	1468	182	1464	183	C-C stretchings of the two adsorbed hexagons
N	1511	187	1521	189	6:6 bond stretchings
O	1539	191	1544	191	6:6 bond stretchings
P	1568	194	1579	196	6:6 bond stretchings
Q	1608	199	1613	200	C-C stretchings mainly localized on the two adsorbed hexagons
R	1617	200	1624	201	C-C stretchings mainly localized on the two adsorbed hexagons

Table VI.10. Label, frequency (cm^{-1}), potential (mV), and description of the vibrational normal modes of the **H** junction dominating the IET spectrum calculated at the B3LYP/cc-pVDZ/LANL2DZ and B3LYP(D)/cc-pVDZ/LANL2DZ levels of approximation, for $d=4.0 \text{ \AA}$.

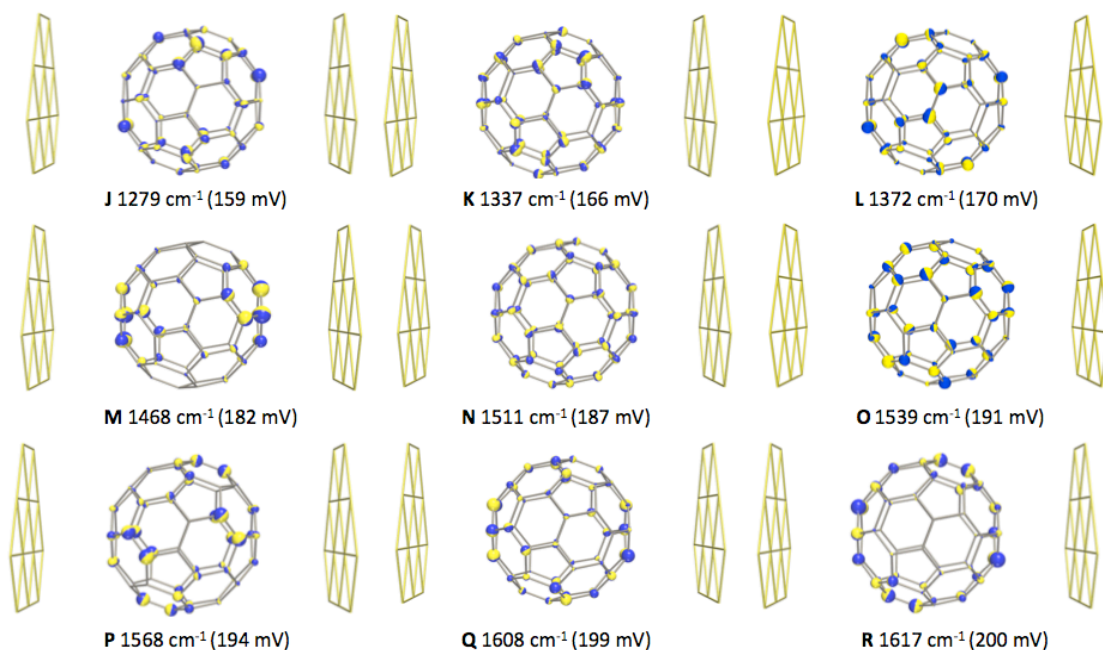


Fig. VI.5. Sketch of the vibrational normal modes corresponding to the dominant peaks of the IET spectrum for a C_{60} molecule-electrode distance equal to 4.0 Å, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

Peak #	d=3.6Å	Gas
J	0.815	0.856
K	0.996	0.993
L	1.000	0.998
M	0.996	0.435
N	1.000	1.000
O	0.966	0.915
P	0.998	0.973
Q	0.997	0.908
R	0.998	0.897

Table VI.11. Overlap values between the IET active vibrational modes of the **H** junction obtained for different molecule-electrode distances, taking as reference the results with $d=4.0\text{Å}$, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

These results highlight the sensitivity of the IET response with respect to the C_{60} -electrode distance and illustrates the different pathways that the electrons follow during the inelastic tunneling process depending on this junction parameter value.

Since the IET signatures depend on the molecule-electrode distances, it is interesting to investigate the IET response of asymmetric molecular junctions, *i.e.* those where the distance between the source and the C_{60} molecule [$d(\text{S}-C_{60})$] differs from the distance between the C_{60} molecule and the drain [$d(C_{60}-D)$]. Alternatively, one of these distances was fixed and the other was varied. First, $d(\text{S}-C_{60})$ is fixed at 2.8 Å, while $d(C_{60}-D)=3.4$ Å or 4.0 Å. Then, $d(\text{S}-C_{60})$ was varied

around the equilibrium position while keeping $d(\text{C}_{60}\text{-D})=4.0$ Å. The IET spectra simulated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation are sketched in Fig. (VI.6) and the frequency and intensity values are reported in Tables (VI.12-15).

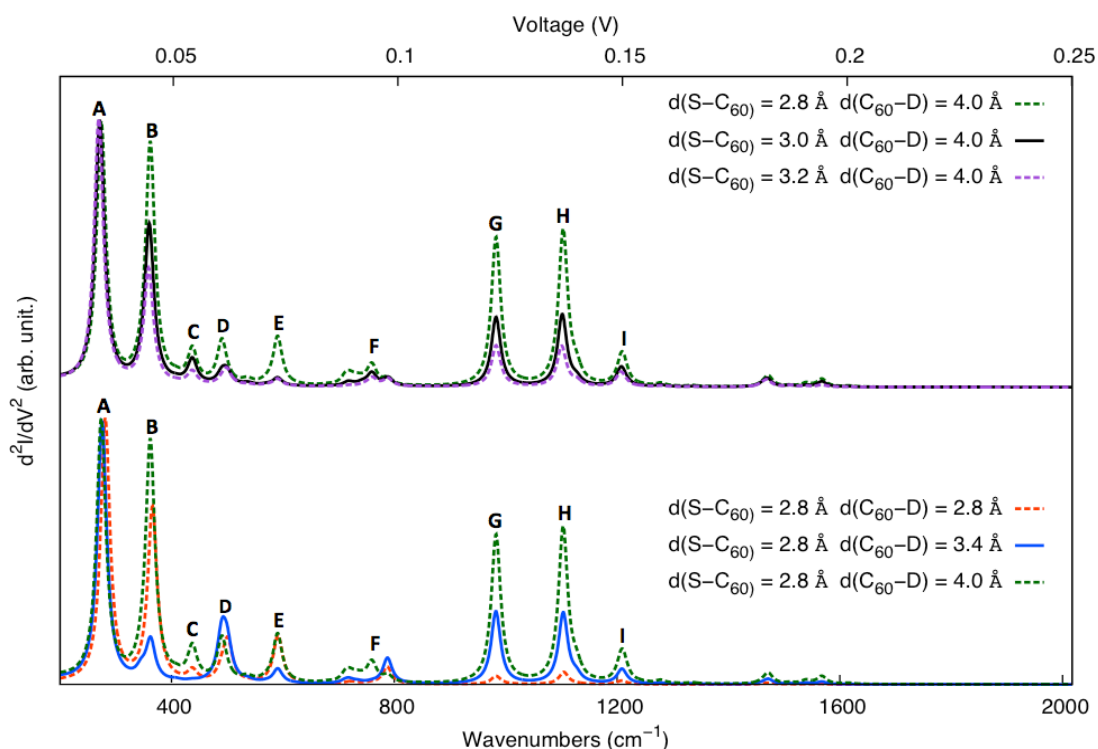


Fig. VI.6. IET spectra of the **H** junction simulated at the B3LYP/cc-pVDZ/LANL2DZ level by considering asymmetric distances between the source and the molecule and between the molecule and the drain.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	275	34	1.56×10^{-14}	1.000
B	362	45	2.84×10^{-15}	0.182
C	437	54	3.63×10^{-16}	0.023
D	500	62	3.51×10^{-15}	0.225
E	591	73	9.50×10^{-16}	0.061
F	788	98	1.58×10^{-15}	0.101
G	984	122	4.32×10^{-15}	0.277
H	1103	137	4.27×10^{-15}	0.274
I	1209	150	9.29×10^{-16}	0.060

Table VI.12. Positions and intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for $d(\text{S-C}_{60})=2.8$ Å and $d(\text{C}_{60}\text{-D})=3.4$ Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	274	34	1.50×10 ⁻¹⁵	1.000
B	362	45	1.39×10 ⁻¹⁵	0.927
C	437	54	2.33×10 ⁻¹⁶	0.155
D	500	62	1.62×10 ⁻¹⁶	0.108
E	591	73	2.88×10 ⁻¹⁶	0.192
F	788	98	6.33×10 ⁻¹⁷	0.042
G	984	122	8.31×10 ⁻¹⁶	0.554
H	1103	137	8.91×10 ⁻¹⁶	0.594
I	1209	150	2.01×10 ⁻¹⁶	0.134

Table VI.13. Positions and intensities of the IET active modes of the **H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d(S-C₆₀)=2.8 Å and d(C₆₀-D)=4.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	271	34	1.70×10 ⁻¹⁶	1.000
B	360	45	1.04×10 ⁻¹⁶	0.612
C	437	54	1.90×10 ⁻¹⁷	0.112
D	499	62	1.41×10 ⁻¹⁷	0.083
E	591	73	6.33×10 ⁻¹⁸	0.037
F	788	98	6.79×10 ⁻¹⁸	0.040
G	983	122	4.47×10 ⁻¹⁷	0.263
H	1102	137	4.65×10 ⁻¹⁷	0.274
I	1208	150	1.33×10 ⁻¹⁷	0.078

Table VI.14. Positions and intensities of the vibrational normal modes of the **H** junction dominating the IET spectrum calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d(S-C₆₀)=3.0 Å and d(C₆₀-D)=4.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	269	33	1.41×10 ⁻¹⁷	1.000
B	359	45	6.27×10 ⁻¹⁸	0.445
C	437	54	9.14×10 ⁻¹⁹	0.065
D	499	62	1.04×10 ⁻¹⁸	0.074
E	591	73	4.54×10 ⁻¹⁹	0.032
F	789	98	5.02×10 ⁻¹⁹	0.036
G	983	122	2.20×10 ⁻¹⁸	0.156
H	1101	137	2.17×10 ⁻¹⁸	0.154
I	1207	150	8.15×10 ⁻¹⁹	0.058

Table VI.15. Positions and intensities of the vibrational normal modes of the **H** junction dominating the IET spectrum calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d(S-C₆₀)=3.2 Å and d(C₆₀-D)=4.0 Å.

Upon increasing $d(C_{60}-D)$, the largest frequency variations are observed for the two lowest frequency IET active modes **A** and **B**. Their frequencies decrease by 7 cm^{-1} and 4 cm^{-1} from $d(C_{60}-D)=2.8\text{ Å}$ to $d(C_{60}-D)=4.0\text{ Å}$, respectively. For the other IET active modes the frequency shifts are negligible. Consistently with the previous analysis, the IET absolute intensities decrease when $d(C_{60}-D)$ is enlarged owing to the diminution of the C_{60} /drain coupling. Still, the relative IET intensities change. Indeed, going from $d(C_{60}-D)=2.8\text{ Å}$ to $d(C_{60}-D)=3.4\text{ Å}$ results in a significant decrease of modes **B** and **E**. At the same time, the relative intensity of modes **G** and **H** increase, and this effect is further enhanced for $d(C_{60}-D)=4.0\text{ Å}$. On the other hand, the relative intensities of modes **B** and **E**, as observed for the symmetric junction, are almost recovered when considering a stronger asymmetry between the $d(S-C_{60})$ and $d(C_{60}-D)$ values. Based on the overlap values reported in Table (VI.16), one observes again a very good correlation between the IET active modes calculated with $d(S-C_{60})=2.8\text{ Å}$ and with $d(C_{60}-D)=2.8\text{ Å}$, 3.4 Å and 4.0 Å . Thereby, the variations of IET intensities discussed before should not be explained in terms of changes of the vibrational normal modes but rather by modifications of the coupling between the electronic structure and the molecular vibrations.

Peak #	$d(S-C_{60})=2.8\text{ Å}$ $d(C_{60}-D)=3.4\text{ Å}$	$d(S-C_{60})=2.8\text{ Å}$ $d(C_{60}-D)=4.0\text{ Å}$
A	0.994	0.992
B	0.995	0.991
C	0.940	0.694
D	0.996	0.993
E	0.972	0.948
F	0.799	0.627
G	0.999	0.999
H	0.999	0.999
I	0.998	0.996

Table VI.16. Overlap values between the IET active vibrational modes of the **H** junction obtained for different C_{60} -drain distances, taking as reference the results with $d(S-C_{60})=d(C_{60}-D)=2.8\text{ Å}$, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

For $d(C_{60}-D)=4.0\text{ Å}$, when going from $d(S-C_{60})=2.8\text{ Å}$ to 3.2 Å , i) the frequency variations are negligible, except for the two lowest frequency modes which change by $3\text{-}5\text{ cm}^{-1}$, ii) the intensities decrease, iii) this effect is stronger for modes **B**, **G**, and **H**, and iv) mode **E** presents the smallest intensity. For this $d(C_{60}-D)=4.0\text{ Å}$ an excellent correlation is observed between the IET active modes calculated with $d(S-C_{60})=2.8\text{ Å}$, 3.0 Å and 3.2 Å [Table (VI.17)], demonstrating the key role played by the electron/phonon coupling.

Peak#	d(S-C ₆₀)=3.0 Å d(C ₆₀ -D)=4.0 Å	d(S-C ₆₀)=3.2 Å d(C ₆₀ -D)=4.0 Å
A	0.999	0.995
B	0.996	0.988
C	0.996	0.997
D	0.999	0.997
E	1.000	1.000
F	0.996	0.945
G	0.995	0.996
H	1.000	0.999
I	0.999	0.998

Table VI.17. Overlap values between the IET active vibrational modes of the **H** junction obtained for different source-C₆₀ distances, taking as reference the results with d(S-C₆₀)=2.8 Å and d(C₆₀-D)=4.0 Å, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

VI.C.2. Effect of dispersion corrections in the XC functional on the IET response

Since dispersion forces play a role in describing the interactions between C₆₀ and gold^[22], this section is devoted to study the effect of adding dispersion corrections to the traditional B3LYP XC functional [Fig. (VI.2)]. The frequencies (cm⁻¹), the transition potentials (mV), and the IET intensities (arb. units) of the dominant modes are reported in Tables (VI.18-23). For the shortest molecule-electrode distance (d=2.0 Å), the same IET signatures are observed by adding dispersion. The largest frequency variations appear for the peak **G** associated to distortions of the C₆₀ molecule with stretchings of the C-C bonds of the two hexagons aligned parallel to the Au(111) surfaces, as its frequency increases by 19 cm⁻¹. For modes with frequencies ranging from 500 cm⁻¹ to 1000 cm⁻¹ the variations attain 10 cm⁻¹, while for the other IET active modes they are less than 4 cm⁻¹. The largest relative intensity change concerns mode **D** with a 47% decrease, while the intensity variations are negligible for the other modes. Based on the overlaps reported in Table (VI.24), this decrease originates from a change in the nature of the vibrational mode. Indeed, mode **D** is split into two contributions when using the B3LYP(D) XC functional, as illustrated in Fig. (VI.7). The smaller contribution of the longitudinal motions of the two hexagons in the direction parallel to the normal to the Au(111) surfaces observed when adding dispersion corrections to the B3LYP XC functional explains this decrease of intensity.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	348	43	5.15×10 ⁻⁸	0.141
B	418	52	2.73×10 ⁻⁷	0.746
D	537	67	2.36×10 ⁻⁷	0.645
E	605	75	3.66×10 ⁻⁷	1.000
F	791	98	6.35×10 ⁻⁸	0.173
G	1018	126	7.70×10 ⁻⁹	0.021
-	1133	140	1.55×10 ⁻⁸	0.042
I	1235	153	1.58×10 ⁻⁸	0.043

Table VI.18. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=2.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	292	36	7.27×10 ⁻¹⁰	1.000
B	370	46	6.18×10 ⁻¹⁰	0.850
C	434	54	3.80×10 ⁻¹¹	0.052
-	492	61	6.27×10 ⁻¹¹	0.086
D	519	64	1.37×10 ⁻¹⁰	0.188
E	602	75	2.41×10 ⁻¹⁰	0.331
F	795	99	6.74×10 ⁻¹¹	0.093
G	988	122	3.63×10 ⁻¹¹	0.050
H	1116	138	4.25×10 ⁻¹¹	0.058
I	1217	151	1.07×10 ⁻¹¹	0.015

Table VI.19. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=2.4 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	288	36	1.82×10 ⁻¹²	1.000
B	369	46	1.36×10 ⁻¹²	0.747
C	438	54	9.89×10 ⁻¹⁴	0.054
-	493	61	2.21×10 ⁻¹³	0.121
D	522	65	2.52×10 ⁻¹³	0.138
E	612	76	3.45×10 ⁻¹³	0.190
F	805	100	7.87×10 ⁻¹⁴	0.043
G	1004	124	3.51×10 ⁻¹⁴	0.019
H	1112	138	7.96×10 ⁻¹⁴	0.044
I	1215	151	2.24×10 ⁻¹⁴	0.012

Table VI.20. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=2.8 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	275	34	3.17×10 ⁻¹⁵	1.000
B	361	45	1.41×10 ⁻¹⁵	0.445
C	438	54	1.42×10 ⁻¹⁶	0.045
-	491	61	2.04×10 ⁻¹⁶	0.064
D	520	64	2.50×10 ⁻¹⁶	0.079
E	614	76	3.19×10 ⁻¹⁶	0.101
F	806	100	6.67×10 ⁻¹⁷	0.021
G	1002	124	4.28×10 ⁻¹⁷	0.014
H	1107	137	1.33×10 ⁻¹⁶	0.042
I	1212	150	5.38×10 ⁻¹⁷	0.017

Table VI.21. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=3.2 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
J	1278	158	8.79×10 ⁻¹⁴	0.103
K	1337	166	4.31×10 ⁻¹⁴	0.051
L	1372	170	7.99×10 ⁻¹⁴	0.094
M	1467	182	8.53×10 ⁻¹³	1.000
N	1522	189	1.64×10 ⁻¹³	0.192
O	1544	191	2.47×10 ⁻¹³	0.290
P	1579	196	2.77×10 ⁻¹³	0.325
Q	1613	200	7.17×10 ⁻¹³	0.841
R	1624	201	8.01×10 ⁻¹³	0.939

Table VI.22. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=3.6 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
J	1278	158	9.86×10 ⁻¹⁵	0.089
K	1337	166	7.32×10 ⁻¹⁵	0.066
L	1372	170	1.24×10 ⁻¹⁴	0.112
M	1464	183	1.13×10 ⁻¹³	0.946
N	1521	189	2.36×10 ⁻¹⁴	0.213
O	1544	191	3.98×10 ⁻¹⁴	0.359
P	1579	196	4.17×10 ⁻¹⁴	0.376
Q	1613	200	1.01×10 ⁻¹³	0.910
R	1624	201	1.11×10 ⁻¹³	1.000

Table VI.23. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=4.0 Å.

Peak #	Overlap value
A	0.800
B	0.999
D	0.612
E	0.992
F	0.999
G	0.979
I	0.812

Table VI.24. Overlap values between the B3LYP and B3LYP(D) IET active vibrational modes of the **H** junction obtained for $d=2.0$ Å, taking as reference the results calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

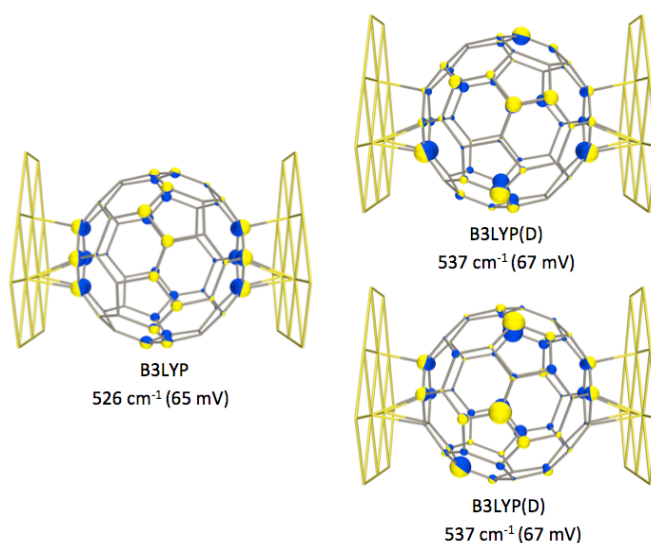


Fig. VI.7. Illustration of the splitting of vibrational mode **D** of the **H** junction into two contributions when using the B3LYP(D) XC functional.

For $d=2.4$ Å - 3.2 Å, a new peak appears close to 500 cm^{-1} (492 cm^{-1} , 493 cm^{-1} and 491 cm^{-1} for $d = 2.4$ Å, 2.8 Å, and 3.2 Å, respectively). It corresponds to longitudinal motions of the two adsorbed hexagons in the direction parallel to the normal to the Au(111) surfaces, as displayed in Fig. (VI.8). The largest frequency shifts are found for modes with frequency values ranging from 500 to 1000 cm^{-1} and they attain about 20 cm^{-1} . Upon inclusion of dispersion interactions, the largest intensity variations are found for peaks **D** and **G** and they originate from modifications of the coupling between the electronic structure and the molecular vibrations since the B3LYP/B3LYP(D) overlaps are larger than 0.95. The same observations concerning the frequency and intensity variations [Tables (VI.25-28)], and the nature of the vibrational modes in terms of B3LYP/B3LYP(D) overlaps are made for the junctions with asymmetric molecule-electrode distances. The only difference is the appearance of an additional peak at 1140 cm^{-1} as illustrated in Fig. (VI.8).

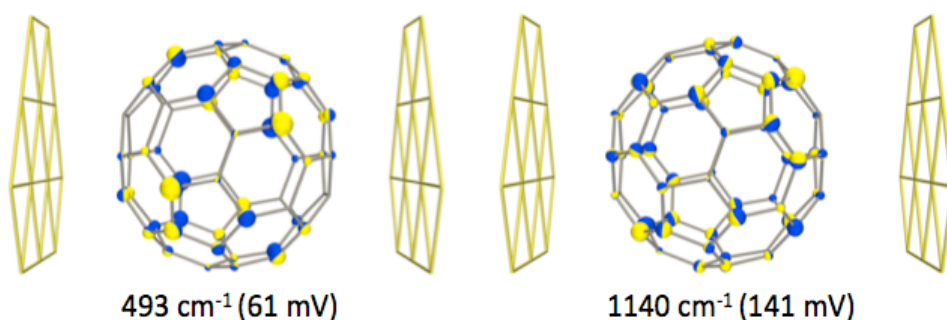


Fig. VI.8. Sketch of the vibrational modes of the **H** junction associated to the additional peaks calculated at the B3LYP(D)/cc-pVDZ level of approximation, with $d(\text{S-C}_{60})=2.8 \text{ \AA}$ and $d(\text{C}_{60}\text{-D})=2.8 \text{ \AA}$ (left) and $d(\text{C}_{60}\text{-D})=3.4 \text{ \AA}$ or $4.0 \text{ \AA}$ (right).

Peak #	Frequency (cm^{-1})	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	280	35	1.36×10^{-14}	1.000
B	364	45	2.14×10^{-15}	0.157
C	438	54	3.44×10^{-16}	0.025
-	491	61	3.27×10^{-15}	0.240
D	521	65	2.33×10^{-15}	0.171
E	613	76	8.39×10^{-16}	0.062
F	806	100	1.38×10^{-15}	0.101
G	1003	124	2.93×10^{-15}	0.215
H	1110	138	3.86×10^{-15}	0.284
-	1140	141	1.25×10^{-15}	0.092
I	1214	151	7.77×10^{-16}	0.057

Table VI.25. Frequency and potential values (cm^{-1} and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for $d(\text{S-C}_{60})=2.8 \text{ \AA}$ and $d(\text{C}_{60}\text{-D})=3.4 \text{ \AA}$.

Peak #	Frequency (cm^{-1})	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	278	34	1.42×10^{-15}	1.000
B	364	45	1.41×10^{-15}	0.993
C	438	54	2.13×10^{-16}	0.150
-	491	61	3.19×10^{-16}	0.225
D	520	64	1.19×10^{-16}	0.084
E	612	76	2.47×10^{-16}	0.174
F	806	100	6.66×10^{-17}	0.047
G	1002	124	7.30×10^{-16}	0.514
H	1109	137	8.17×10^{-16}	0.575
-	1140	141	2.34×10^{-16}	0.165
I	1214	151	1.69×10^{-16}	0.119

Table VI.26. Frequency and potential values (cm^{-1} and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for $d(\text{S-C}_{60})=2.8 \text{ \AA}$ and $d(\text{C}_{60}\text{-D})=4.0 \text{ \AA}$.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	274	34	1.66×10 ⁻¹⁶	1.000
B	361	45	1.08×10 ⁻¹⁶	0.651
C	438	54	1.94×10 ⁻¹⁷	0.117
-	491	61	9.02×10 ⁻¹⁸	0.054
D	519	64	1.05×10 ⁻¹⁷	0.063
E	612	76	3.45×10 ⁻¹⁸	0.021
F	807	100	9.82×10 ⁻¹⁸	0.059
G	1002	124	2.72×10 ⁻¹⁷	0.164
H	1107	137	4.35×10 ⁻¹⁷	0.262
-	1140	141	1.04×10 ⁻¹⁷	0.063
I	1212	150	1.16×10 ⁻¹⁷	0.070

Table VI.27. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d(S-C₆₀)=3.0 Å and d(C₆₀-D)=4.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	271	34	1.40×10 ⁻¹⁷	1.000
B	359	45	6.36×10 ⁻¹⁸	0.454
C	438	54	9.31×10 ⁻¹⁹	0.067
-	491	61	4.85×10 ⁻¹⁹	0.035
D	519	64	8.92×10 ⁻¹⁹	0.064
E	612	76	5.01×10 ⁻¹⁹	0.036
F	807	100	5.54×10 ⁻¹⁹	0.040
G	1001	124	1.37×10 ⁻¹⁸	0.098
H	1106	137	2.05×10 ⁻¹⁸	0.146
-	1139	141	6.20×10 ⁻¹⁹	0.044
I	1212	150	7.25×10 ⁻¹⁹	0.052

Table VI.28. Frequency and potential values (cm⁻¹ and mV), IET intensities (arb. unit) and relative intensities of the IET active modes of the **H** junction calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d(S-C₆₀) =3.2 Å and d(C₆₀-D)=4.0 Å.

For larger molecule-electrode distances (d=3.6 Å and d=4.0 Å), the largest frequency shifts are observed for modes **N** and **P** with differences attaining 10 cm⁻¹. Then, the dominant mode **M** observed at 1468 cm⁻¹ presents the largest intensity variations as it decreases by 20% and 26% for d=3.6 Å and d=4.0 Å, respectively, what leads to close intensity values for the IET peaks **M**, **Q** and **R**.

On the basis of this analysis of the IET responses of a single C₆₀ molecule embedded between gold electrodes as a function of molecule-electrode distances, a comparison with experimental measurements^[15] can be performed. The derivative of the symmetric part of dI/dV

with respect to bias reversal, corresponding to vibronic excitations of the C_{60} molecule shows a dominant peak at 34 mV that can be attributed to the spherical/prolate C_{60} distortion (mode **A**) as well as another significant feature at 114 mV associated to mode **G** in our calculations. The best agreement with experiment is found when considering a molecular junction with $d(S-C_{60}) = 2.8 \text{ \AA}$ and $d(C_{60}-D) = 3.4 \text{ \AA}$. The study of Böhler and co-workers has also evidenced that some peaks may have a different origin than the intrinsic vibrational modes of the system, e.g. the deformation of the molecular contact. These peaks cannot be systematically reproduced from one experiment to another as they are greatly dependent on the structure itself, like for example the peak observed at 64 mV, which also appears in our simulation (mode **D**).

VI.C.3. Influence of the orientation of the C_{60} molecule on the IET response.

The IET signatures are now analyzed for other orientations of the C_{60} molecule on the gold electrode plane, corresponding to the **P**, **H-H**, and **H-P** adsorption configurations illustrated in Fig. (VI.1). The peaks associated to vibrational modes only active when considering the **P**, **H-P**, and **H-H** junctions are labeled as **A1**..., **A2**... and **A3**..., respectively.

As observed in the case of the **H** junction, the equilibrium C_{60} molecule-electrode distance is $2.8 \text{ \AA}$ when using the B3LYP(D) functional ($3.2 \text{ \AA}$ with B3LYP) for the **P**, **H-H**, and **H-P** adsorption configurations. Considering the equilibrium distances, when using the B3LYP(D) functional, the **H** configuration is the most stable (with a difference of 4.7 kcal/mol with respect to the one presenting the highest energy *i.e.* the **H-H** junction, and of 0.1 kcal/mol with respect to the **P** junction), while the B3LYP functional leads to similar energy values for the 4 configurations (only 1 kcal/mol of difference between the lowest and highest energy values).

Concerning the **P** junctions, the vibrational frequencies (cm^{-1}) and corresponding transition potentials (mV), and the IET intensities of the dominant vibrational modes are reported in Tables (VI.29-34), while Table (VI.35) describes the major IET signatures obtained for $d = 2.8 \text{ \AA}$. One observes the same variations of the IET response (compared to the **H** junctions) as a function of the molecule-electrode distance (Fig. (VI.9)) defined in this case as the distance between the center of the pentagon aligned parallel to the Au(111) surfaces and the hcp site. Indeed, for d ranging from $2.4 \text{ \AA}$ to $3.2 \text{ \AA}$, two peaks labeled **A1** and **B1** dominate the IET spectrum and they are associated respectively to the deformation of the C_{60} molecule between a spherical and prolate shape and to longitudinal motions of the pentagons moving from one electrode to the other, as shown in Fig. (VI.10). However, for $d = 2.4\text{-}2.8 \text{ \AA}$, peak **B1** dominates the spectrum, while for $d = 3.2 \text{ \AA}$ the major contribution is attributed to peak **A1**.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A1	337	42	1.00×10 ⁻⁷	0.043
B1	415	51	5.70×10 ⁻⁷	0.248
C1	456	57	2.29×10 ⁻⁷	0.100
-	527	65	6.38×10 ⁻⁷	0.277
-	541	67	5.21×10 ⁻⁷	0.227
F1	608	75	2.30×10 ⁻⁶	1.000
G1	695	86	5.26×10 ⁻⁸	0.023
-	772	96	3.37×10 ⁻⁷	0.147
-	781	97	3.03×10 ⁻⁷	0.132
I1	978	121	1.86×10 ⁻⁷	0.081
J1	1116	138	1.83×10 ⁻⁷	0.080

Table VI.29. Positions and intensities of the IET active modes of the **P** adsorption configuration, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A1	294	36	1.89×10 ⁻⁹	0.620
B1	362	45	3.05×10 ⁻⁹	1.000
C1	441	55	1.06×10 ⁻⁹	0.348
D	503	62	4.02×10 ⁻¹⁰	0.132
E1	533	66	1.51×10 ⁻¹⁰	0.050
F1	589	73	7.38×10 ⁻¹⁰	0.242
G1	689	85	1.05×10 ⁻⁹	0.344
F	785	97	4.95×10 ⁻¹⁰	0.162
I1	978	121	2.18×10 ⁻¹⁰	0.071
J1	1123	139	2.17×10 ⁻¹⁰	0.071

Table VI.30. Positions and intensities of the IET active modes of the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.4 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A1	278	34	1.47×10 ⁻¹¹	0.870
B1	351	44	1.69×10 ⁻¹¹	1.000
C1	440	55	5.02×10 ⁻¹²	0.297
D	500	62	1.29×10 ⁻¹²	0.076
E1	535	66	1.13×10 ⁻¹²	0.067
F1	591	73	1.83×10 ⁻¹²	0.108
G1	706	88	4.97×10 ⁻¹²	0.294
F	787	98	1.02×10 ⁻¹²	0.060
I1	980	122	3.80×10 ⁻¹³	0.022
J1	1125	139	3.32×10 ⁻¹³	0.020

Table VI.31. Positions and intensities of the IET active modes of the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.8 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A1	270	33	1.35×10 ⁻¹³	1.000
B1	347	43	1.17×10 ⁻¹³	0.867
C1	438	54	3.82×10 ⁻¹⁴	0.283
D	499	62	9.47×10 ⁻¹⁵	0.070
E1	536	66	1.45×10 ⁻¹⁴	0.107
F1	590	73	8.60×10 ⁻¹⁵	0.064
G1	715	89	2.76×10 ⁻¹⁴	0.204
M	1468	182	3.19×10 ⁻¹⁵	0.024
O	1537	191	5.12×10 ⁻¹⁵	0.038
P	1567	194	6.30×10 ⁻¹⁵	0.047
Q	1608	199	1.20×10 ⁻¹⁴	0.089
R	1615	200	1.38×10 ⁻¹⁴	0.102

Table VI.32. Positions and intensities of the IET active modes of the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=3.2 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
K	1279	159	4.93×10 ⁻¹⁵	0.033
L	1335	166	4.71×10 ⁻¹⁵	0.031
M	1468	182	1.50×10 ⁻¹³	1.000
N	1511	187	2.37×10 ⁻¹⁴	0.158
O	1539	191	4.45×10 ⁻¹⁴	0.297
P	1568	194	2.23×10 ⁻¹⁴	0.149
Q	1608	199	9.00×10 ⁻¹⁴	0.600
R	1616	200	1.04×10 ⁻¹³	0.693

Table VI.33. Positions and intensities of the IET active modes of the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=3.6 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
K	1279	159	3.60×10 ⁻¹⁵	0.031
L	1337	166	6.49×10 ⁻¹⁵	0.055
M	1467	182	1.18×10 ⁻¹³	1.000
N	1511	187	1.50×10 ⁻¹⁴	0.127
O	1539	191	1.87×10 ⁻¹⁴	0.158
P	1568	194	1.15×10 ⁻¹⁴	0.097
Q	1609	199	4.20×10 ⁻¹⁴	0.383
R	1617	200	4.52×10 ⁻¹⁴	0.356

Table VI.34. Positions and intensities of the IET active modes of the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=4.0 Å.

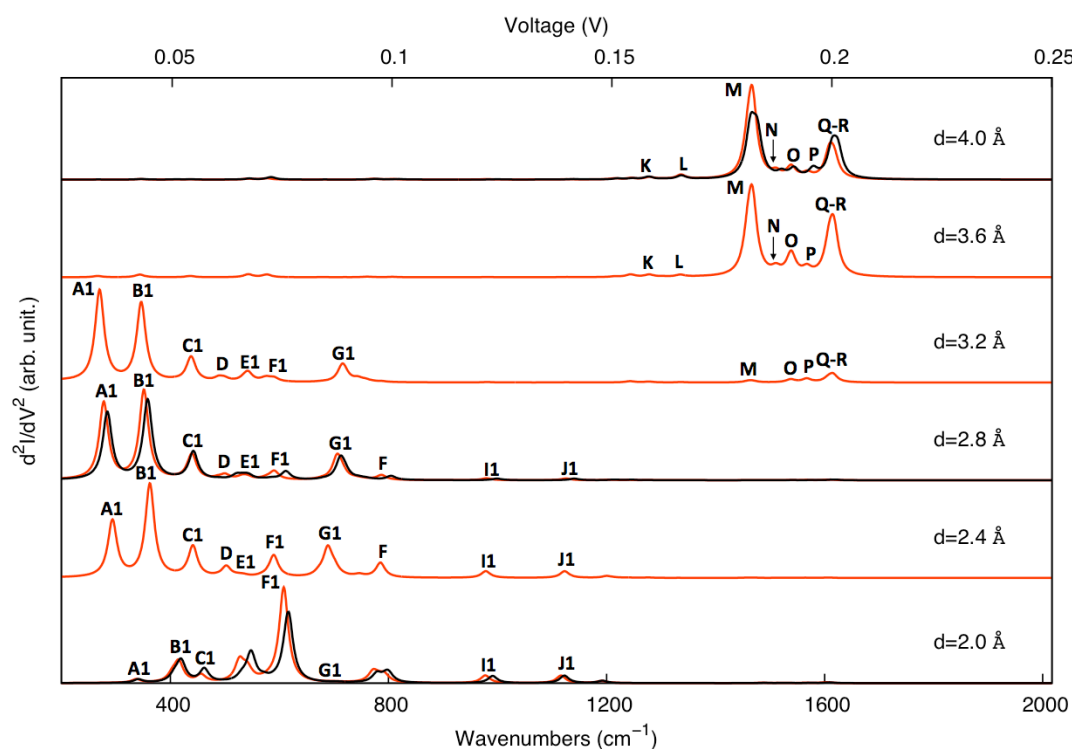


Fig. VI.9. IET spectra of the **P** junctions calculated at the B3LYP/cc-pVDZ/LANL2DZ (red line) and B3LYP(D)/cc-pVDZ/LANL2DZ (black line) levels of approximation by considering molecule-electrode distances ranging from 2.0 Å to 4.0 Å.

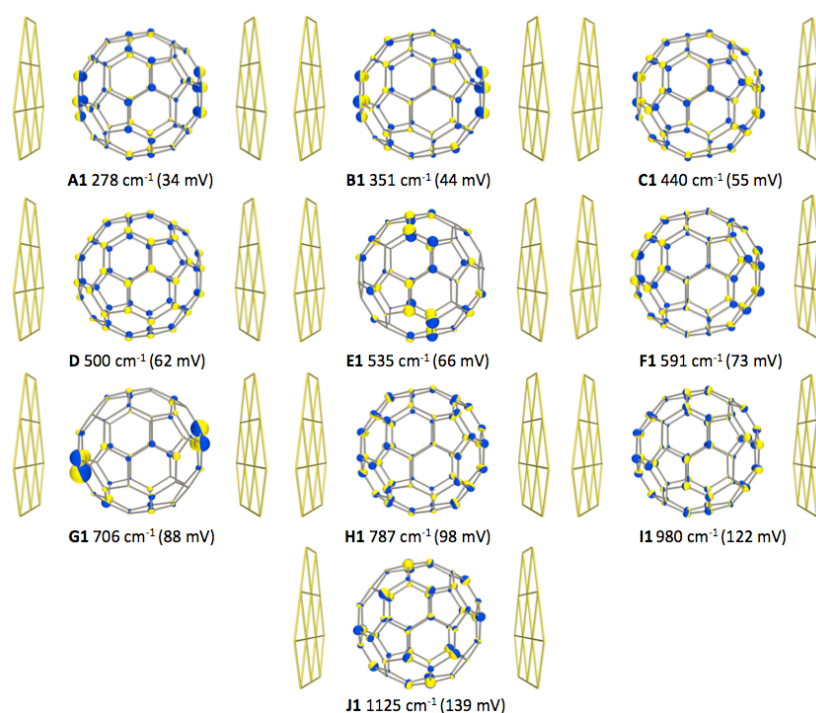


Fig. VI.10. Sketch of the vibrational normal modes corresponding to the dominant peaks of the IET spectrum for a C₆₀ molecule-electrode distance equal to 2.8 Å for the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

Peak label	B3LYP		B3LYP(D)		Mode description
	Freq (cm ⁻¹)	Potential (mV)	Freq (cm ⁻¹)	Potential (mV)	
A1	278	34	284	35	spherical-to-prolate distortion corresponding to symmetric displacements of the adsorbed pentagon rings with respect to the electrodes
B1	351	44	358	44	anti-symmetric displacements of the adsorbed pentagon rings with respect to the electrodes
C1	440	55	442	55	symmetric displacements of the adsorbed pentagon rings with respect to the electrodes
D	500	62	521	65	C ₆₀ breathing mode
E1	535	66	536	66	distortions of the C ₆₀ molecule
F1	591	73	612	76	distortions of the adsorbed pentagons swaying between the electrodes
G1	706	88	712	88	distortions of the two adsorbed pentagon rings
F	787	98	805	100	distortions of the C ₆₀ molecule
I1	980	122	999	124	C-C stretchings of the adsorbed pentagon rings
J1	1125	139	1141	141	C-C stretchings of the adsorbed pentagon rings

Table VI.35. Label, frequency (cm⁻¹), potential (mV), and description of the vibrational normal modes dominating the IET spectrum of the **P** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ and B3LYP(D)/cc-pVDZ/LANL2DZ levels of approximation, for d=2.8 Å.

By going from d=3.2 Å to d=2.0 Å, the relative intensities of peaks **A1**, **B1**, **C1** and **G1** decrease, while it increases for peak **F1**. These intensity variations find their origin in changes of the vibrational modes, as illustrated in Fig. (VI.11). Indeed, from d=2.8 Å to d=2.0 Å, the amplitude of the motions localized on the two pentagons aligned parallel to the Au(111) surfaces gets smaller for modes **A1**, **B1**, **C1** and **G1**, while larger for mode **F1**. For larger molecule-electrode distances (d>3.6 Å), the major IET signatures involve C-C stretching motions, and the three dominant vibrational modes associated to distortions of the pentagon rings aligned parallel to the Au(111) surfaces are sketched in Fig. (VI.12).

We can draw a general conclusion for the IET response of the **H** and **P** adsorption configurations as a function of the molecule-electrode distance. At short distances, there are strong interactions between the molecule and the gold electrodes, so that longitudinal motions localized on the two rings facing the Au(111) surfaces (hexagons for the **H** configuration, pentagons for the **P** configuration) are responsible of the IET activity. On the other hand, at larger

molecule-electrode distances we mainly find C-C stretchings that are associated to the paths that electrons follow during the tunneling process.

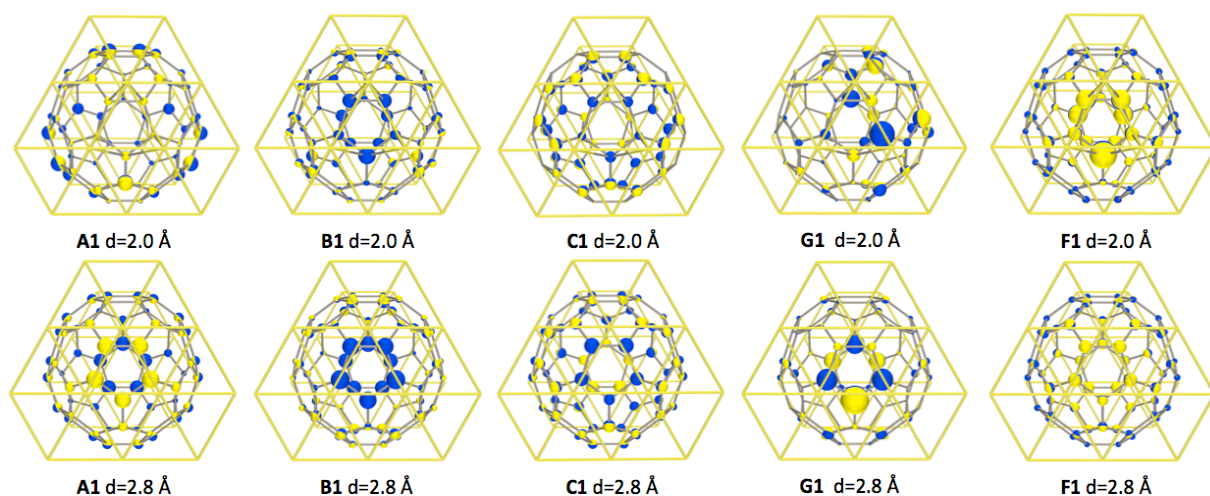


Fig. VI.11. Illustration of the correlation table between the vibrational normal modes of the **P** adsorption configuration obtained with $d=2.0$ Å and of its $d=2.8$ Å analog. The overlap values between the pairs of modes **A1**, **B1**, **C1**, **G1** and **F1** obtained for $d=2.0$ Å/ 2.8 Å are equal to 0.630, 0.629, 0.718, 0.574 and 0.871, respectively.

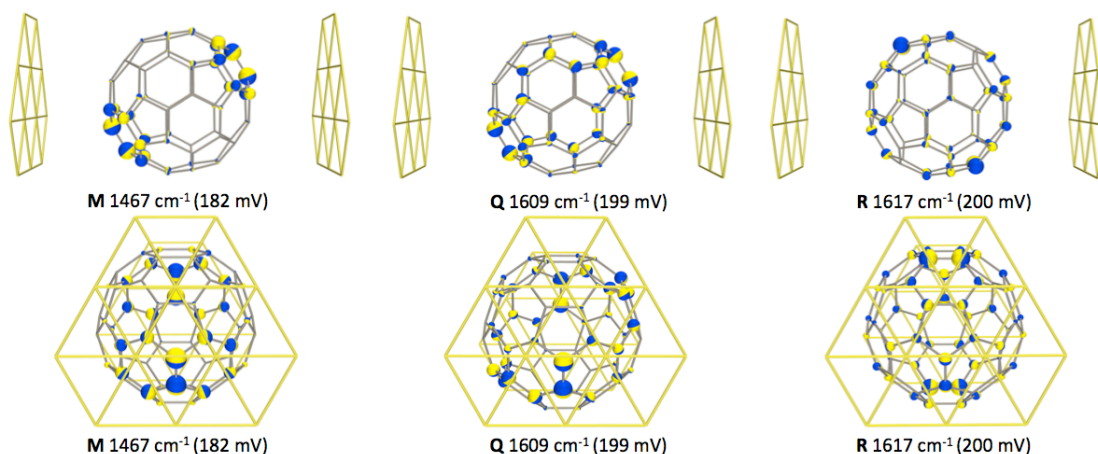


Fig. VI.12. Sketch of the vibrational normal modes (side and top views) corresponding to the dominant peaks of the IET spectrum for a C_{60} molecule-electrode distance equal to 4.0 Å for the **P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

In the cases of the **H-P** and **H-H** adsorption configurations a stronger sensitivity is observed for the IET response as function of the molecule-electrode distance, defined as the distance between the center of the 6:5 bond (6:6 bond for **H-H**) oriented parallel to the Au(111) surface and the hcp site [Figs. (VI.13) and (VI.16)]. The vibrational frequencies (cm^{-1}) and corresponding transition potentials (mV), and the IET intensities of the dominant vibrational modes (Tables (VI.36-38) and (VI.40-42) for the **H-P** and **H-H** junctions respectively). For $d=2.8$ Å, the IET active modes characteristic to the **H-P** (**H-H**) junctions are sketched in Fig. (VI.14) (Fig. (VI.17)) and are

described in Table (VI.39) (Table (VI.43)). The analysis focuses on three molecule-electrode distances highlighting the main variations of the IET response: $d=2.0$ Å, 2.8 Å and 4.0 Å.

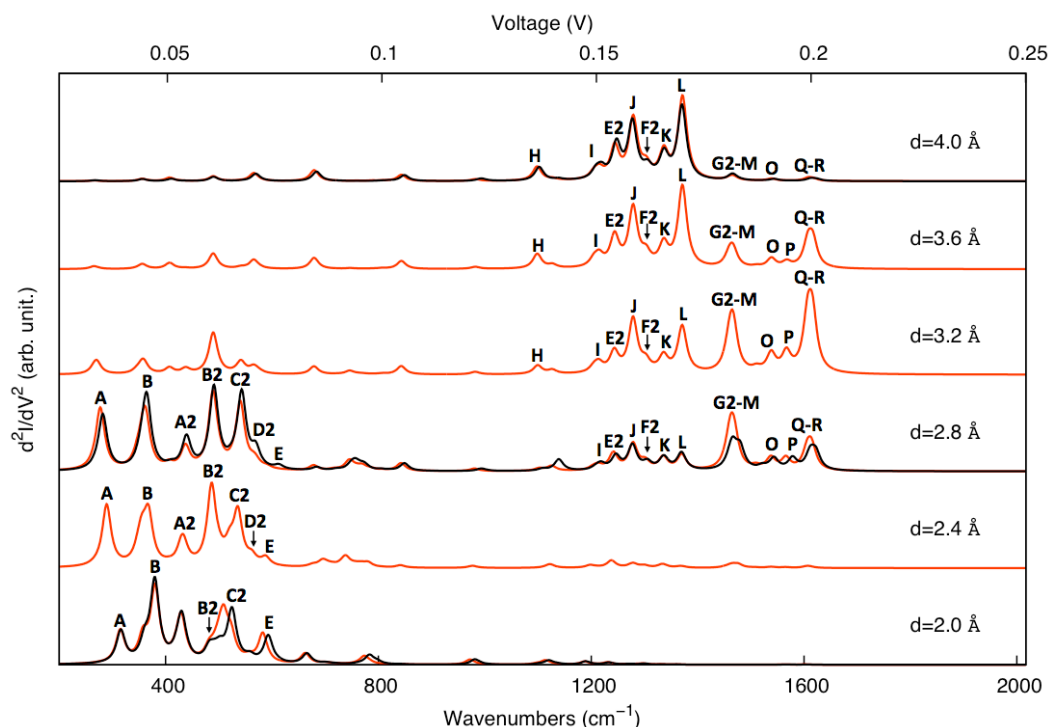


Fig. VI.13. IET spectra of the **H-P** junctions calculated at the B3LYP/cc-pVDZ/LANL2DZ (red line) and B3LYP(D)/cc-pVDZ/LANL2DZ (black line) levels of approximation by considering molecule-electrode distance values ranging from 2.0 Å to 4.0 Å.

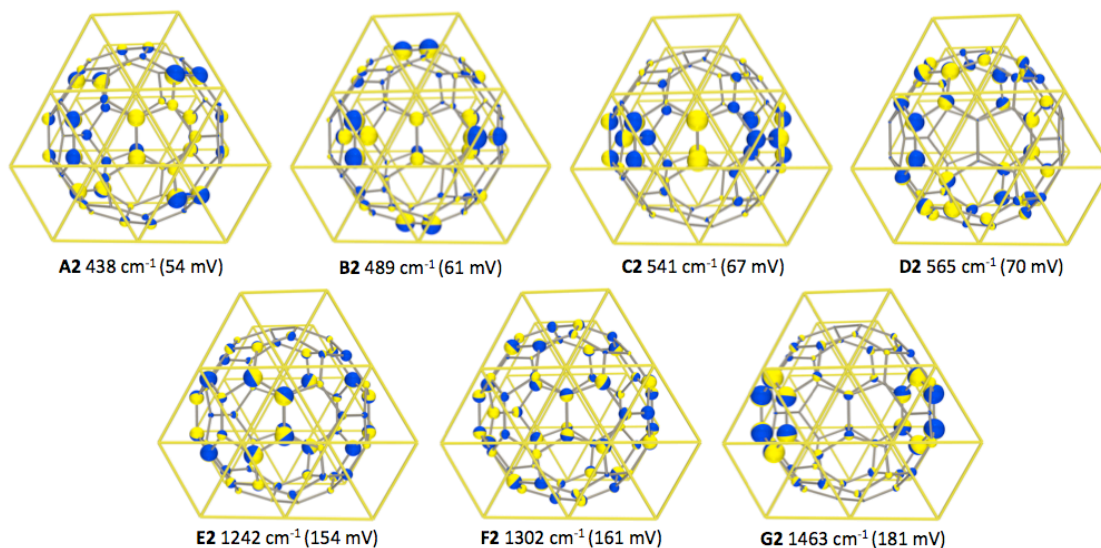


Fig. VI.14. Sketch of the IET active modes characteristic of the **H-P** junction for a C_{60} molecule-electrode distance equal to 2.8 Å, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	315	39	4.47×10 ⁻⁷	0.438
-	357	44	4.78×10 ⁻⁷	0.469
B	380	47	1.02×10 ⁻⁶	1.000
-	429	53	6.60×10 ⁻⁷	0.647
B2	482	60	3.34×10 ⁻⁷	0.327
-	509	63	7.56×10 ⁻⁷	0.741
C2	523	65	5.34×10 ⁻⁷	0.524
E	583	72	4.04×10 ⁻⁷	0.396
-	662	82	1.49×10 ⁻⁷	0.146
-	773	96	1.13×10 ⁻⁷	0.111

Table VI.36. Positions and intensities of the IET active modes of the **H-P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	277	34	3.64×10 ⁻¹¹	0.790
B	362	45	3.73×10 ⁻¹¹	0.809
A2	438	54	1.57×10 ⁻¹¹	0.341
B2	489	61	4.61×10 ⁻¹¹	1.000
C2	541	67	4.02×10 ⁻¹¹	0.872
D2	565	70	1.13×10 ⁻¹¹	0.245
E	591	73	4.17×10 ⁻¹²	0.090
I	1213	150	5.01×10 ⁻¹²	0.109
E2	1242	154	1.13×10 ⁻¹¹	0.245
J	1279	159	1.67×10 ⁻¹¹	0.362
F2	1302	161	7.96×10 ⁻¹²	0.173
K	1335	166	9.12×10 ⁻¹²	0.198
L	1369	170	1.01×10 ⁻¹¹	0.219
G2	1463	181	3.32×10 ⁻¹¹	0.720
M	1469	182	3.32×10 ⁻¹¹	0.720
O	1537	191	8.99×10 ⁻¹²	0.195
P	1566	194	8.91×10 ⁻¹²	0.193
Q	1606	199	1.84×10 ⁻¹¹	0.399
R	1614	200	1.91×10 ⁻¹¹	0.414

Table VI.37. Positions and intensities of the IET active modes of the **H-P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.8 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
H	1098	136	2.80×10 ⁻¹⁵	0.174
I	1215	151	3.30×10 ⁻¹⁵	0.205
E2	1244	154	7.31×10 ⁻¹⁵	0.454
J	1279	159	1.25×10 ⁻¹⁴	0.776
F2	1303	162	4.81×10 ⁻¹⁵	0.299
K	1338	166	6.78×10 ⁻¹⁵	0.421
L	1371	170	1.61×10 ⁻¹⁴	1.000
G2	1466	182	1.19×10 ⁻¹⁵	0.074
M	1468	182	1.13×10 ⁻¹⁵	0.070
O	1539	191	5.37×10 ⁻¹⁶	0.033
Q	1607	199	7.79×10 ⁻¹⁶	0.048
R	1617	200	7.01×10 ⁻¹⁶	0.044

Table VI.38. Positions and intensities of the IET active modes of the **H-P** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=4.0 Å.

Peak label	Freq B3LYP (cm ⁻¹) (mV)		Freq B3LYP(D) (cm ⁻¹) (mV)		Mode description
A2	438	54	439	54	longitudinal motions of the two carbons of the 6:5 bonds parallel to the Au(111) surfaces
B2	489	61	491	61	distortions of the hexagon and pentagon close to the electrodes
C2	541	67	543	67	distortions of the hexagon and pentagon close to the electrodes
D2	565	70	569	71	distortions of the hexagon close to the electrodes
E2	1242	154	1246	154	6:5 bond stretchings
F2	1302	161	1306	162	6:5 bond stretchings
G2	1463	181	1465	182	C-C stretchings mainly localized on the two hexagons linked to the ones facing each electrode

Table VI.39. Label, frequencies (cm⁻¹ and mV), and description of the vibrational normal modes characteristic to the **H-P** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ and B3LYP(D)/cc-pVDZ/LANL2DZ levels of approximation for d=2.8 Å.

For the **H-P** junctions, the IET spectrum obtained for d=2.0 Å is dominated by peak **B** observed at 380 cm⁻¹ associated to longitudinal motions of the 6:5 bonds aligned parallel to the Au(111) surfaces. Two other significant contributions are found at 429 cm⁻¹ and 509 cm⁻¹: the first one corresponds to longitudinal displacements of the two carbon atoms of the 6:5 bonds parallel to the Au(111) surfaces; while the mode appearing at 509 cm⁻¹ is associated to distortions of the hexagon-pentagon moieties facing each electrode.

When going from $d=2.0$ Å to $d=2.8$ Å, an increase of the relative intensity of peak **A** (spherical/prolate mode) is observed and is attributed to a greater contribution of motions localized on the hexagon closest to each electrode, as displayed in Fig. (VI.15). The relative intensity of peaks **B2** and **C2** also increases while the peak **E** almost disappears. These modes are associated to distortions of the hexagon and pentagon close to the electrodes and the intensity increases (decrease) are related to greater (weaker) amplitude of distortion motions [Fig. (VI.15)]. Besides, peaks appear at higher frequencies and are mostly associated to C-C stretchings. Larger molecule-electrode distances mainly exhibit similar stretching motions and, in particular for $d=4.0$ Å, the two dominant peaks **J** and **L** observed respectively at 1279 cm^{-1} and 1371 cm^{-1} are associated to symmetric and anti-symmetric stretchings of the 6:5 bonds all over the C_{60} molecule.

This observation stresses the role of the junction configuration (i.e. rings or edges facing the gold surfaces) in the exaltation of the peaks appearing in the IET spectra. Indeed, contrary to the **H** and **P** configurations new peaks appear at larger frequencies.

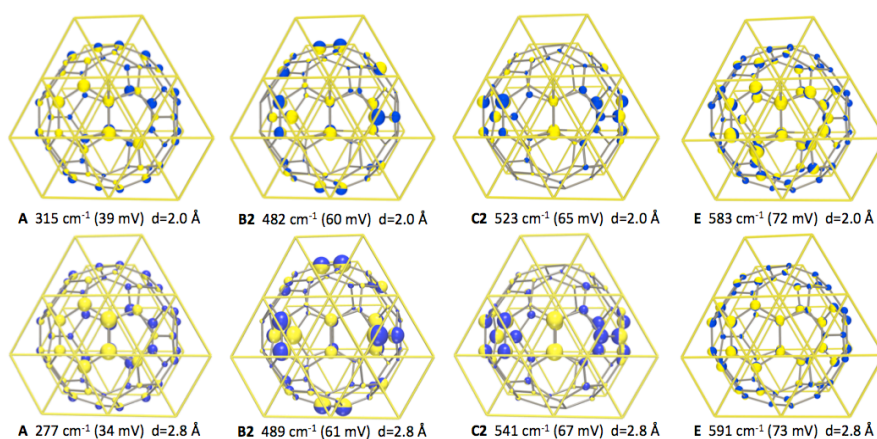


Fig. VI.15. Illustration of the vibrational modes of the **H-P** adsorption configuration characterized by significant intensity variations when going from $d=2.0$ Å to $d=2.8$ Å. The overlap values between the frequency modes obtained for $d=2.0$ Å/ $d=2.8$ Å pairs of modes **A**, **B2**, **C2** and **E** are equal to 0.931, 0.936, 0.915, and 0.694 respectively.

Concerning the **H-H** junctions, for $d=2.0$ Å the main signatures are observed in the $300\text{--}535\text{ cm}^{-1}$ range as illustrated in Fig. (VI.16). The dominant peak **C3** appearing at 376 cm^{-1} is associated to longitudinal displacements of the two carbon atoms of the 6:6 bonds parallel to the Au(111) surfaces, and the other peaks correspond to distortions of the C_{60} molecule mainly localized on the two hexagons closest to each gold electrode. By considering a molecule-electrode distance of 2.8 Å, we can notice a decrease of the relative intensity of these peaks, as shown for mode **C3** for which the intensity decrease is attributed to a weaker amplitude of the motions involving the two carbon atoms of the 6:6 bonds parallel to the Au(111) surfaces [Fig. (VI.18)]. The intensity decreases of modes **A2** and **B2** are explained similarly by weaker amplitudes of the distortion

motions localized on the two hexagons closest to each gold electrode. For $d=2.8$ Å and larger molecule-electrode distances the dominant IET signatures are found in the 1460-1615 cm^{-1} range and are associated to C-C stretchings mainly localized on the two 6:6 bonds aligned parallel to the Au(111) surfaces: *e.g.* the major peak **M** observed at 1467 cm^{-1} is associated to anti-symmetric stretchings of the 6:6 bonds aligned parallel to the Au(111) surfaces. We can point out that these IET signatures were also observed in the case of the **H** and **P** configurations (for large distances), while their IET intensities are weak when considering the **H-P** junction.

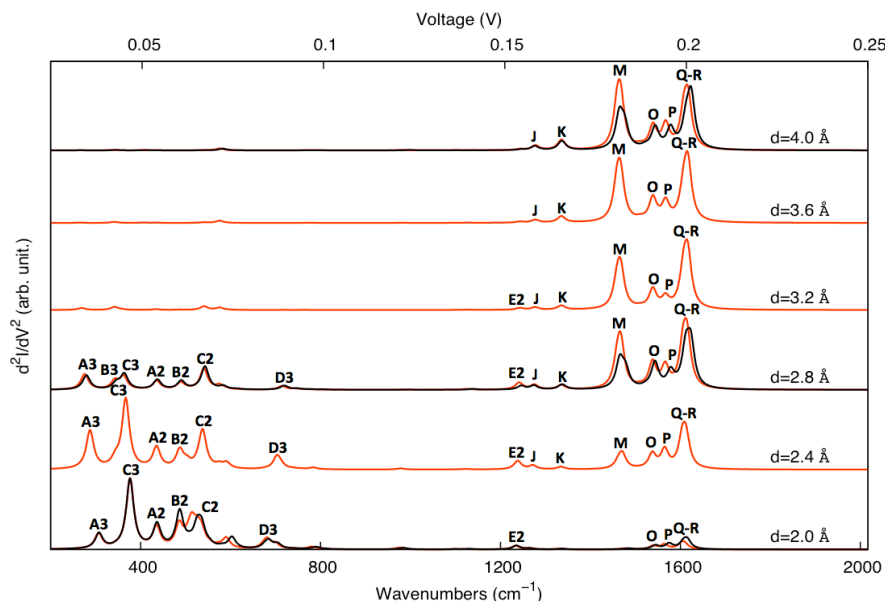


Fig. VI.16. IET spectra of the **H-H** junctions calculated at the B3LYP/cc-pVDZ/LANL2DZ (red line) and B3LYP(D)/cc-pVDZ/LANL2DZ (black line) levels of approximation by considering molecule-electrode distance values ranging from 2.0 Å to 4.0 Å.

Peak #	Frequency (cm^{-1})	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A3	306	38	1.27×10^{-6}	0.236
C3	376	47	5.39×10^{-6}	1.000
A2	436	54	1.87×10^{-6}	0.347
B2	486	60	2.22×10^{-6}	0.412
-	513	64	2.82×10^{-6}	0.523
C2	535	66	2.16×10^{-6}	0.401
-	590	73	9.53×10^{-7}	0.177
D3	681	84	9.19×10^{-7}	0.171
E2	1233	153	2.84×10^{-7}	0.053
O	1539	191	3.18×10^{-7}	0.059
P	1564	194	4.32×10^{-7}	0.080
Q	1603	199	5.93×10^{-7}	0.110
R	1609	199	6.33×10^{-7}	0.117

Table VI.40. Positions and intensities of the IET active modes of the **H-H** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for $d=2.0$ Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A3	276	34	1.42×10 ⁻¹⁰	0.231
B3	343	43	1.05×10 ⁻¹⁰	0.171
C3	362	45	1.32×10 ⁻¹⁰	0.215
A2	436	54	8.38×10 ⁻¹¹	0.136
B2	489	61	7.17×10 ⁻¹¹	0.117
C2	541	67	1.94×10 ⁻¹⁰	0.316
D3	713	88	3.48×10 ⁻¹¹	0.057
E2	1241	154	6.81×10 ⁻¹¹	0.111
J	1275	158	5.08×10 ⁻¹¹	0.083
K	1335	166	4.64×10 ⁻¹¹	0.076
M	1467	182	5.25×10 ⁻¹⁰	0.855
O	1538	191	2.73×10 ⁻¹⁰	0.445
P	1566	194	2.55×10 ⁻¹⁰	0.415
Q	1606	199	5.87×10 ⁻¹⁰	0.956
R	1615	200	6.43×10 ⁻¹⁰	1.000

Table VI.41. Positions and intensities of the IET active modes of the **H-H** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=2.8 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
J	1278	158	5.68×10 ⁻¹⁵	0.075
K	1336	166	1.16×10 ⁻¹⁴	0.153
M	1467	182	7.56×10 ⁻¹⁴	1.000
O	1539	191	2.97×10 ⁻¹⁴	0.393
P	1567	194	3.22×10 ⁻¹⁴	0.426
Q	1608	199	6.23×10 ⁻¹⁴	0.824
R	1617	200	7.00×10 ⁻¹⁴	0.898

Table VI.42. Positions and intensities of the IET active modes of the **H-H** junction, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation, for d=4.0 Å.

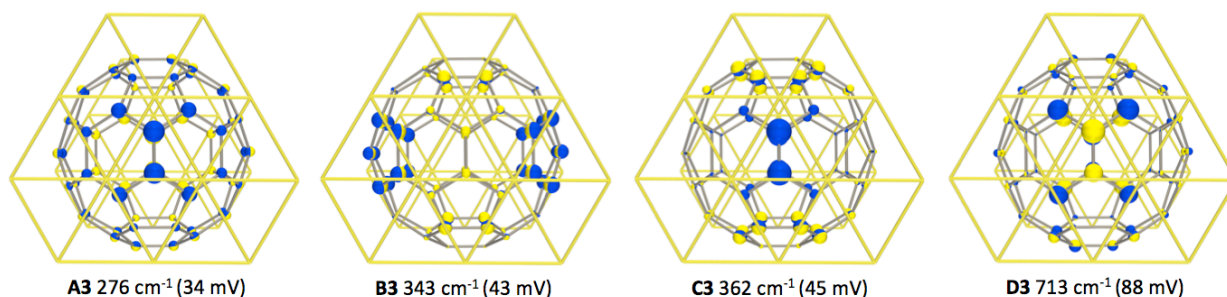


Fig. VI.17. Sketch of the IET active modes characteristic of the **H-H** junction for a C₆₀ molecule-electrode distance equal to 2.8 Å, calculated at the B3LYP/cc-pVDZ/LANL2DZ level of approximation.

Peak label	Freq B3LYP (cm ⁻¹) (mV)		Freq B3LYP(D) (cm ⁻¹) (mV)		Mode description
A3	276	34	279	35	longitudinal displacements of the two carbons of the 6:6 bonds parallel to the Au(111) surfaces
B3	343	43	346	43	out-of-plane motions of C-C bonds of pentagons
C3	362	45	364	45	longitudinal displacements of the two carbons of the 6:6 bonds parallel to the Au(111) surfaces
D3	713	88	718	89	distortions of the two hexagons close to each electrode

Table VI.43. Label, frequencies (cm⁻¹ and mV), and description of the vibrational normal modes characteristic of the **H-H** junction calculated at the B3LYP/cc-pVDZ/LANL2DZ and B3LYP(D)/cc-pVDZ/LANL2DZ levels of approximation, for d=2.8 Å.

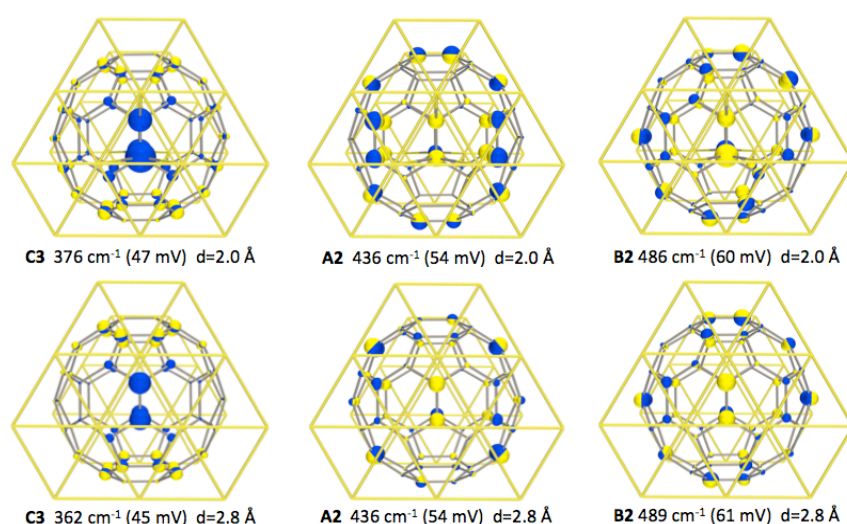


Fig. VI.18. Illustration of the vibrational modes of the **H-H** adsorption configuration characterized by significant intensity variations when going from d=2.0 Å to 2.8 Å. The overlap values between the frequency modes obtained for d=2.0 Å/2.8 Å pairs (376 cm⁻¹/362 cm⁻¹), (436 cm⁻¹/436 cm⁻¹) and (486 cm⁻¹/489 cm⁻¹) are equal to 0.923, 0.720 and 0.946, respectively.

As a final remark, we stress out the fact that changes in terms of nature of the IET active modes observed when increasing the molecule-electrode distances for each adsorption configuration can not be described by a general statement. Indeed, even if these transitions appear to be continuous for every system, we note that the “threshold” distance around which such transitions occur depends on the studied system. Moreover, the width of the distance interval required to observe a neat change in the IET signature also varies as a function of the system. For example, we observe after additional calculations considering intermediate molecule-electrode distances that the transition interval is [3.4 Å-3.6 Å] for configuration **H** [Fig. (VI.19)], [3.2 Å-3.6 Å] for configuration **P** [Fig. (VI.21)], while [2.4 Å-3.2 Å] [Fig. (VI.13)] and [2.0 Å-3.2 Å]

[Fig. (VI.16)] for configurations **H-P** and **H-H**, respectively.

The rationalization of the sensitivity of the IET responses is not always straightforward. In the present case, we observe an interesting consistency between the variations of the IET signatures and the changes in the frontier molecular orbitals topologies, especially the HOMO. Taking the example of the **H** configuration, we observe that the description of the HOMOs related to C_{60} molecule-electrode distance in the [2.0 Å-3.4 Å] involves isosurfaces localized at the interface between the molecule and the metallic electrode, *i.e.* in the contact region [Fig. (VI.19)]. This can be attributed to the significant overlap occurring between the molecule and the electrodes, and correlates well with the nature of the dominant IET modes active for these distances involving longitudinal motions between the contact moieties (*i.e.* the hexagon rings) and the electrodes, e.g. peaks **D** and **E** for $d=2.0$ Å and peaks **A** and **B** for $d=2.8$ Å [Fig. (VI.20)]. On the other hand, for distances larger than 3.6 Å the isosurfaces corresponding to the HOMO are mainly localized on the C_{60} molecule, and do not involve orbital overlaps between the C_{60} molecule and the metallic electrodes. The corresponding IET signatures are associated to stretching motions localized only on the C_{60} molecule (e.g. peak **R**) [Fig. (VI.20)]. Note that such molecular response properties dependency on the molecule-electrode orbitals overlap has already been demonstrated in a study focusing on the NLO properties of a C_{60} molecule adsorbed on a SiO_2 surface^[23]. In a similar way, we can correlate the HOMOs with the IET signatures of the **P** configuration. The analysis remains identical with the case of the **H** configuration in terms of correlation between the nature of the IET active vibrational modes and the topology of the HOMOs. However, we can note that the IET spectrum related to $d=3.4$ Å [Fig. (VI.21)] is characterized by peaks involving longitudinal motions between the C_{60} molecule and the electrodes and also C-C stretchings, illustrated in Fig. (VI.22). This can be correlated to the progressive evolution of the HOMOs topology around the transition interval [3.2 Å-3.6 Å]. Considering the Mulliken charges presented in Table (VI.44) for the **H** and **P** configurations, we observe a clear decrease of the charge transfer from the C_{60} molecule to the electrodes when increasing the C_{60} molecule-electrode distances. This is coherent with the analysis of HOMO topologies, for which the overlap between the molecule and the electrodes decrease when increasing the distance between the C_{60} molecule and the electrodes. Furthermore, this charge transfer tendency is consistent with the results presented by Leszczynski et al.^[24], who have shown that, for a C_{60} molecule sandwiched between clusters containing 2 to 8 gold atoms on each side ($d(S-Au)\sim 2.4$ Å) investigated at a similar level of calculation, there is an electronic charge transfer from the C_{60} molecule to the gold clusters.

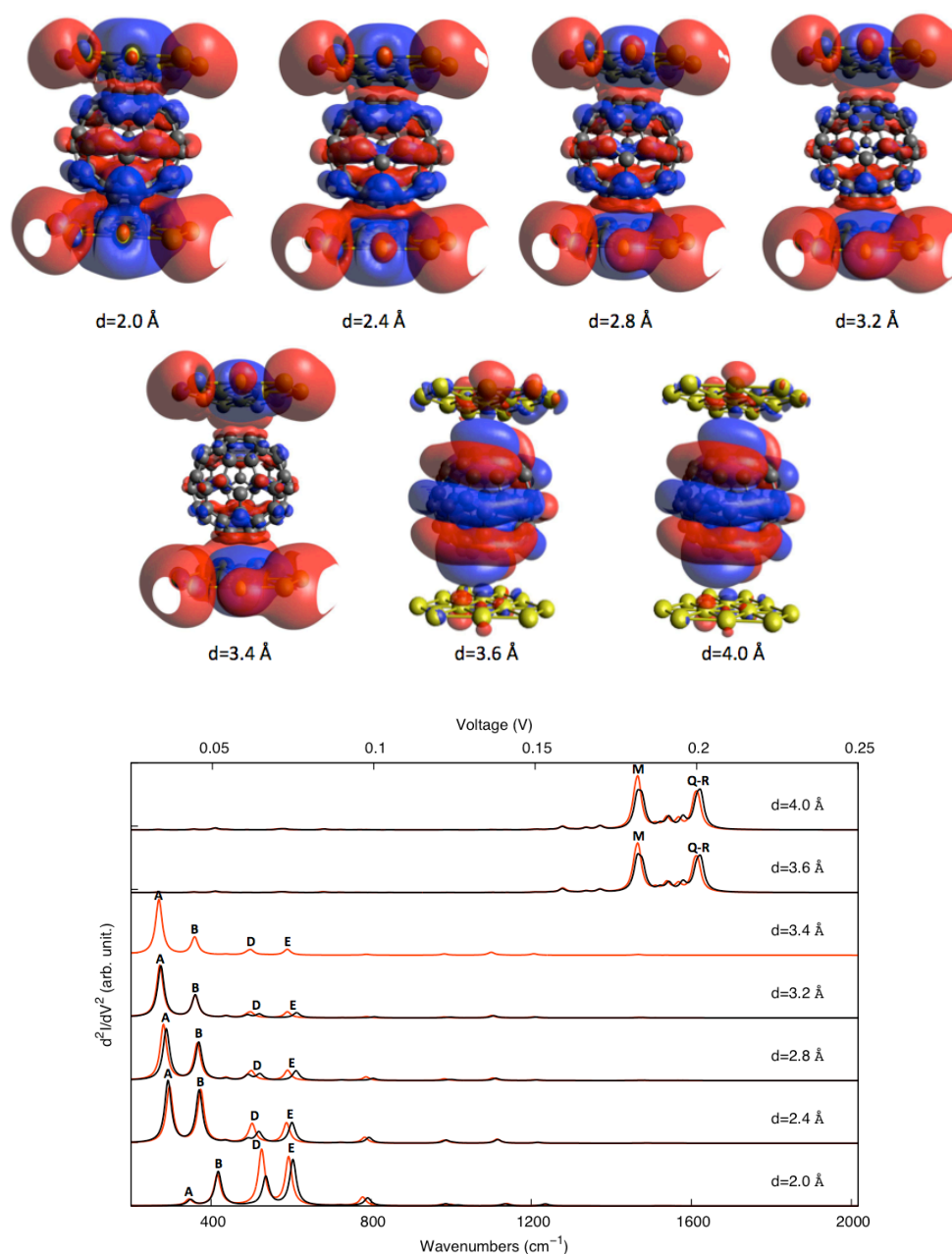


Fig.VI.19. Representation of the isosurfaces of the HOMO of the **H** junction for several C₆₀ molecule-electrode distances (top) and IET spectra of the **H** junctions calculated at the B3LYP/cc-pVDZ/LANL2DZ (red line) and B3LYP(D)/cc-pVDZ/LANL2DZ (black line) levels of approximation (bottom).

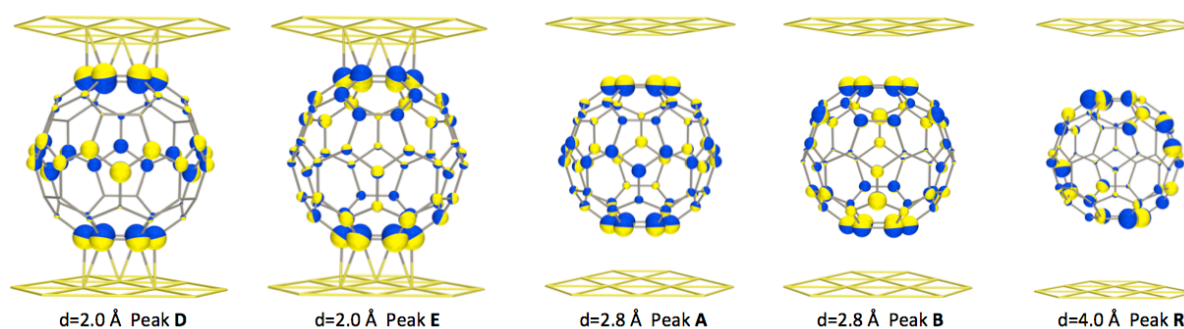


Fig.VI.20. Illustration of dominant IET modes of the **H** junction for different C₆₀ molecule-electrode distance values.

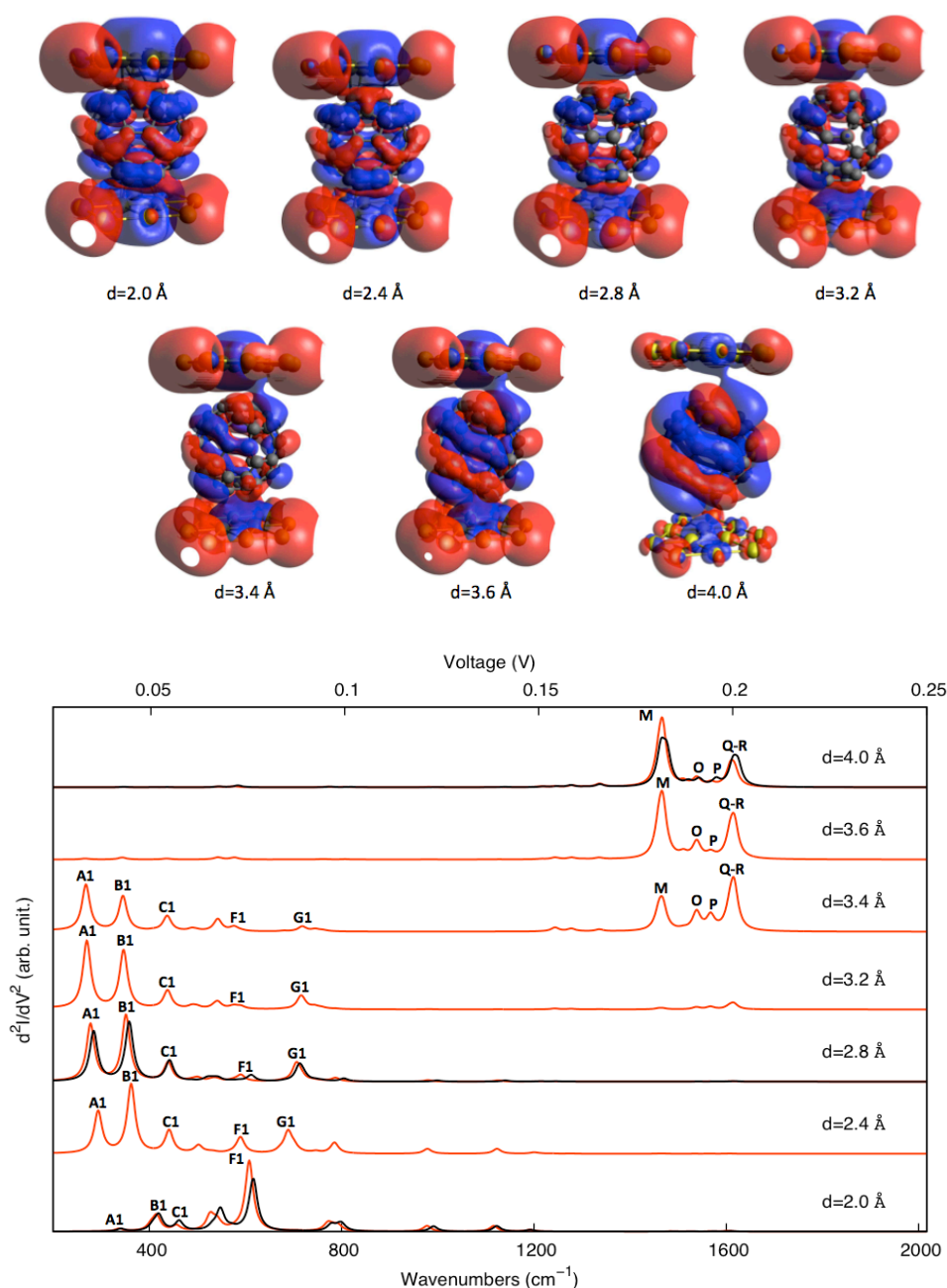


Fig.VI.21. Representation of the isosurfaces of the HOMO of the **P** junction for several C₆₀ molecule-electrode distances (top) and IET spectra of the **P** junctions calculated at the B3LYP/cc-pVDZ/LANL2DZ (red line) and B3LYP(D)/cc-pVDZ/LANL2DZ (black line) levels of approximation (bottom).

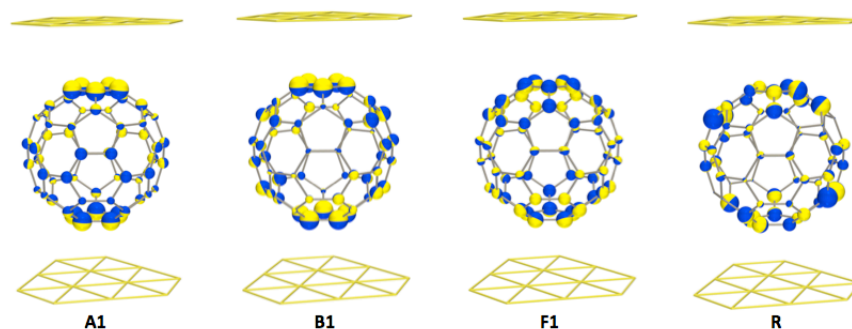


Fig.VI.22. Sketch of some IET active modes of the **P** junction for a C₆₀ molecule-electrode distance of $3.4 \text{ \AA}$.

H	Source	C₆₀	Drain
d=2.0 Å	-0.0397	0.0285	0.0112
d=2.4 Å	-0.3193	0.5704	-0.2511
d=2.8 Å	-0.2057	0.3709	-0.1652
d=3.2 Å	-0.1057	0.1941	-0.0884
d=3.6 Å	-0.0532	0.0999	-0.0467
d=4.0 Å	-0.0341	0.0661	-0.0319

P	Source	C₆₀	Drain
d=2.0 Å	-0.0338	0.0670	-0.0332
d=2.4 Å	-0.2175	0.4348	-0.2173
d=2.8 Å	-0.1433	0.2867	-0.1434
d=3.2 Å	-0.0796	0.1593	-0.0796
d=3.6 Å	-0.0457	0.0914	-0.0457
d=4.0 Å	-0.0343	0.0686	-0.0344

Table VI.44. Mulliken charges (au) for the different parts constituting the **H** and **P** molecular junctions.

VI.C.4. Dispersion correction effects on the IET response of the **P**, **H-P** and **H-H** junctions

Concerning the **P** junctions with a molecule-electrode distance value of 2.0 Å, the largest intensity variations are observed for B3LYP (B3LYP(D)) modes appearing at 456 cm⁻¹ (462 cm⁻¹) associated to mode **C1**, at 541 (548 cm⁻¹), at 527 cm⁻¹ (532 cm⁻¹) and at 608 cm⁻¹ (617 cm⁻¹) related to mode **F1**, as their values increase by 61%, 51% and decrease by 43% and 26%, respectively [Tables (VI.29) and (VI.45)]. These intensity decreases (increases) can be attributed to weaker (greater) amplitude of the motions involving the two pentagons facing the gold electrodes, as illustrated in Fig. (VI.23). For d=2.8 Å, the inclusion of dispersion interactions involves no significant changes in terms of relative intensity among the dominant IET peaks, while for a larger molecule-electrode distance (d=4.0 Å), the largest intensity variations (sketched in Fig. (VI.24)) appear for the B3LYP modes **M** and **R** as their value respectively decrease by 29% and 17%, as also found for the **H** junction. As a general conclusion, the analysis of the IET responses of the **P** junctions (Fig. (VI.9)) allows to show a small impact of the inclusion of dispersion interactions on the IET spectra, the largest intensity variations concerning the dominant IET peaks being observed for modes **F1** (d=2.0 Å) and modes **M** (d=4.0 Å).

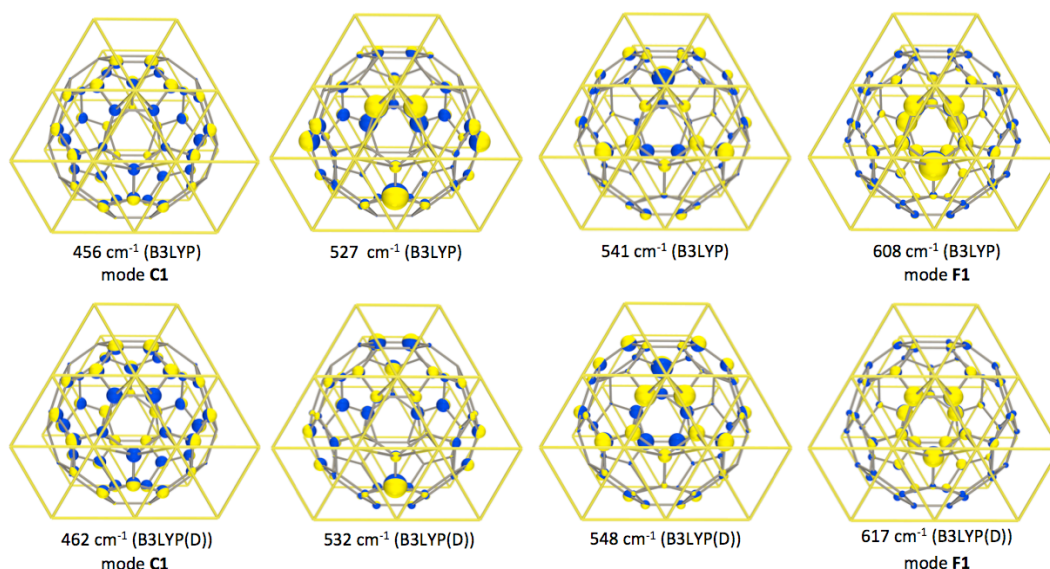


Fig.VI.23. Illustration of the vibrational modes of the **P** adsorption configuration ($d=2.0$ Å) characterized by significant intensity variations when adding dispersion corrections in the B3LYP XC functional. The overlap values between the B3LYP/B3LYP(D) frequency modes for pairs ($456\text{ cm}^{-1}/462\text{ cm}^{-1}$), ($527\text{ cm}^{-1}/532\text{ cm}^{-1}$), ($541\text{ cm}^{-1}/548\text{ cm}^{-1}$) and ($608\text{ cm}^{-1}/617\text{ cm}^{-1}$) are equal to 0.991, 0.731, 0.866 and 0.902, respectively.

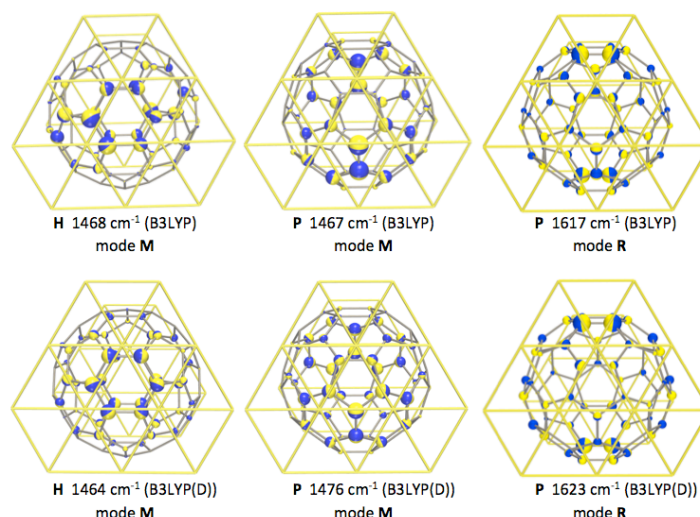


Fig. VI.24. Illustration of the vibrational modes of the **H** and **P** adsorption configurations ($d=4.0$ Å) characterized by significant intensity variations when adding dispersion corrections in the B3LYP XC functional. The overlap value between the B3LYP/B3LYP(D) pair of modes **M** of the **H** junction is equal to 0.889, and the overlap values between the B3LYP/B3LYP(D) pairs of modes **M** and **R** of the **P** junction are equal to 0.768, 0.935, respectively.

In the case of a **H-P** junction with a small molecule-electrode distance ($d=2.0$ Å), we do not observe significant intensity variations when adding dispersion corrections, as all the IET intensity shifts are smaller than 14% (Tables (VI.36) and (VI.46)), except for the B3LYP (B3LYP(D)) mode observed at 509 cm^{-1} (502 cm^{-1}) as its intensity decreases by 52% when adding dispersion corrections due to a weaker amplitude of the displacement motions involving the carbon atoms localized on the 6:5 bonds and the Au(111) surfaces. In addition, we can point out that in the 480-

530 cm^{-1} range, the B3LYP mode providing the largest intensity value (mode appearing at 509 cm^{-1}) is not correlated to the B3LYP(D) mode dominating this frequency range (mode **C2** observed at 525 cm^{-1}), as the overlap value is smaller than 0.1. These two dominant modes are associated to distortions of the C_{60} molecule, but are not localized on the same ring: in the B3LYP spectrum the atomic motions of the dominant vibrational mode are mainly localized on the hexagon ring close to the H-P edge, while for the B3LYP(D) IET response the dominant peak is associated to distortions of both the pentagon and hexagon rings close to the H-P edge. For a molecule-electrode distance of 2.8 Å, the largest intensity variations appear for modes **M**, **G2**, **R**, as their values decrease respectively by 48%, 41% and 26%, and for modes **D2** and **A2** as their value respectively increases by 52% and 34% [Tables (VI.37) and (VI.47)]. The IET intensity decreases observed for modes **M** and **R** is related to the weakening of the C-C stretchings involved in the 6:5 bonds close to each electrode, as shown in Fig. (VI.25). In the case of modes **A2** and **D2**, the IET intensity increase can be attributed to a greater longitudinal displacement of the 6:5 bonds in the direction parallel to the normal to the Au(111) surfaces [Fig. (VI.25)]. Finally, the intensity decrease of mode **G2** when adding dispersion corrections can be attributed to weaker C-C stretchings mainly localized on the two hexagons linked to the ones facing each electrode. For $d=4.0$ Å, we can observe that the inclusion of dispersion corrections does not affect the relative intensities of the dominant peaks.

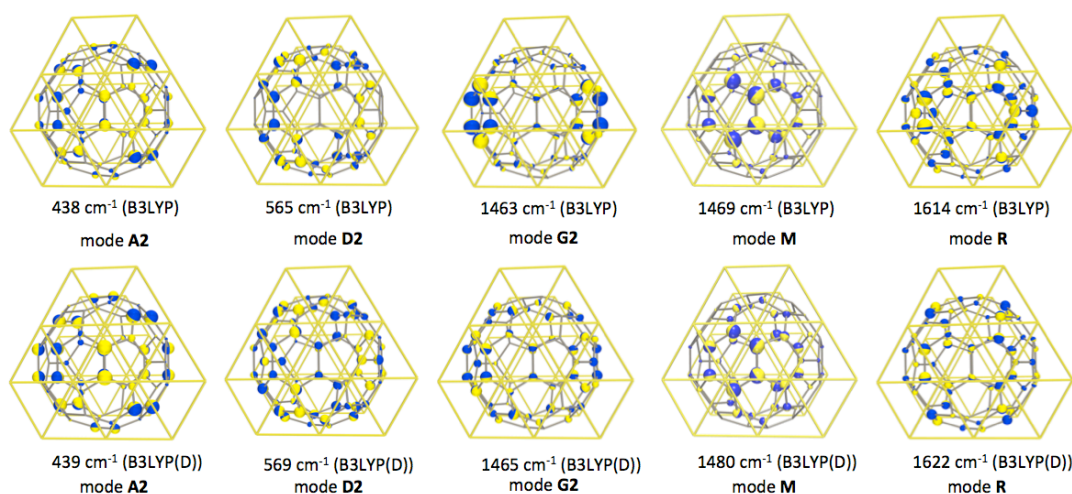


Fig. VI.25. Illustration of the vibrational modes of the **H-P** adsorption configuration ($d=2.8$ Å) characterized by significant intensity variations when adding dispersion corrections in the B3LYP XC functional. The overlap values between the B3LYP/B3LYP(D) pairs of modes **A2**, **D2**, **G2**, **M** and **R** are equal to 0.950, 0.688, 0.783, 0.738 and 0.882, respectively.

Finally, considering the **H-H** junctions for $d=2.0$ Å, the addition of dispersion corrections induces the largest IET intensity variations (among the dominant peaks) for mode **B2**, as its value

increases by 38% [Tables (VI.40) and (VI.48)]. This is explained by a greater amplitude of the longitudinal displacements of the two 6:6 bonds involved in the molecule-electrode contact [Fig. (VI.26)]. Moreover, one can note that the dominant peaks appearing in the 500-540 cm^{-1} range are not correlated: the mode appearing on the B3LYP spectrum at 513 cm^{-1} is characterized by distortions of the hexagon rings surrounding the 6:6 bonds facing the gold electrodes, while the B3LYP(D) mode observed at 526 cm^{-1} involves longitudinal displacements of these 6:6 bonds. For molecule-electrode distances of 2.8 Å and 4.0 Å, the largest intensity variation is observed in each case for mode **M**, and originates from a weaker amplitude of the stretching motions involving the 6:6 bonds parallel to the Au(111) surfaces, as illustrated in Fig. (VI.26) for $d=2.8$ Å.

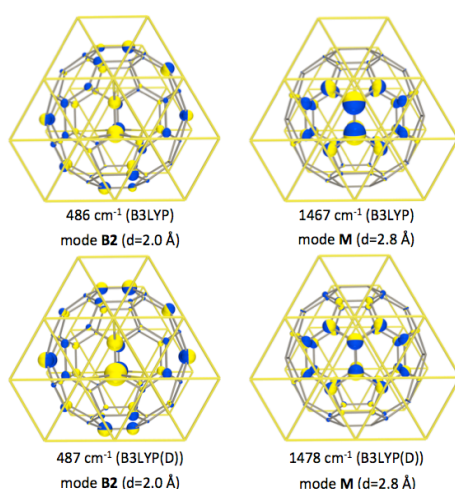


Fig. VI.26. Illustration of the vibrational modes of the **H-H** junction characterized by significant intensity variations when adding dispersion corrections in the B3LYP XC functional. The overlap values between the B3LYP/B3LYP(D) pairs of modes **B2** ($d=2.0$ Å) and pairs of modes **M** ($d=2.8$ Å) are equal to 0.937 and 0.680, respectively.

Peak #	Frequency (cm^{-1})	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A1	341	42	9.95×10^{-8}	0.058
B1	420	52	5.90×10^{-7}	0.345
C1	462	57	3.69×10^{-7}	0.216
-	532	66	3.61×10^{-7}	0.211
-	548	68	7.89×10^{-7}	0.461
F1	617	76	1.71×10^{-6}	1.000
G1	699	87	4.82×10^{-8}	0.028
-	779	97	2.84×10^{-7}	0.166
-	794	98	3.09×10^{-7}	0.181
I1	991	123	1.73×10^{-7}	0.101
J1	1123	139	1.82×10^{-7}	0.106

Table VI.45. Positions and intensities of the IET active modes of the **P** junction, calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for $d=2.0$ Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	316	39	4.44×10 ⁻⁷	0.404
-	360	45	4.79×10 ⁻⁷	0.435
B	380	47	1.10×10 ⁻⁶	1.000
-	430	53	6.76×10 ⁻⁷	0.615
B2	482	60	3.04×10 ⁻⁷	0.276
-	502	62	3.60×10 ⁻⁷	0.327
C2	525	65	7.22×10 ⁻⁷	0.656
E	593	74	3.75×10 ⁻⁷	0.341
-	666	83	1.46×10 ⁻⁷	0.133
-	783	97	1.29×10 ⁻⁷	0.117

Table VI.46. Positions and intensities of the IET active modes of the **H-P** junction, calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=2.0 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A	282	35	3.27×10 ⁻¹¹	0.663
B	365	45	4.48×10 ⁻¹¹	0.909
A2	439	54	2.10×10 ⁻¹¹	0.426
B2	491	61	4.93×10 ⁻¹¹	1.000
C2	543	67	4.67×10 ⁻¹¹	0.947
D2	569	71	1.72×10 ⁻¹¹	0.349
E	613	76	4.31×10 ⁻¹²	0.087
I	1218	151	5.77×10 ⁻¹²	0.117
E2	1246	154	1.01×10 ⁻¹¹	0.205
J	1278	158	1.59×10 ⁻¹¹	0.323
F2	1306	162	7.19×10 ⁻¹²	0.146
K	1335	166	9.26×10 ⁻¹²	0.188
L	1370	170	1.11×10 ⁻¹¹	0.225
G2	1465	182	1.96×10 ⁻¹¹	0.398
M	1480	183	1.73×10 ⁻¹¹	0.351
O	1542	191	8.31×10 ⁻¹²	0.169
P	1578	196	8.68×10 ⁻¹²	0.176
Q	1612	200	1.47×10 ⁻¹¹	0.298
R	1622	201	1.42×10 ⁻¹¹	0.288

Table VI.47 Positions and intensities of the IET active modes of the **H-P** junction, calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=2.8 Å.

Peak #	Frequency (cm ⁻¹)	Potential (mV)	Intensity (arb. units.)	Relative Intensity
A3	307	38	1.29×10 ⁻⁶	0.239
C3	376	47	5.39×10 ⁻⁶	1.000
A2	437	54	2.09×10 ⁻⁶	0.388
B2	487	60	3.07×10 ⁻⁶	0.570
-	526	65	2.57×10 ⁻⁶	0.477
C2	536	66	2.43×10 ⁻⁶	0.451
-	603	75	9.94×10 ⁻⁷	0.184
D3	685	85	8.06×10 ⁻⁷	0.150
E2	1235	153	3.05×10 ⁻⁷	0.057
O	1544	191	3.57×10 ⁻⁷	0.066
P	1575	195	5.15×10 ⁻⁷	0.096
Q	1607	199	8.82×10 ⁻⁷	0.164
R	1615	200	9.42×10 ⁻⁷	0.175

Table VI.48. Positions and intensities of the IET active modes of the **H-H** junction, calculated at the B3LYP(D)/cc-pVDZ/LANL2DZ level of approximation, for d=2.0 Å.

VI.D. Conclusion

In this study, we have simulated the IET response of a single C₆₀ molecule embedded between two gold electrodes by using the QCME code which is based on the Green's function formalism within the harmonic approximation for evaluating the vibronic couplings. The sensitivity of the IET spectroscopy to junction parameters has been evidenced by considering four different orientations of the C₆₀ molecule and by varying the molecule-electrode distance. For all the adsorption configurations (**H**, **P**, **H-P**, **H-H**) and considering a small molecule-electrode distance (d=2.0 Å) the dominant peaks are associated to longitudinal displacements of the contact moieties (hexagon cycles for the **H** configuration, pentagon cycles for the **P** configuration, 6:5 bonds for the **H-P** configuration, 6:6 bonds for the **H-H** configuration). When considering d=2.8 Å, depending on the configuration the dominant signatures are not associated to the same atomic motions. In particular, for the **H** and **P** fixed with a molecule-electrode distance d=2.8 Å, the two dominant peaks are associated to deformations of the C₆₀ molecule between a spherical and a prolate shape and to longitudinal motions of the hexagons cycles in the **H** junction (pentagon cycles in the **P** junction) moving from one electrode to the other. For the **H-P** junction fixed with d=2.8 Å the two dominant peaks correspond to longitudinal motions of the 6:5 bonds in the direction of the normal to the gold surfaces. Moreover, in this specific case we can observe the apparition of small peaks at higher frequencies corresponding to C-C stretchings. For the **H-H** junction fixed with

$d=2.8$ Å we also observe the apparition of high-frequency modes which have the higher relative intensities, the two dominant peaks being associated to C-C stretchings of the 6:6 bonds aligned parallel to the Au(111) surfaces. On the other hand, for $d=4.0$ Å the four adsorption configurations only exhibit peaks corresponding to C-C stretching modes. In the case of the **H** junction, the dominant peaks are associated to large endocyclic stretchings of the contact hexagons, while for the **P** junction the major signatures are associated to deformations of the contact pentagons. In the case of the edge contacts (**H-H** and **H-P**) the dominant peaks are associated to C-C stretchings mainly localized on the 6:6 or 6:5 bonds aligned parallel to the Au(111) surfaces. The rationalization of the sensitivity of the IET response as a function of the C_{60} molecule-electrode distance has highlighted an interesting consistency between the variations of the IET signatures and the changes in the HOMO topologies. Indeed, when considering small C_{60} molecule-electrode distances the dominant IET peaks involving longitudinal motions between the contact moieties and the electrodes are associated to isosurfaces localized at the interface between the C_{60} and the electrodes, while for larger distances the dominant contribution of the C-C stretchings motions in the IET response is correlated to a delocalization of the HOMO on the C_{60} molecule, and does not involve orbital overlaps between the C_{60} and the electrodes.

The best agreement between the experimental measurements^[15] and our theoretical calculations has been found when considering a molecular junction characterized by two hexagons of the C_{60} molecule aligned parallel to the Au(111) surfaces and centered on a hcp site, with a distance between the center of the hexagon (aligned parallel to the Au(111) surface) and the hcp site of the source reservoir of 2.8 Å, and with a distance between the center of the hexagon and the hcp site of the drain reservoir of 3.4 Å. In this case, the dominant signature is associated to the spherical/prolate C_{60} distortion mode, which is correlated to a H_g mode of a free C_{60} molecule, active in Raman spectroscopy^[25]. This observation is consistent with previous studies focusing on the IET response of a single C_{60} molecule in contact with Pb(111), Ag(110), and Al(100) surfaces showing that H_g modes are strongly coupled to transport^[26].

Finally, the study of Böhler and co-workers has also evidenced that some signatures do not originate from the intrinsic vibrational modes of the system, but rather from the deformation of the molecular contact as found for the peak observed at 64 mV (correlating to the A_g breathing mode also active in Raman spectroscopy). Our approach can therefore be of great help in understanding, beside the intrinsic vibrational behavior of one compound, the small structural variations induced by the proximity to the metallic electrodes.

VI.E. References.

- [1] (a) Porath, D.; Levi, Y.; Tarabiah, M.; Millo, O. *Phys. Rev B* **1997**, *56*, 9829-9833; (b) Zeng, C.; Wang, H.; Wang, B.; Yang, J.; Hou, J. G. *Appl. Phys. Lett.* **2000**, *77*, 3595; (c) Zheng, X.; Lu, W.; Abtew, T. A.; Meunier, V.; Bernholc, J. *ACS Nano* **2010**, *4*, 7205-7210.
- [2] (a) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983 ; (b) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *Chem. Comm.* **1990**, *20*, 1423-1425.
- [3] (a) Schlüter, M. A.; Lannoo, M.; Needels, M.; Baraff, G. A.; Tomanék, D. *Mater. Sci. Eng. B* **1993**, *19*, 129-134; (b) Winkelmann, C. B.; Roch, N.; Wernsdorfer, W.; Bouchiat, V.; Balestro, F. *Nature Phys.* **2009**, *5*, 876-879.
- [4] (a) Joachim, C.; Gimzewski, J. K.; Schlittler, R.R.; Chavy, C. *Phys. Rev. Lett.* **1995**, *74*, 2102; (b) Joachim, C.; Gimzewski, J. K. *Chem. Phys. Lett.* **1997**, *265*, 353-357; (c) Gimzewski, J. K.; Joachim, C. *Science* **1999**, *283*, 1683.
- [5] (a) Joachim, C.; Gimzewski, J. K. ; Tang, H. *Phys. Rev. B* **1998**, *58*, 16407-16417. (b) Alavi, S. ; Larade, B. ; Taylor, J. ; Guo, H. ; Seideman, T. *Chem. Phys.* **2002**, *281*, 293-303; (c) Park, H.; Park, J.; Lim, A. K. L.; Anderson, E. H.; Alivisatos, A. P.; McEuen, P. L. *Nature* **2000**, *407*, 57.
- [6] (a) Nakaya, M.; Tsukamoto, S.; Kuwahara, Y.; Aono, M.; Nakayama, T. *Adv. Mater.* **2010**, *22*, 1622-1625; (b) Kim, H. S.; Lee, J.; Kim, Y-H. *Carbon* **2014**, *67*, 48-57.
- [7] Szymańska, I.; Radecka, H.; Radecki, J.; Kikut-Ligaj, D. *Biosens Bioelectron.* **2001**, *16*, 911-915.
- [8] (a) Nara, J.; Geng, W. T.; Kino, H.; Kobayashi, N.; Ohno, T. *J. Chem. Phys.* **2004**, *121*, 6485; (b) Chen, F.; Li, X.; Hihath, J.; Huang, Z.; Tao, N. *J. Am. Chem. Soc.* **2006**, *128*, 15874-15881; (c) Liu, H.; Wang, N.; Zhao, J.; Guo, Y.; Yin, X.; Boey, F. Y. C.; Zhang, H. *ChemPhysChem* **2008**, *9*, 1416-1424; (d) Cho, Y.; Kim, W. Y.; Kim, K. S. *J. Phys. Chem. A* **2009**, *113*, 4100-4104.
- [9] Cuevas, J. C. Scheer, E. *Molecular Electronics: An Introduction to Theory and Experiment*, World scientific, Singapore, 2010.
- [10] (a) Joachim, C.; Gimzewski, J. K. *Europhys. Lett.* **1995**, *30*, 409; (b) Hou, J. G.; Yang, J.; Wang, H.; Li, Q.; Zeng, C.; Lin, H.; Bing, W.; Chen, D. M.; Zhu, Q. *Phys. Rev. Lett.* **1999**, *83*, 3001; (c) Pascual, J. I.; Gómez-Herrero, J.; Rogero, C.; Baró, A. M.; Sánchez-Portal, D.; Artacho, E.; Ordejón, P.; Soler, J. M. *Chem. Phys. Lett.* **2000**, *321*, 78-82; (d) Rogero, C.; Pascual, J. I.; Gómez-Herrero, J.; Baró, A. M. *J. Chem. Phys.* **2002**, *116*, 832; (e) Ho, W. *J. Chem. Phys.* **2002**, *117*, 11033-11061; (f) Pradhan, N. A.; Liu, N.; Ho, W. *J. Phys. Chem. B* **2005**, *109*, 8513-8518; (g) Schull, G.; Néel, N.; Becker, M.; Kröger, J.; Berndt, R. *New. J. Phys.* **2008**, *10*, 065012.
- [11] (a) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P. *Science* **1997**, *278*, 252; (b) Xiang, D.; Jeong, H.; Lee, T.; Mayer, D. *Adv. Mater.* **2013**, *25*, 4818.
- [12] (a) Jaklevic, R. C.; Lambe, J. *Phys. Rev. Lett.* **1966**, *17*, 1139; (b) Adkins, C. J.; Phillips, W. A. *J. Phys. C: Solid State Phys.* **1985**, *18*, 1313-1346; (c) Hipps, K. W.; Mazur, U. *J. Phys. Chem.* **1993**, *97*, 7803-7814; (d) Reed, M. A. *Mater. Today* **2008**, *11*, 46-50; (e) Okabayashi, N.; Paulsson, M.; Komeda, T. *Prog. Surf. Sci.* **2013**, *88*, 1-38.

- [13] (a) Troisi, A.; Ratner, M. A. *Phys. Chem. Chem. Phys.* **2007**, *9*, 2421; (b) Leng, J. C.; Lin, L. L.; Song, X. N.; Li, Z. L.; Wang, C. K. *J. Phys. Chem. C* **2009**, *113*, 18353.
- [14](a) Taniguchi, M.; Tsutsui, M.; Yokota, K.; Kawai, T. *Nanotechnology* **2009**, *20*, 434008; (b) Tsutsui, M.; Taniguchi, M.; Shoji, K.; Yokota, K.; Kawai, T. *Nanoscale* **2009**, *1*, 164-170; (c) Kim, Y.; Song, H.; Strigl, F.; Pernau, H-F.; Lee, T.; Scheer, E. *Phys. Rev. Lett.* **2011**, *106*, 196804; (d) Fock, J.; Sørensen, J. K.; Lörtscher, E.; Vosch, T.; Martin, C. A.; Riel, H.; Kilså, K.; Bjørnholm, van der Zant, H. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14325-14332.
- [15] Böhler, T.; Edtbauer, A.; Scheer, E. *Phys. Rev. B* **2007**, *76*, 125432.
- [16] Lin, L. L.; Wang C. K.; Luo, Y. *ACS Nano* **2011**, *5*, 2257.
- [17] Ségerie, A.; Lin, L-L.; Liégeois, V.; Luo, Y.; Champagne, B. *Spectrochim. Acta Part A: Mol. and Biomol. Spectrosc.* **2014**, *119*, 34-41.
- [18] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comp. Chem.* **2011**, *32*, 1456-65.
- [19] (a) Fedorovsky, M. PyVib2, A Program for Analyzing Vibrational Motion and Vibrational Spectra; 2007; <http://pyvib2.sourceforge.net>. (b) Fedorovsky, M. *Comput. Lett.* **2006**, *2*, 233. (c) Liégeois, V.; Champagne, B. *Theor. Chem. Acc.* **2012**, *131*, 1284.
- [20] Wang, L-L.; Cheng, H-P. *Phys. Rev. B* **2004**, *69*, 165417.
- [21] (a) Chavy, C.; Joachim, C. Altibelli, A. *Chem. Phys. Lett.* **1993**, *214*, 569; (b) Ruoff, R. S.; Hickman, A. P. *J. Phys. Chem.* **1993**, *97*, 2494; (c) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes* (academic Press, New York, 1996); (d) Pérez-Jiménez, A. J.; Palacios, J. J.; Louis, E.; SanFabian, E.; Vergés, J. A. *ChemPhysChem* **2003**, *4*, 388-392.
- [22] Hamada, I.; Tsukada, M. *Phys. Rev B* **2011**, *83*, 245437.
- [23] Nénon, S.; Champagne, B. *J. Phys. Chem. Lett.* **2014**, *5*, 149.
- [24] Shukla, M. K.; Dubey, M.; Leszczynski, J. *ACS Nano* **2008**, *2*, 227.
- [25] Kuzmany, H.; Pfeiffer, R.; Hulman, M.; Kramberger, C. *Phil. Trans. R. Soc. Lond. A* **2004**, *362*, 2375-2406.
- [26] (a) Pascual, J. I.; Gomez-Herrero, J.; Sanchez-Portal, D.; Rust, H.-P. *J. Chem. Phys.* **2002**, *117*, 9531-9534. (b) Sergueev, N.; Demkov, A. A.; Guo, H. *Phys. Rev. B* **2007**, *75*, 233418; (c) Franke, K. J.; Schulze, G.; Pascual, J. I. *Phys. Chem. Lett.* **2010**, *1*, 500-504.

**IET spectra simulation of complex C₆₀-porphyrin
derivatives within TINTIN project**

VII. IET spectra simulation of complex C₆₀-porphyrin derivatives within TINTIN project

In the context of the ARC proposal TINTIN, we have extended our calculations to complex systems which are constituted of two C₆₀-porphyrin based molecules sketched in Fig. (VII.1) and denoted **S1** and **S2** in our study. Their synthesis is realized in the frame of the PhD thesis of Sylvia Forensi under the supervision of Professor Davide Bonifazi in the Laboratoire de Chimie Organique des Matériaux Supramoléculaires (COMS) in the University of Namur. The optimization of the geometrical structures, the vibrational frequencies as well as the first-order derivatives of the wavefunction with respect to the normal mode coordinates have been calculated at the B3LYP/6-31G(d) level of approximation. Note that the huge computational needs required for the calculation of the vibrational frequencies of **S1** and **S2** (having respectively 642 and 768 normal modes) have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifique de Belgique (F.R.S.-FNRS). The simulation of the IET spectra has been performed by considering isolated molecules, *i.e.* the gold surfaces have been considered implicitly. In this case, the coupling between the molecule and the electrodes is defined as a constant parameter set to 0.05 eV, and the temperature is fixed to 4.2 K.

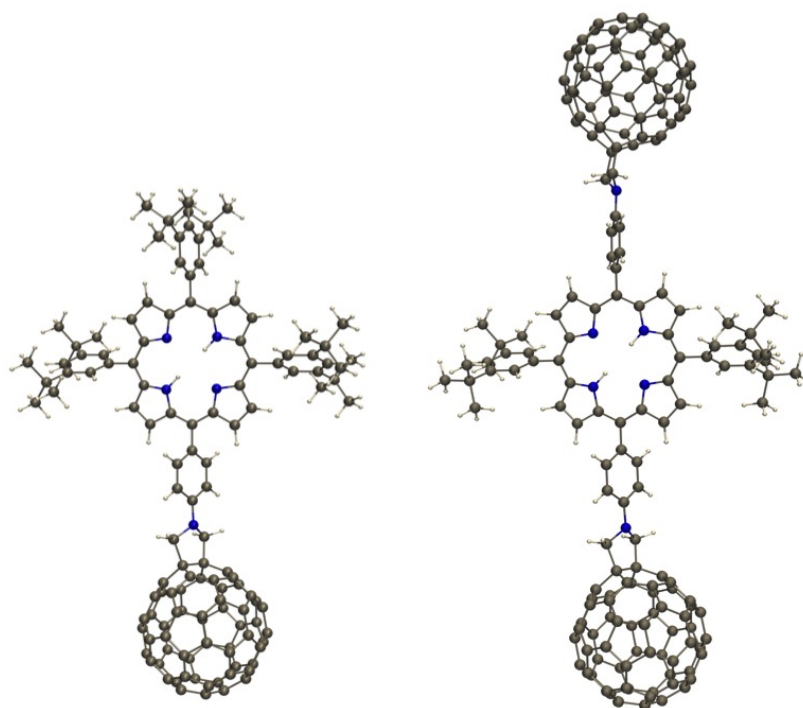


Fig. VII.1. Representation of the C₆₀-porphyrin based molecules **S1** (left) and **S2** (right) optimized at the B3LYP/6-31G(d) level of calculation.

The IET spectra obtained for **S1** and **S2** are illustrated in Fig. (VII.2). The vibrational frequencies (cm^{-1}) and corresponding transition potentials (mV), and the IET intensities (arb. units) of the dominant vibrational modes of **S1** and **S2** are respectively reported in Tables (VII.1-2).

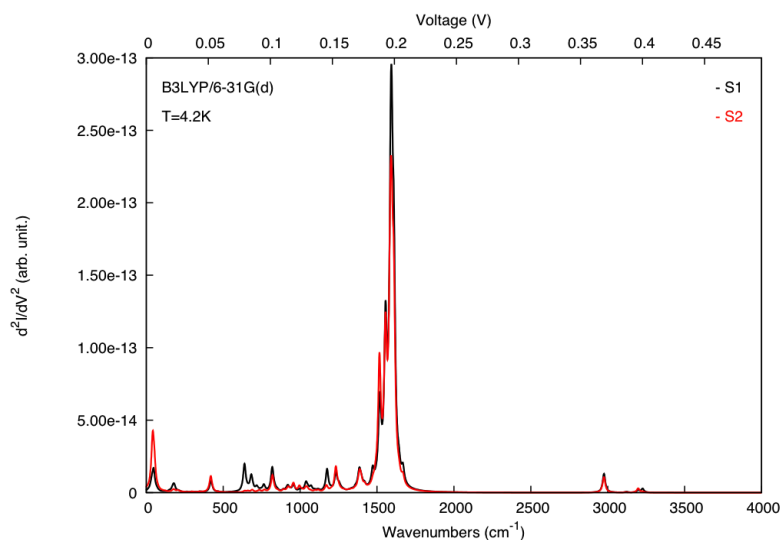


Fig. VII.2. IET spectra of **S1** (black) and **S2** (red) calculated at the B3LYP/6-31G(d) level of approximation. The temperature is fixed to 4.2 K and the FWHM of the IET spectra to 20 cm^{-1} .

Frequency	Potential	Intensity	Mode description
1517	188	6.93×10^{-14}	C-H motions of the tert-butyl groups together with C-C stretchings of the bridges separating the pyrrole rings and C-C stretchings of the pyrrole rings
1555	193	1.32×10^{-13}	C-C stretchings and C-H bendings of the pyrrole rings
1589	197	2.75×10^{-13}	C-C stretchings of the bridges separating the pyrrole rings
1595	198	2.92×10^{-13}	N-H and C-H bending motions of the pyrrole rings and C-C stretchings of the bridges separating the pyrrole rings
1608	199	2.15×10^{-13}	C-C stretchings and C-H bendings of the pyrrole rings

Table VII.1. Frequency (cm^{-1}), potential (mV), intensity (arb. units), and description of the vibrational normal modes dominating the IET spectrum of **S1** calculated at the B3LYP/6-31G(d) level of approximation.

Frequency	Potential	Intensity	Mode description
1516	188	9.69×10^{-14}	C-C stretchings of the bridges separating the pyrrole rings and C-C stretchings of the pyrrole rings
1555	193	1.24×10^{-13}	C-C stretchings and C-H bendings of the pyrrole rings
1587	197	2.20×10^{-13}	C-C stretchings of the bridges separating the pyrrole rings
1595	198	2.27×10^{-13}	N-H and C-H bending motions of the pyrrole rings and C-C stretchings of the bridges separating the pyrrole rings
1608	199	1.76×10^{-13}	C-C stretchings and C-H bendings of the pyrrole rings

Table VII.2. Frequency (cm^{-1}), potential (mV), and description of the vibrational normal modes dominating the IET spectrum of **S2** calculated at the B3LYP/6-31G(d) level of approximation.

For both compounds, the dominant IET signatures appear at similar frequencies in the 1515-1610 cm^{-1} (188-200 mV) range, and are associated to five vibrational modes reported in Tables (VII.1) and (VII.2). The two major peaks observed in the spectrum corresponding to **S1** (**S2**) are illustrated in Fig. (VII.3) (Fig. (VII.4)) and emerge at 1589 cm^{-1} (1587 cm^{-1}) and 1595 cm^{-1} (1595 cm^{-1}). The first pair of modes is characterized by C-C stretchings of the bridges separating the pyrrole rings, while the second is associated to N-H and C-H bending motions of the pyrrole rings together with C-C stretchings of the bridges separating the pyrrole rings.

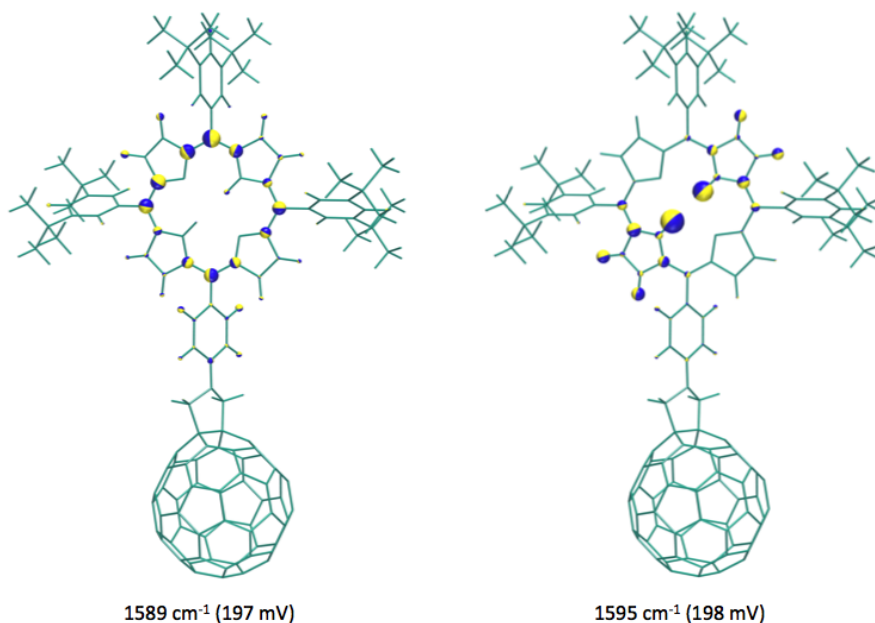


Fig. VII.3. Sketch of the two dominant IET vibrational modes of **S1** calculated at the B3LYP/6-31G(d) level of approximation.

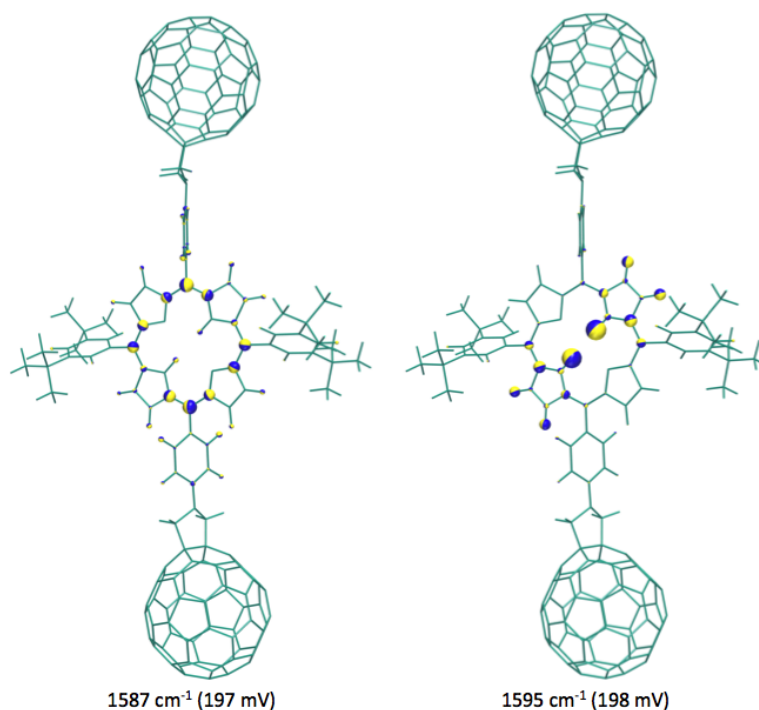


Fig. VII.4. Sketch of the two dominant IET vibrational modes of **S2** calculated at the B3LYP/6-31G(d) level of approximation.

Moreover, the peaks found at 1555 cm^{-1} and 1608 cm^{-1} on both spectra also involve atomic motions localized on the porphyrin moiety, and more particularly C-C stretchings and C-H bendings of the pyrrole rings as sketched in Figs. (VII.5) and (VII.6).

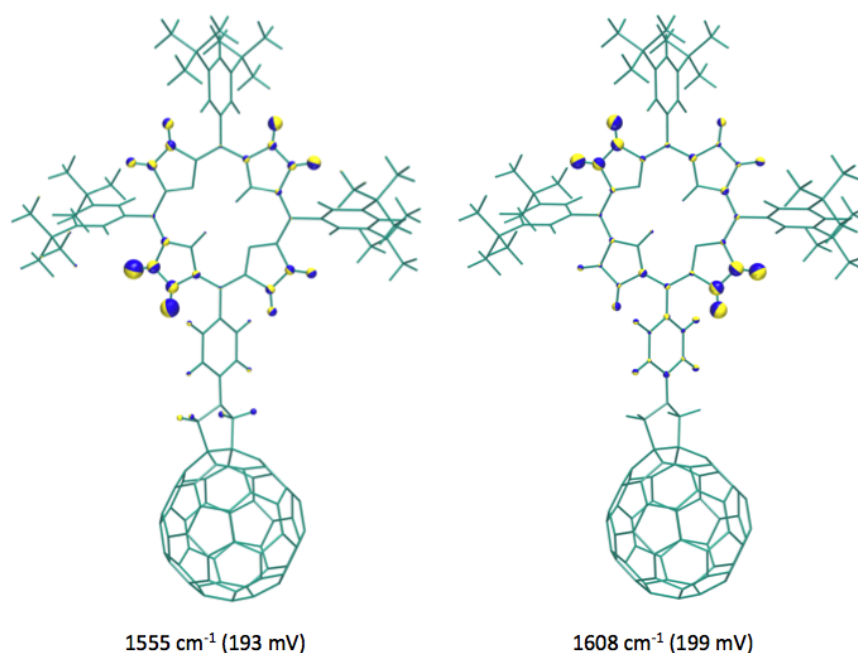


Fig. VII.5. Sketch of active IET vibrational modes of **S1** calculated at the B3LYP/6-31G(d) level of approximation.

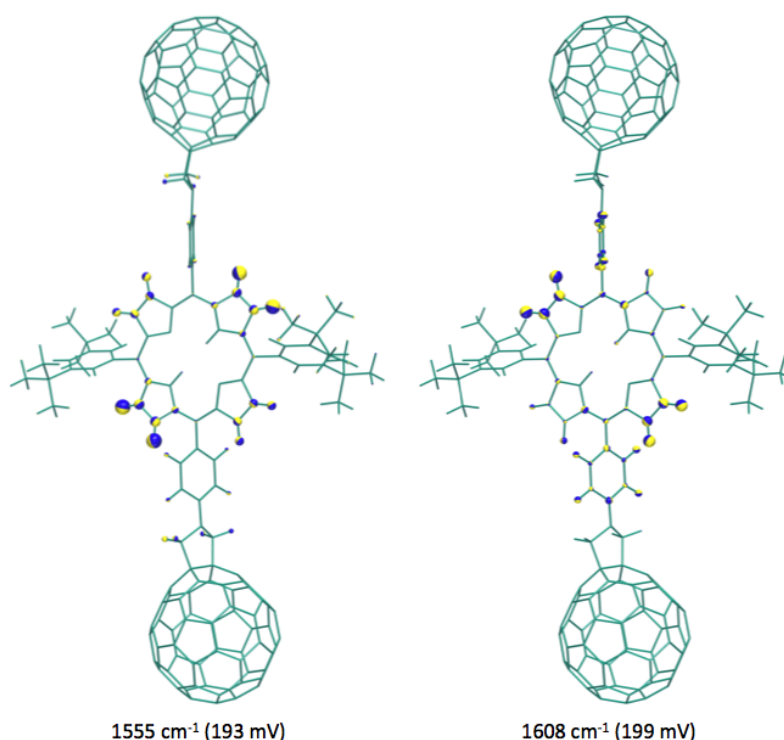


Fig. VII.6. Sketch of active IET vibrational modes of **S2** calculated at the B3LYP/6-31G(d) level of approximation.

Considering the dominant signatures, the largest variation of relative intensity is observed for the peak appearing at 1517 cm^{-1} (1516 cm^{-1}) when considering **S1** (**S2**) and can be explained by a

change of the nature of the vibrational mode, as illustrated in Fig. (VII.7). Indeed, the smaller contribution of the peak observed in the case of **S1** can be attributed to a decrease of the amplitude of the C-C stretching motions of the bridges separating the pyrrole rings with respect to **S2**, while the contribution of motions localized on tert-butyl groups becomes significant. This brings additional evidence that motions localized on the porphyrin moiety have a direct impact on the IET activity, while none of the IET peaks (even the less intense) is associated to atomic motions localized on the C₆₀ moieties.

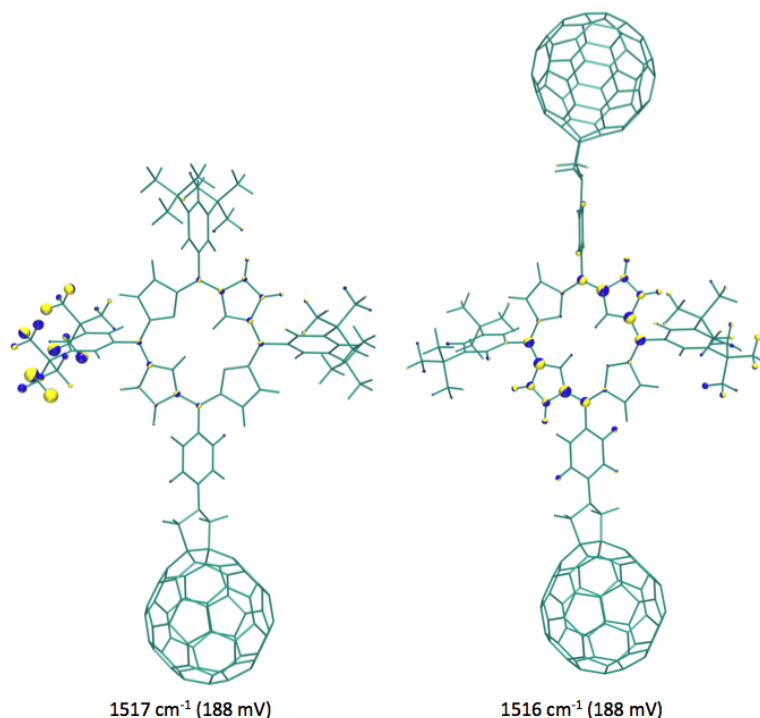


Fig. VII.7. Sketch of the two vibrational modes of **S1** (left) and **S2** presenting the largest variation of intensity calculated at the B3LYP/6-31G(d) level of approximation.

Finally, concerning the less intense peaks the largest variations of intensity are observed for modes of **S1** (**S2**) appearing at 639 cm⁻¹ (640 cm⁻¹) and 1175 cm⁻¹ (1170 cm⁻¹). In the first case, it is not associated to a change of the nature of the vibrational modes [Fig. (VII.8)], while for the second the intensity decrease observed for the **S2** derivative is attributed to a smaller amplitude of the motions localized on the tert-butyl groups, as sketched in Fig. (VII.8).

A further extension of this preliminary study would be to describe explicitly the gold electrodes, what may require a reduction of the size of the system in order to reduce the computational needs. This could be achieved by replacing the tert-butyl groups by smaller substituents. Note that in the frame of our collaborative work, these structures and spectra are open to comparisons with experiment.

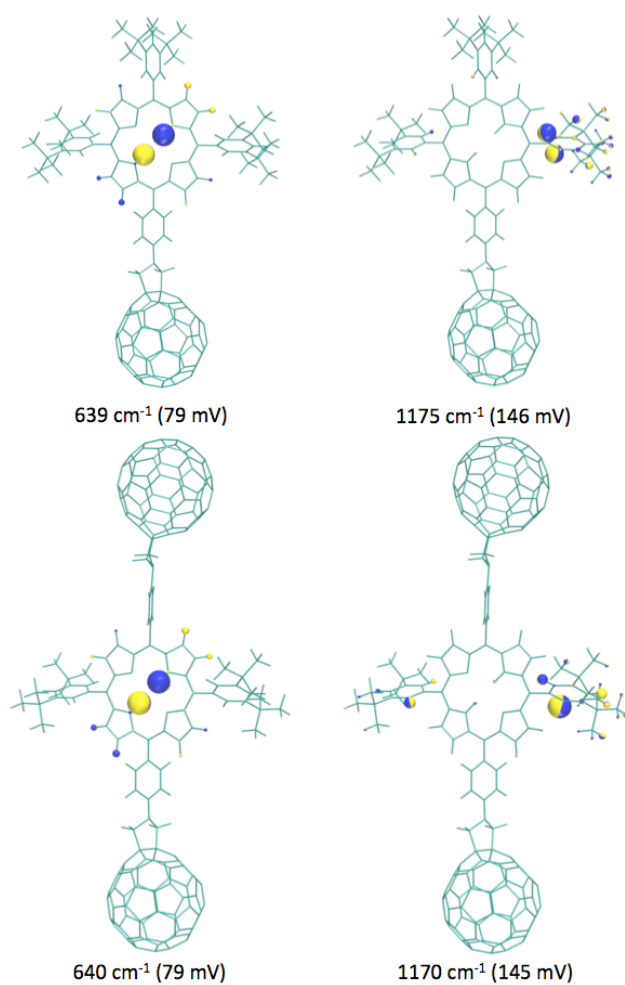


Fig. VII.8. Sketch of the two vibrational modes of **S1** (top) and **S2** (bottom) characterized by significant variations of relative intensities, calculated at the B3LYP/6-31G(d) level of approximation.

Conclusions and outlooks

VIII. Conclusions and outlooks

This thesis has aimed at predicting, determining and interpreting the inelastic electron tunneling responses of molecular junctions of interest for molecular electronics. All the IET simulations carried out on these junctions, constituted of a single molecule sandwiched between gold electrodes, have been performed by using the Quantum Chemistry for Molecular Electronics (QCME) code that implements a generalized quantum chemical model for simulating the IET responses of molecular systems. One original aspect of our approach consists in rationalizing the results provided by this code via the sophisticated graphical support of the Pyvib2 program, bringing new perspectives for future analytical applications of the IET technique.

Successive investigations have been carried out, considering single-molecular junctions of increasing size and complexity. The IET technique is known for being sensitive to many junction parameters, such as the molecular conformation, the orientation of the molecule with respect to the metal electrodes, the molecule-electrode distance and the nature of molecule-electrode anchoring. Our investigations have therefore demonstrated the important role of IETS as an analytical tool to provide essential information about the structure and nature of a given molecular junction.

The first study has focused on the selection of an appropriate level of calculation to evaluate IET responses, providing a good compromise between accuracy and computational needs. This preliminary work is justified by the lack of information available in the literature. The impact of the atomic basis set and of the exchange-correlation (XC) functional on the inelastic electron tunnelling (IET) spectra have been investigated by considering the prototypical 1,4-benzenedithiol molecule. We have first noticed that the basis set effects on the IET characteristics are larger than those of the XC functional. We observed that the cc-pVTZ, cc-pVQZ, and aug-cc-pVDZ basis sets provide consistent IET intensities, and that the cc-pVTZ basis set offers the best compromise between accuracy and computational needs. As for the XC functional, B3LYP turned out to be suitable to predict the relative vibrational frequencies. The ability of the selected B3LYP/cc-pVTZ level of approximation to predict accurate relative vibrational frequencies has been supported by tackling the reliability of IR absorption spectra of our system. Indeed, provided a scaling factor is used, the root mean square error on the vibrational frequencies goes down to 18 cm^{-1} .

The second study has consisted in simulating and interpreting the Inelastic Electron Tunneling (IET) spectra of an anil molecule switching between an enol-imine (**E**) and a keto-amine (**K**) forms (via an intramolecular proton transfer). Despite the lack of IET experimental data, it represents a straight continuation of a previous study concerning their nonlinear optical switching behavior in the solid state. The interest of this work has been to assess the responses of such systems in view of practical application in the field of molecular electronics and constitutes a prerequisite step for future simulations and experimental measurements. We have considered each tautomeric form of the molecule in two situations: isolated and sandwiched between gold electrodes. We have shown that the IET spectra of the isolated molecules vary significantly as a function of the chemical functions characteristic of each tautomeric form. When considering the **E** and **K** forms of the molecule sandwiched between the gold electrodes, the dominant IET peaks appear at similar voltages but their intensities are clearly different. In addition, we have consistently observed the activity of vibrational modes involving atomic motions localized on moieties specific to each tautomeric form. Therefore, IET is an analytical technique suitable to the characterization of the molecular state of switches. This study also showed that, for all the investigated configurations, in-plane longitudinal atomic motions contribute significantly to the IET activity of vibrational modes and are thereby associated to the paths followed by the electrons as they tunnel through the molecular junctions.

The variation of the IET activity observed when adding the gold electrodes has motivated the investigation of the influence of the contact configuration, *i.e.* of the size and shape of the gold cluster modeling the electrodes. We have considered junctions based on three different hydrocarbons that have already been investigated experimentally (C_{11} , OPE and OPV) for which we have modulated the electrodes size and shape, the molecule-electrode distances and the nature of the anchoring group. Considering the C_{11} -based junctions, the variation of the molecular orientation and of the molecule-electrode distance allowed us to determine the structure presenting the best agreement with the experimental IET spectrum, highlighting the high sensitivity of the IET spectroscopy and its ability to identify the best configuration to match experimental data. Regarding the OPE and OPV drain-less structures, we have observed a weak influence of the shape of the source electrode on the IET activity, while the explicit description of the drain electrode affects significantly the IET responses and makes the choice of the source shape significant. A systematic feature in this case is the contribution of longitudinal C-S stretching to the major IET active peaks playing a key role in the modulation of the coupling between the molecule and the electrodes. We noticed that considering weak or strong molecule-electrode

couplings (*i.e.* implicit or explicit description of the drain electrode) is not always enough to match the experimental signatures in a satisfying way. This should lead to further simulations taking into account the asymmetry of the molecular junction, *i.e.* considering molecular junctions for which the source-molecule distance is different from the molecule-drain distance. As it was already evidenced in the study of anil derivatives, the IET spectroscopy is able to make the distinction between similar systems presenting small variations in their chemical functionalities and, in this case, allowed to differentiate thiol- and thiolate-terminated OPE and OPV structures. This result supports the idea that the IET technique is perfectly suitable for chemical analysis, in the same way as usual vibrational spectroscopies such as Infrared and Raman, requesting a proper rationalization of propensity rules that remains challenging.

We have then extended our simulations on larger systems, based at first on a single C₆₀ molecule sandwiched between two gold electrodes. In the same trend as the previous study on the C₁₁-based junction, we observed a strong sensitivity of the IET response towards structural parameters such as the nature of the anchoring moiety defined by the C₆₀ orientation and the C₆₀-electrode distance. Depending on the value of this distance, different natures of atomic motions involving the moieties making the contact between the C₆₀ and the electrodes contribute to the dominant IET peaks. For $d=2.0$ Å they are associated to longitudinal displacements while for the largest distance considered in this study ($d=4.0$ Å) they are related to C-C stretching motions. On the other hand, for an intermediate distance value ($d=2.8$ Å) the dominant signatures are not associated to the same atomic motions depending on the nature of the contact moiety. In particular, we found that the symmetric junction involving hexagon cycles as contact moieties allows to reproduce the major IET peak associated to the deformation of the C₆₀ molecule between a spherical and a prolate shape observed in experimental measurements. The rationalization of the sensitivity of the IET response with respect to the C₆₀ molecule-electrode distance has put in evidence a coherence between the changes in the HOMO topologies and the variations of the IET signatures. Indeed, when considering small C₆₀ molecule-electrode distances, the observation of isosurfaces localized at the interface between the C₆₀ and the electrodes is correlated to the dominant IET peaks involving longitudinal motions between the contact moieties and the electrodes, while for larger distances, the delocalization of the HOMO on the C₆₀ molecule is associated to the dominant contribution of the C-C stretching motions in the IET response. Taking into account the need to consider the asymmetry of the junction we pointed out in the study of the OPE-based junction, the best agreement with the experiment has been found for the molecular junction involving two hexagon rings facing the electrodes for which the distance

between the center of the hexagon and the hcp site of the source (drain) electrode is fixed to 2.8 Å (3.4 Å). Beside the intrinsic vibrational behavior of this system, our approach has proven to be helpful to detect the small structural variations originating from the vicinity with the gold surfaces.

Within the frame of the ARC proposal TINTIN, we have finally extended our investigations to two C₆₀-porphyrin based molecules for which we have implicitly considered the gold surfaces due to the heavy computational requirements. The dominant signatures are associated to C-C stretching localized on the bridges between the pyrrole rings and to N-H bending motions. In order to decrease the computational needs, an alternative could be to replace the tert-butyl groups with smaller substituents and then allow to consider explicitly the gold surfaces in the IET simulation. Such investigation of the IET spectra of very large systems (constituted of 216 and 258 atoms) within a quantum chemistry approach is new in the computational chemistry field and opens perspectives in our ability to predict the vibrational responses of large π -conjugated systems.

In the light of these results, we can propose a series of future developments. Given the ability of the IET spectroscopy to predict the influence of the adsorption configuration on the resulting spectrum, one can go further in investigating the effect of intermolecular interactions on the IET response, referring to the experimental situation where the molecules of interest are packed in the form of monolayers. Indeed, this would be interesting to bring an additional knowledge for the rationalization of experimental results and characterization of experimental configurations.

Even if we mainly focused our investigations on systems for which the molecule is anchored to the gold surfaces via thiol/thiolate groups, a natural development would be to investigate the influence of the chemical nature of the anchoring group on the IET response.

Another phenomenon to consider in our simulations concerns the potential polarization and deformation of the molecule due to the application of a bias voltage, what could lead to a better description of the dynamics of the IET process.

Finally, in spite of a long-running effort to rationalize the propensity rules characteristic of the IET technique, it remains a recurring challenge because of the difficulty to understand the key factors modulating the IET activity such as the symmetry matching between the electronic states with the nuclear motions associated to the IET active vibrational modes. Such attempt must be verified by trial on a set of large and non-ideal systems to ensure their reliability when applied on systems of interest of similar complexity to those presented hereabove.