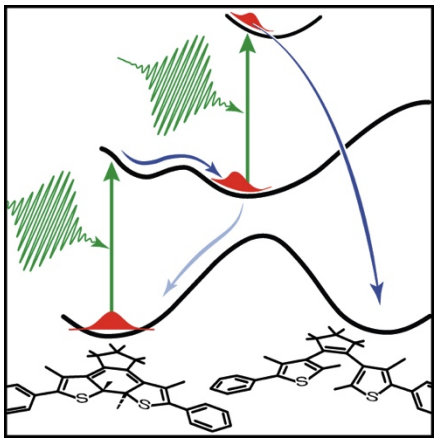
Two-Photon Excitation of Conjugated Molecules in Solution: Spectroscopy and Excited-State Dynamics

Chris Elles

72nd International Symposium on Molecular Spectroscopy

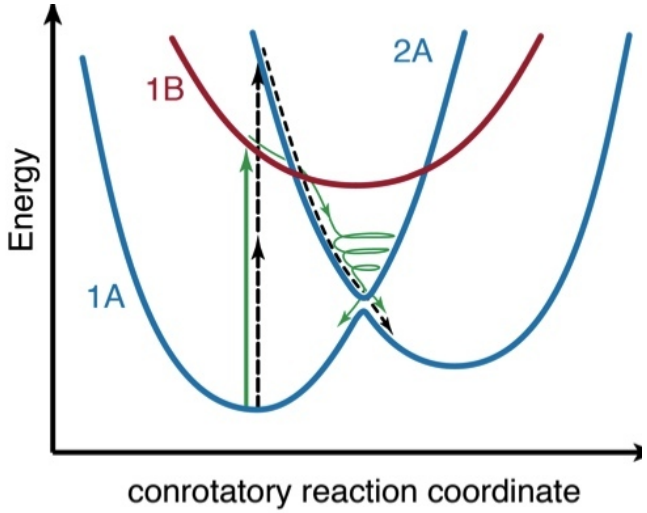
Multiple Potential Energy Surfaces

21 June 2017



Fundamental reaction dynamics

Dynamics of higher-lying excited states (above S_1)

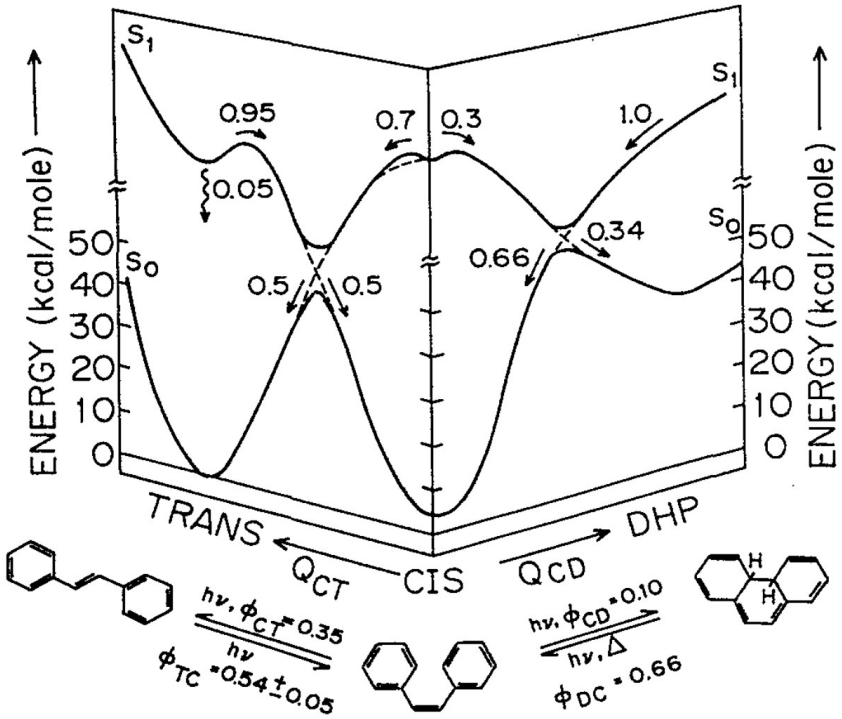


Challenges for experiment <u>and</u> theory:

- *ultrafast electronic relaxation,*
- *high density of states,*
- *multi-configurational and doubly-excited states (e.g. $\pi^*\pi^*$), etc.*

Excited-state dynamics of stilbene

Well-known excited-state dynamics, perfect model to explore higher-lying states!



Sension, *et al.*, *JCP*, **98**, 6291(1993)

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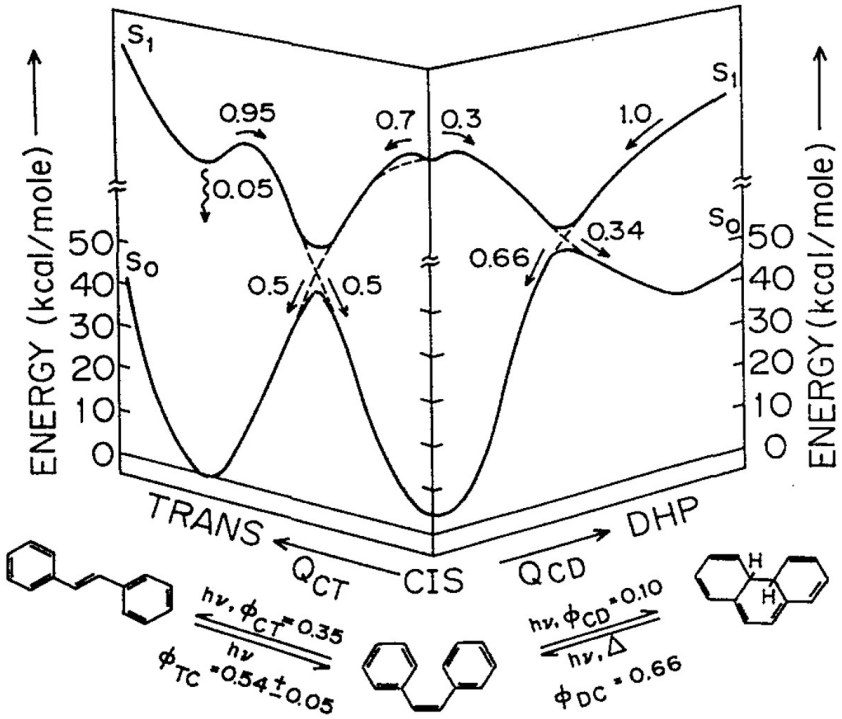

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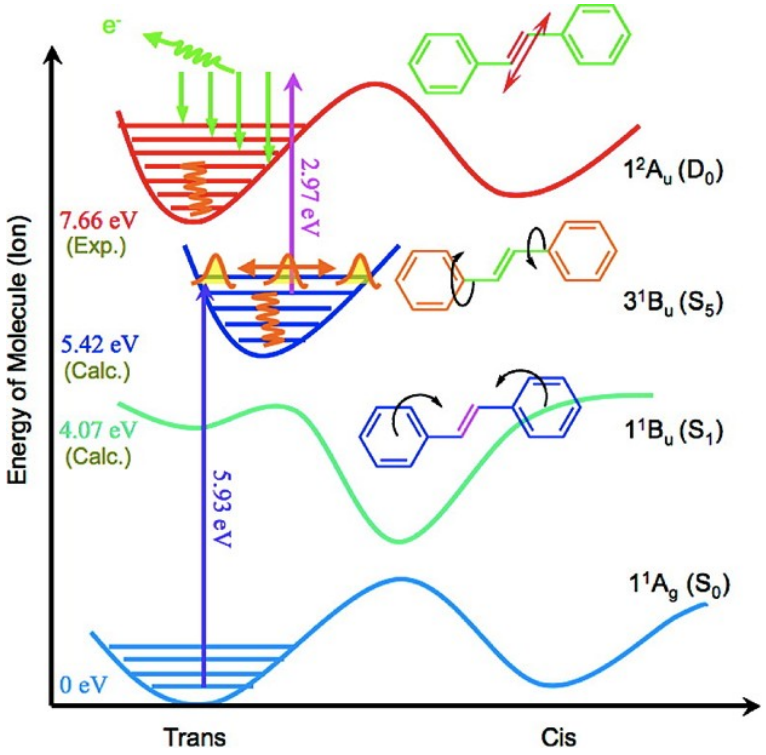
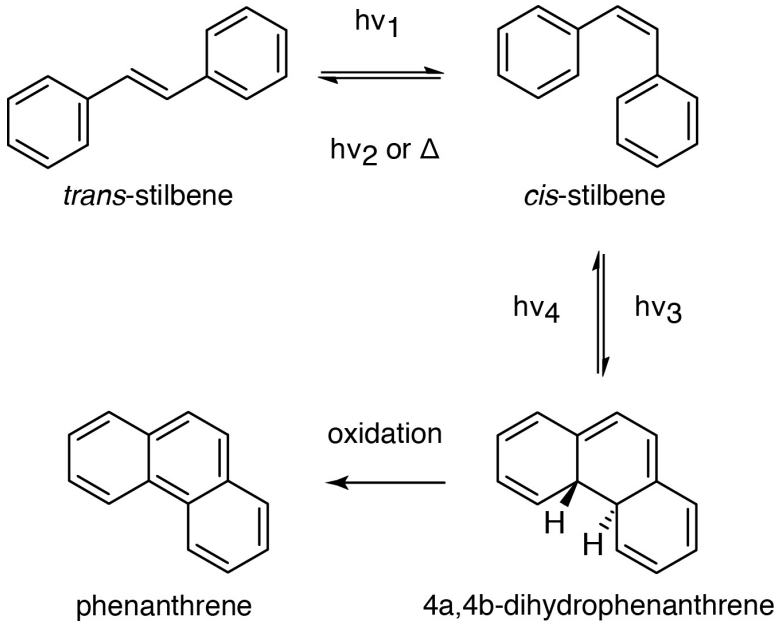


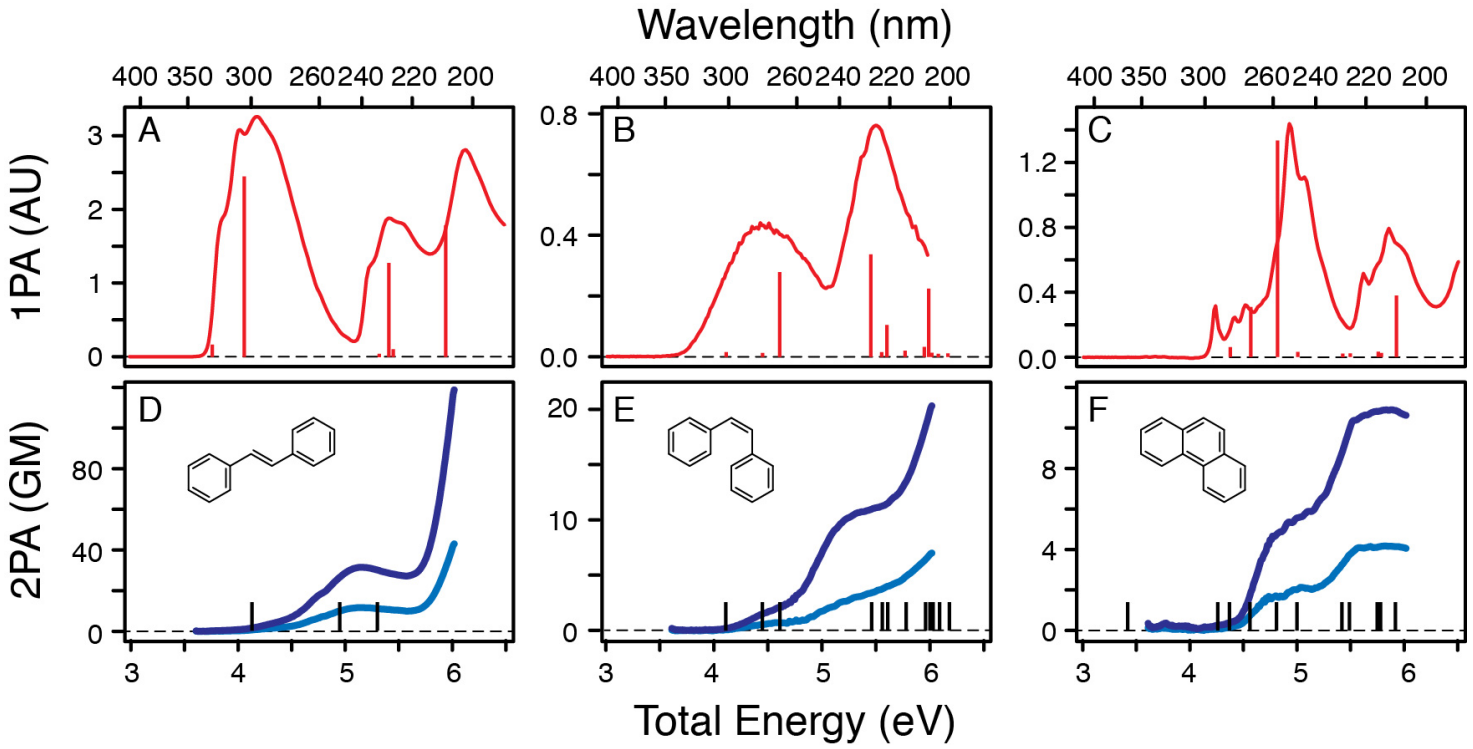
Bao and Weber, *JACS,* **133**, 4164 (2011)

– Gas phase photoelectron spectroscopy

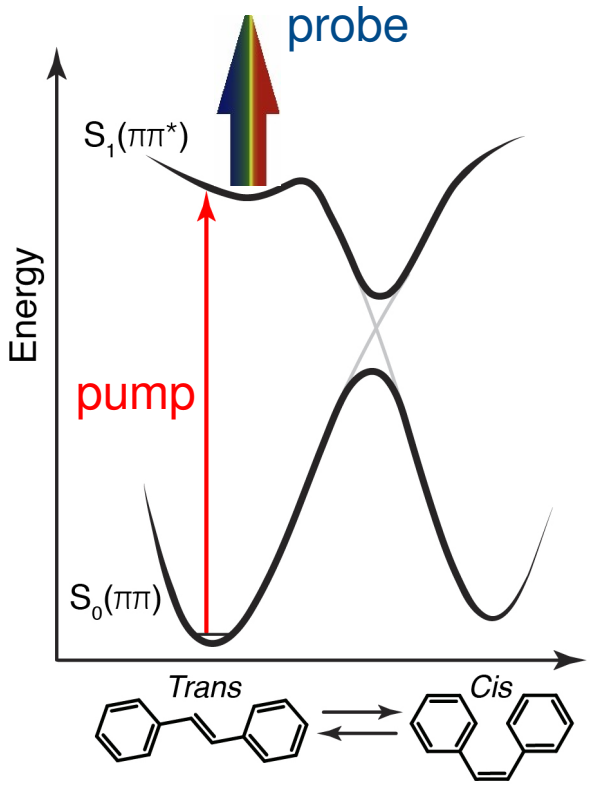
Reactions of stilbene(s)

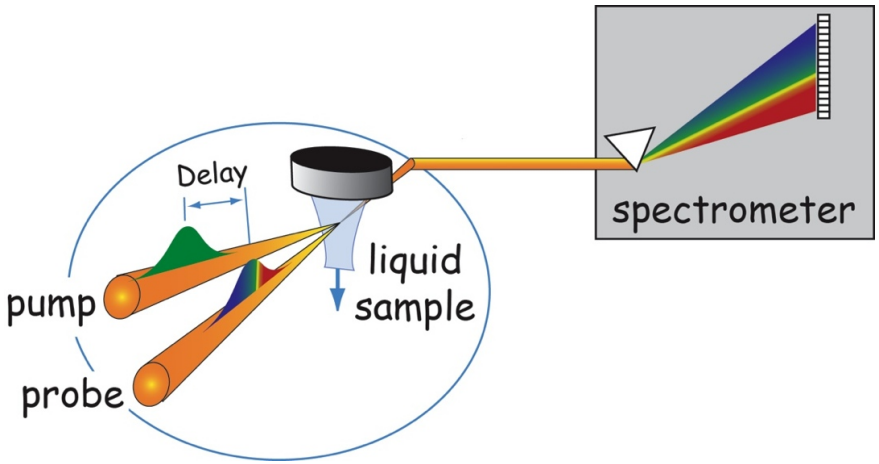


Spectroscopy of stilbene(s)



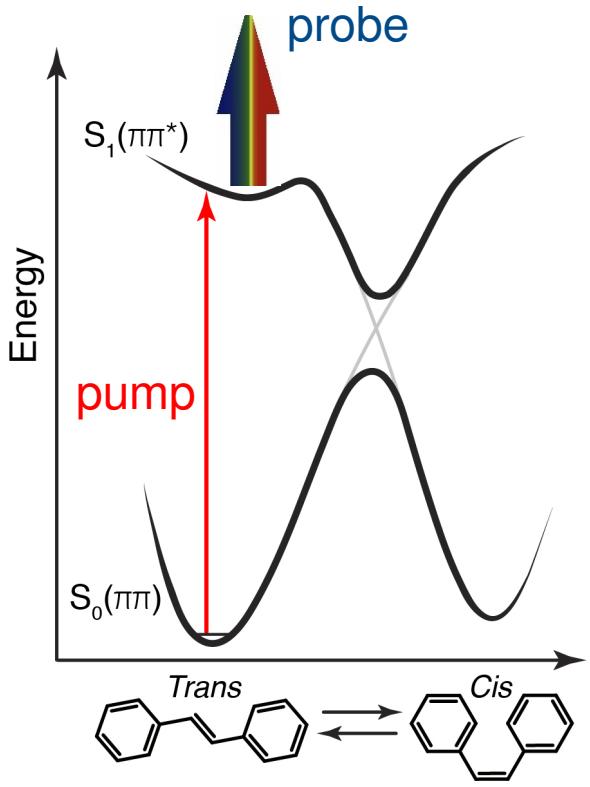
Dynamics of *trans*-stilbene: Transient absorption spectroscopy

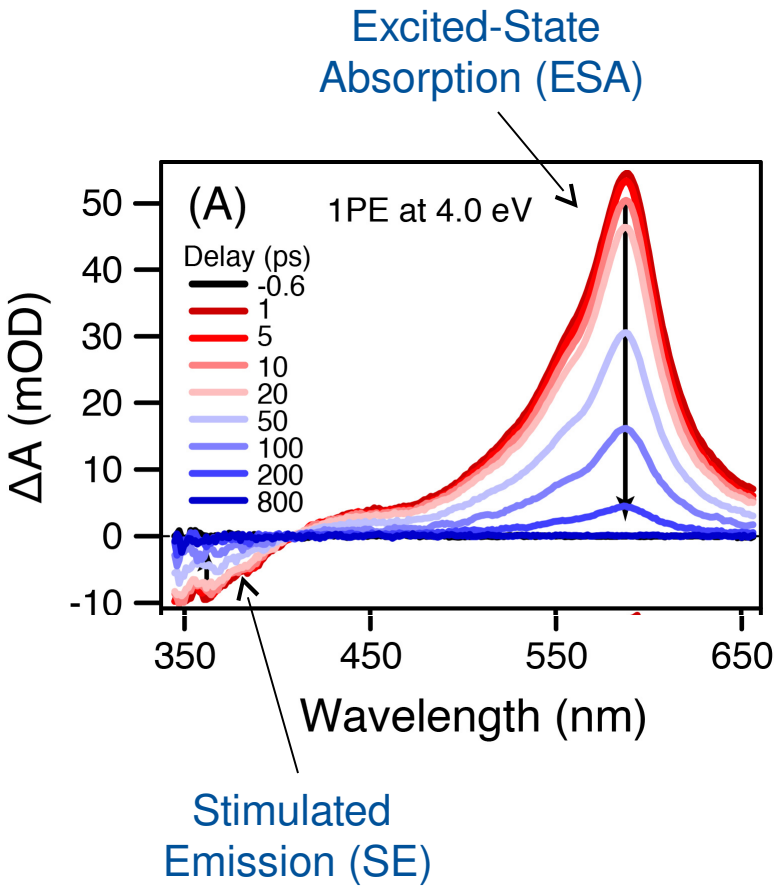




Excited state dynamics of *trans*-stilbene

Amanda Houk

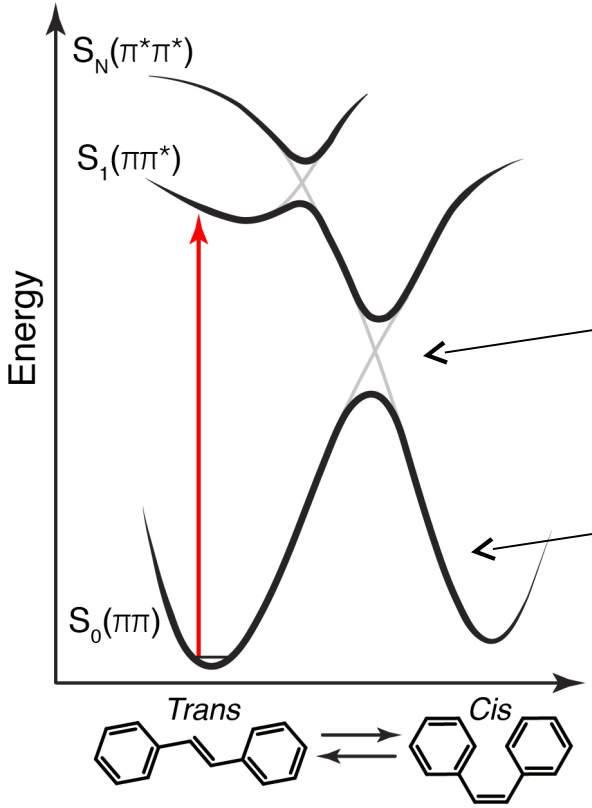




– *Barrier crossing in excited state (torsion) within ~80 ps*

– *Fast $S_1 \rightarrow S_0$ relaxation with 1:1 branching ratio*

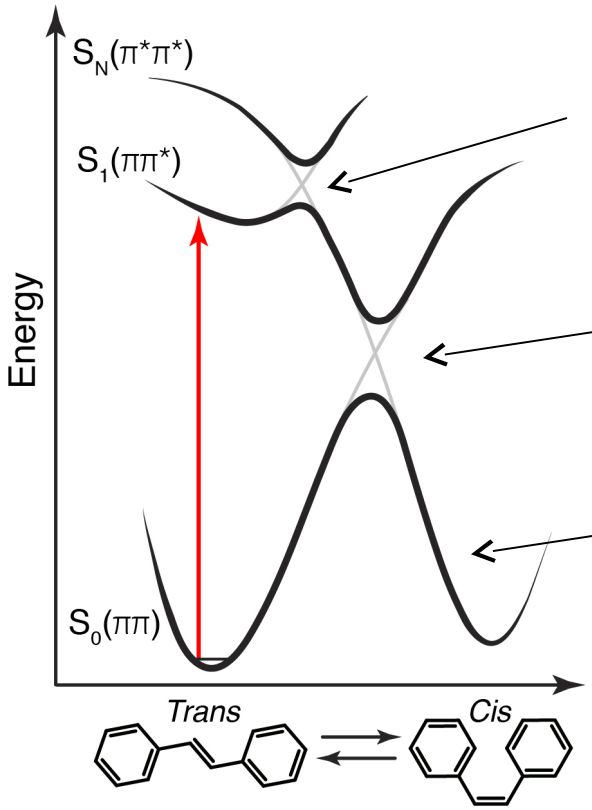
Dynamics of *trans*-stilbene: Two-photon excitation



Conical intersection (CI) at perpendicular geometry

π*π* excited state configuration correlates to ππ ground state!

Dynamics of *trans*-stilbene: Two-photon excitation



Role of S_N–S_1 CI?

Conical intersection (CI) at perpendicular geometry

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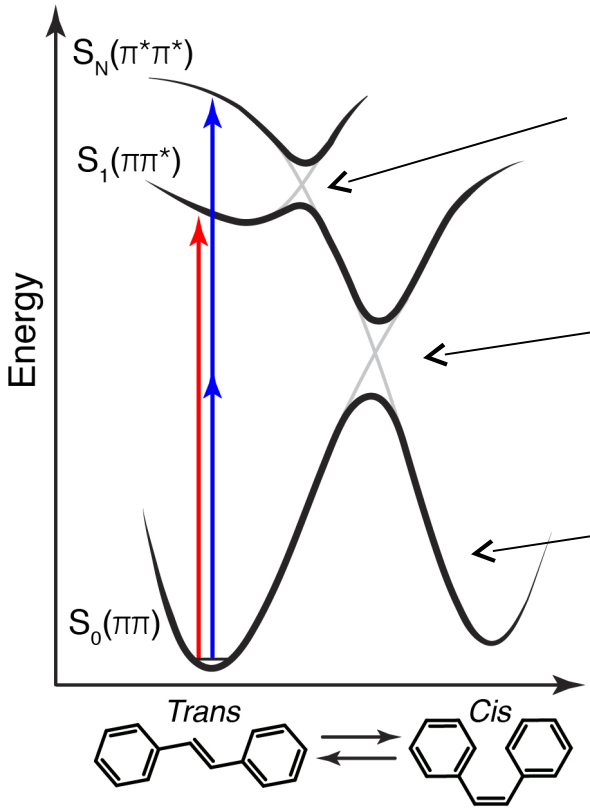
Dynamics of *trans*-stilbene: Two-photon excitation



Role of S_N–S_1 CI?

Conical intersection (CI) at perpendicular geometry

π*π* excited state configuration correlates to ππ ground state!

Parity selection rules (C_{2h}) :

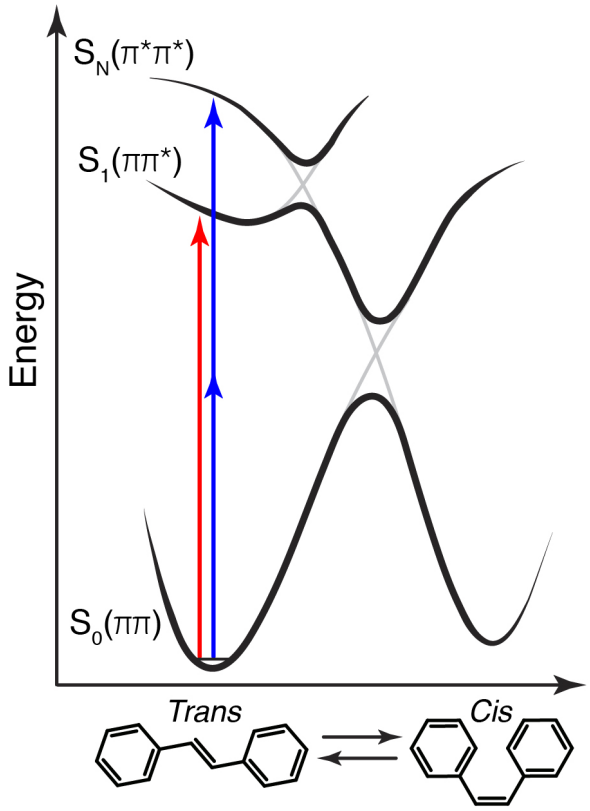
ππ → π*π* is 1PA forbidden, 2PA allowed

ππ → π π* is 1PA allowed, 2PA forbidden

Orlandi, *et al.*, *JACS*, **101**, 3492 (1979)

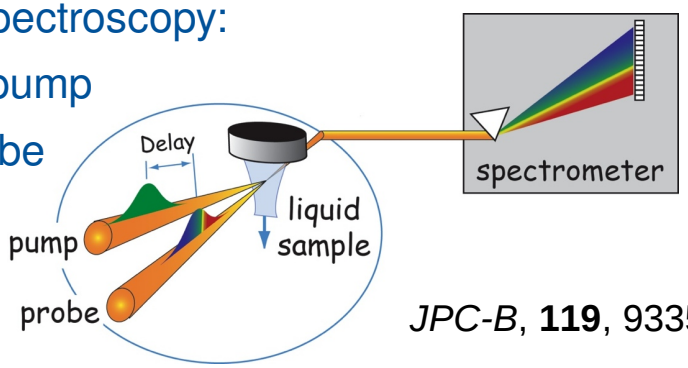
Fuke, *et al.*, *Chem. Phys. Lett.*, **74**, 546 (1980)

Two-photon absorption spectroscopy of *trans*-stilbene

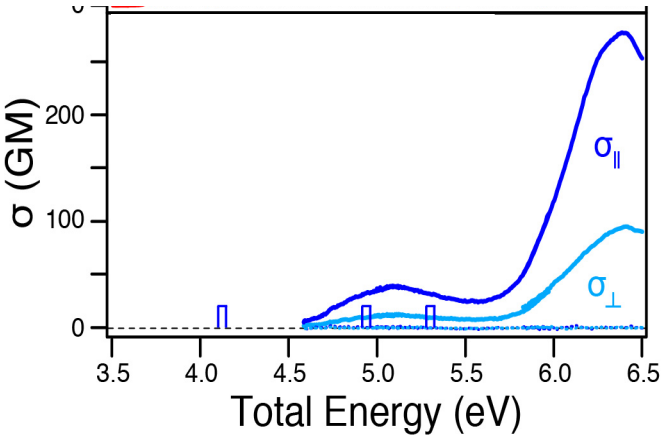


Broadband 2PA spectroscopy:

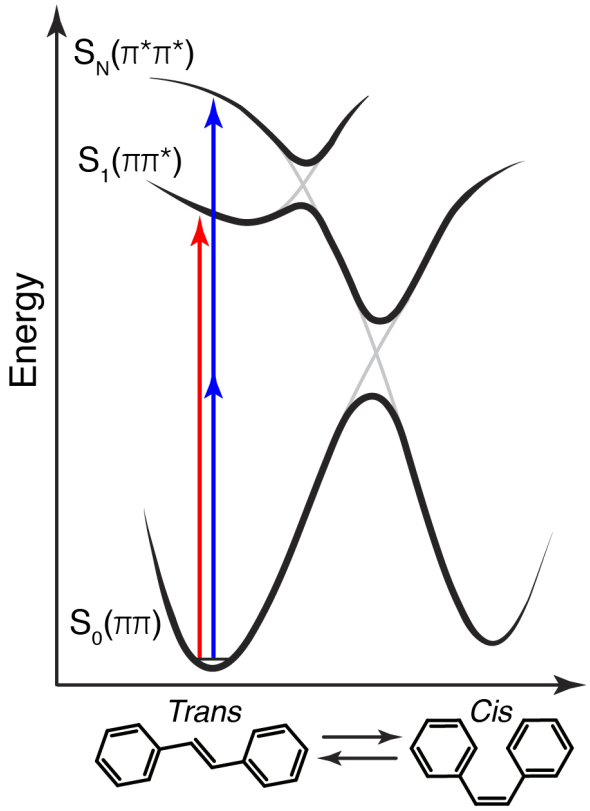
- Non-resonant pump
- Broadband probe

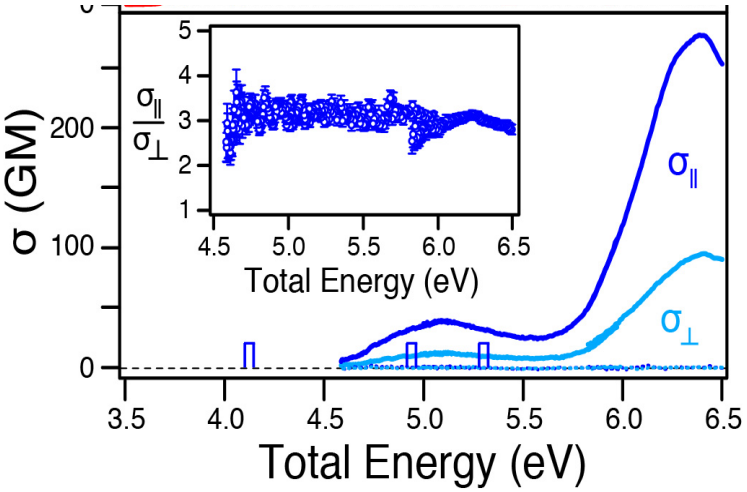


JPC-B, **119**, 9335 (2015)



Two-photon absorption spectroscopy of *trans*-stilbene

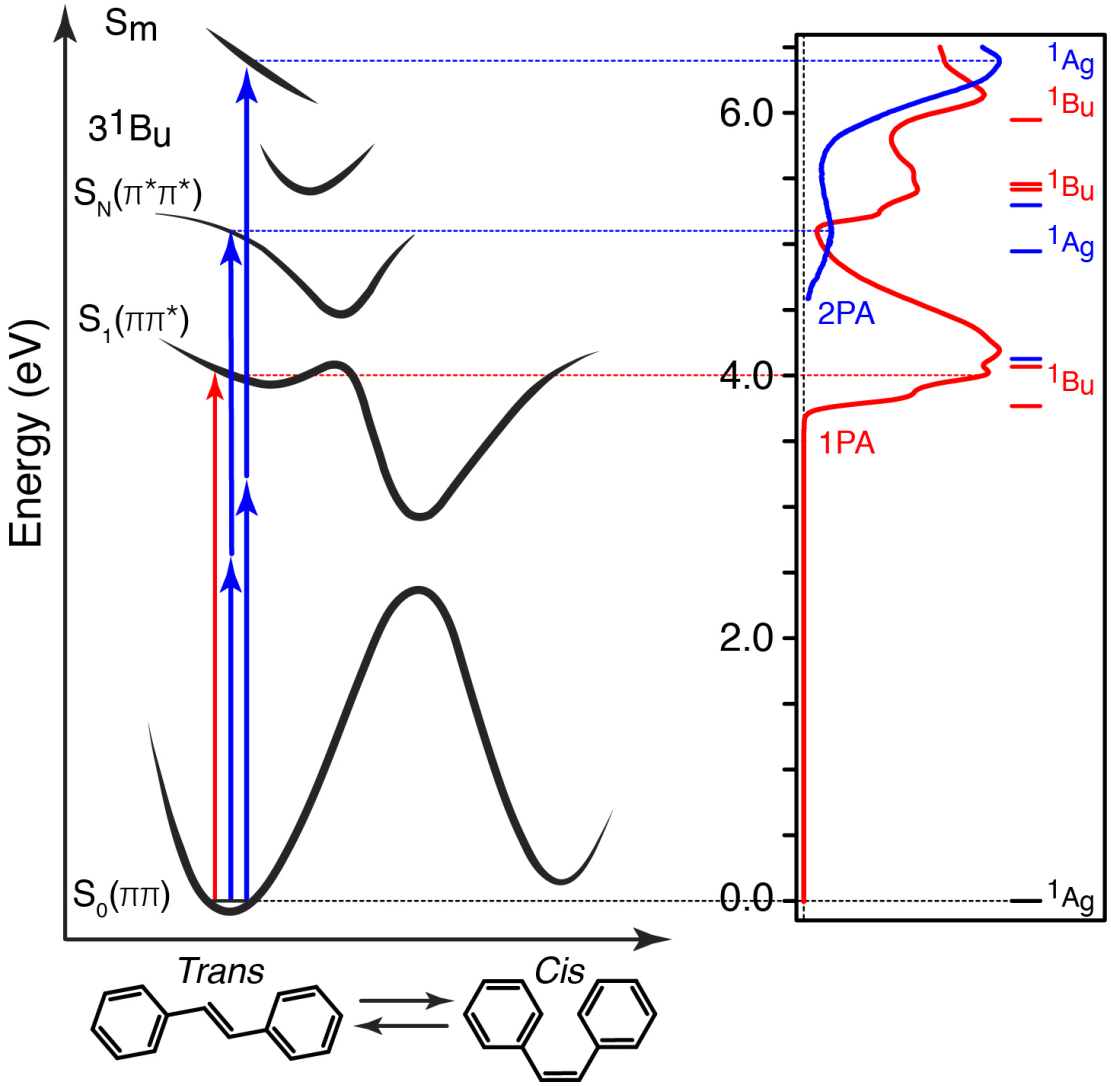




Advantages of broadband 2PA method:

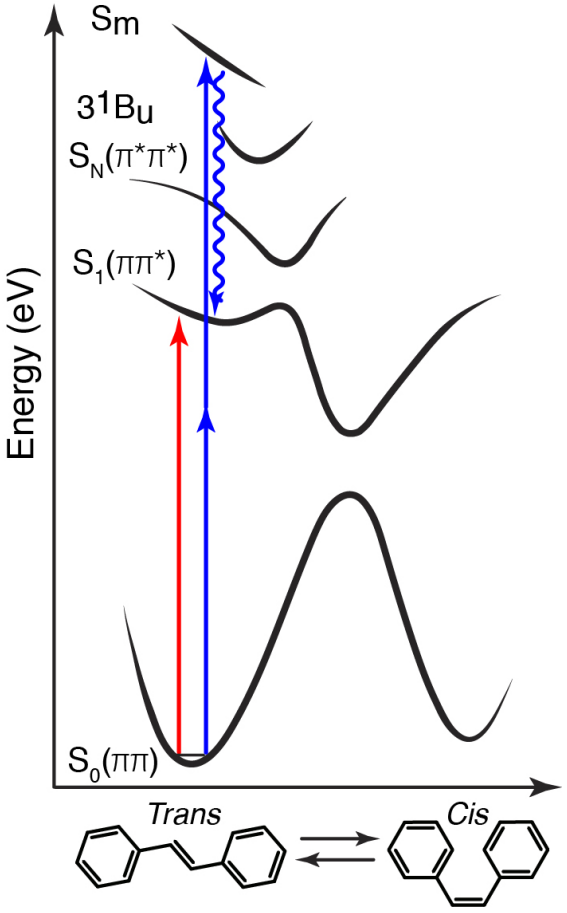
- *direct two-photon absorption*
- *continuous*
- *polarization anisotropy*

Two-photon absorption spectroscopy of *trans*-stilbene

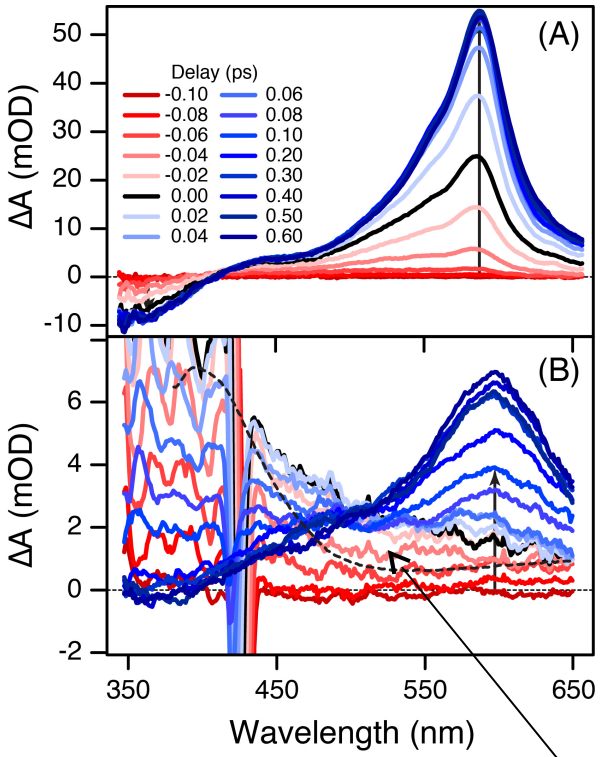


Houk, *et al.*, *JPC-B*, **119**, 9335 (2015)

Dynamics of *trans*-stilbene: Two-photon excitation



First 500 fs of transient absorption…



1PE at 4.0 eV

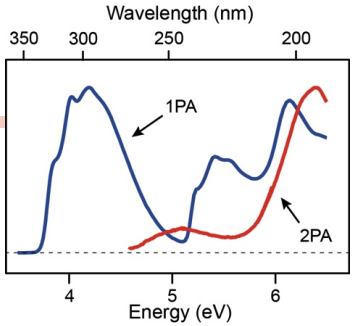
2PE at 6.5 eV

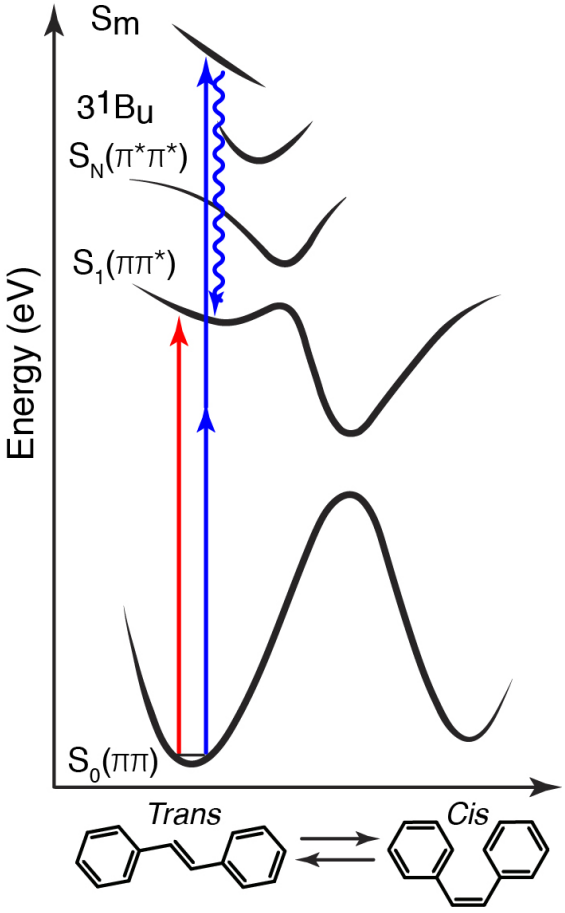
Excited state absorption (S_N)

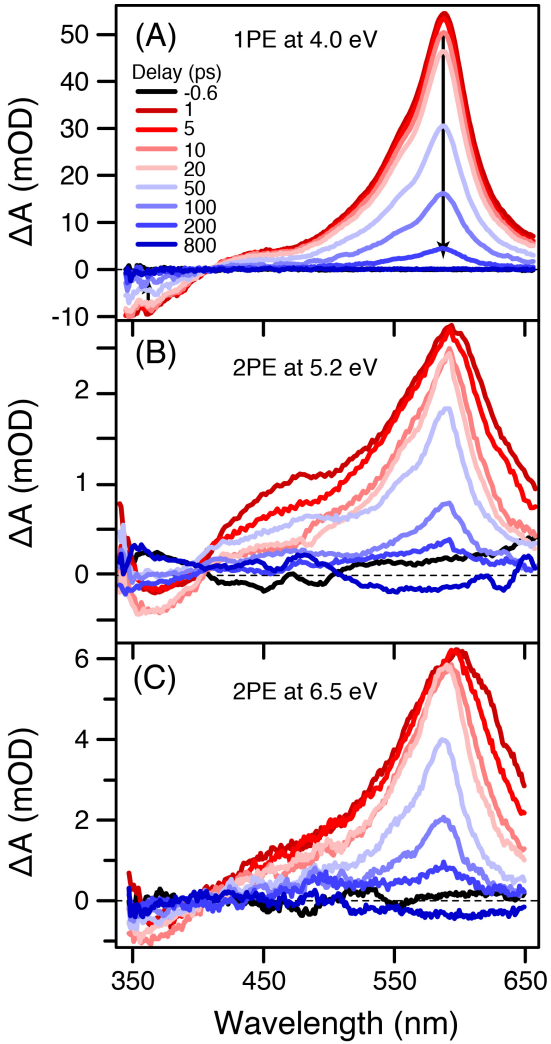
Decays in ~100 fs!

Houk, *et al.*, *JPC-B*, **119**, 9335 (2015)

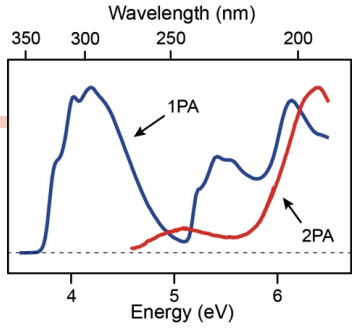
Dynamics of *trans*-stilbene: Two-photon excitation



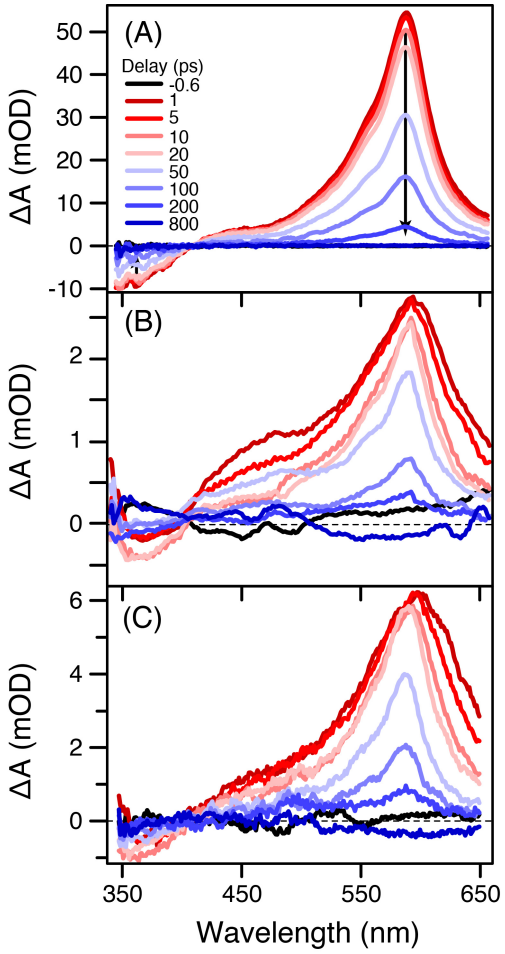




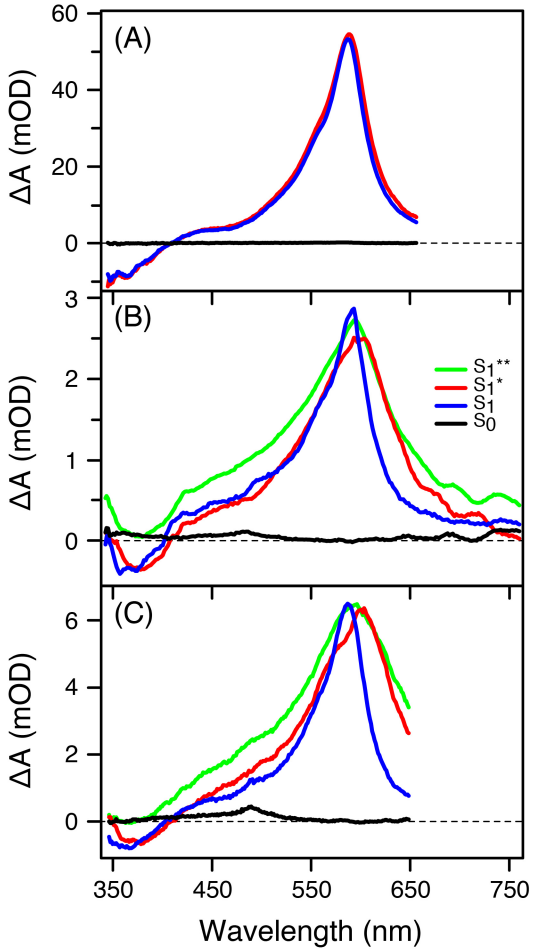
Dynamics of *trans*-stilbene: Two-photon excitation



Picosecond evolution:



Species-associated spectra (SAS)



1PE at 4.0 eV

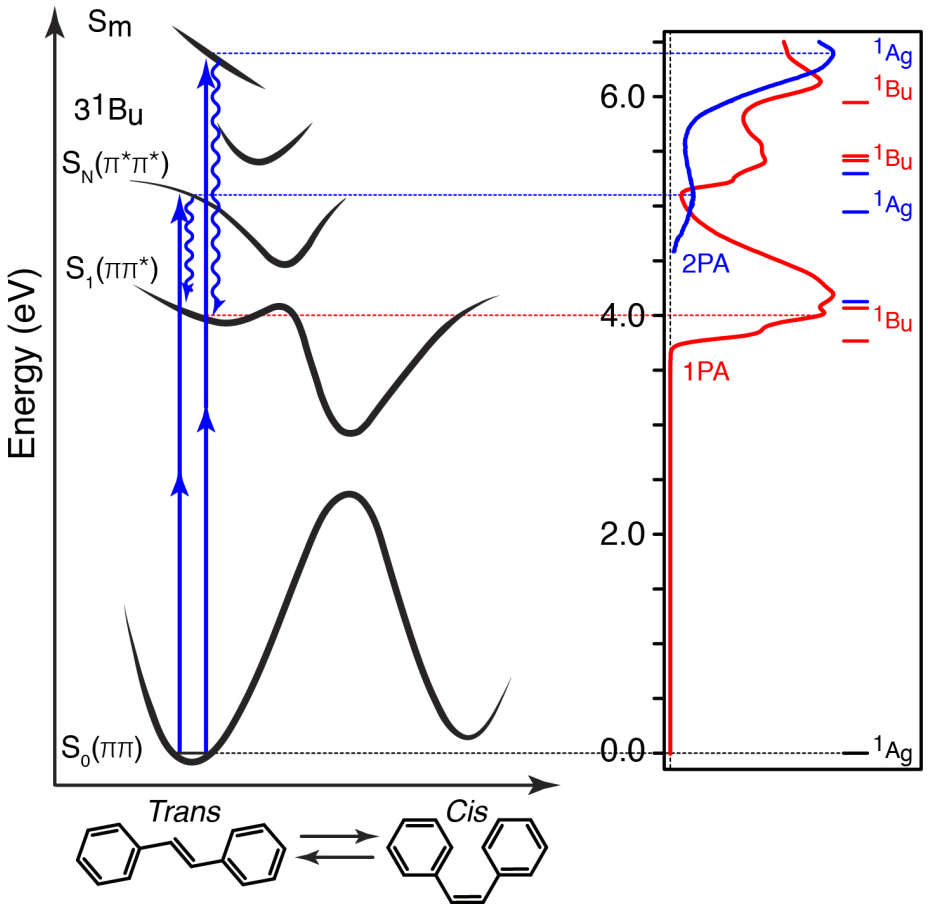
$S_1^* \rightarrow S_1 \rightarrow S_0$

2PE at 5.2 and 6.5 eV

$S_1^{**} \rightarrow S_1^* \rightarrow S_1 \rightarrow S_0$

τ_{IVR} ~ 2 ps τ_{VC} ~ 8 ps τ_{IC} ~ 80 ps

Summary of *trans*-stilbene dynamics



– Electronic relaxation $S_n \rightarrow S_1$ in ~100 fs

– Rapid dissipation of excess vibr. energy (up to ~180 cm^{-1} per mode!)

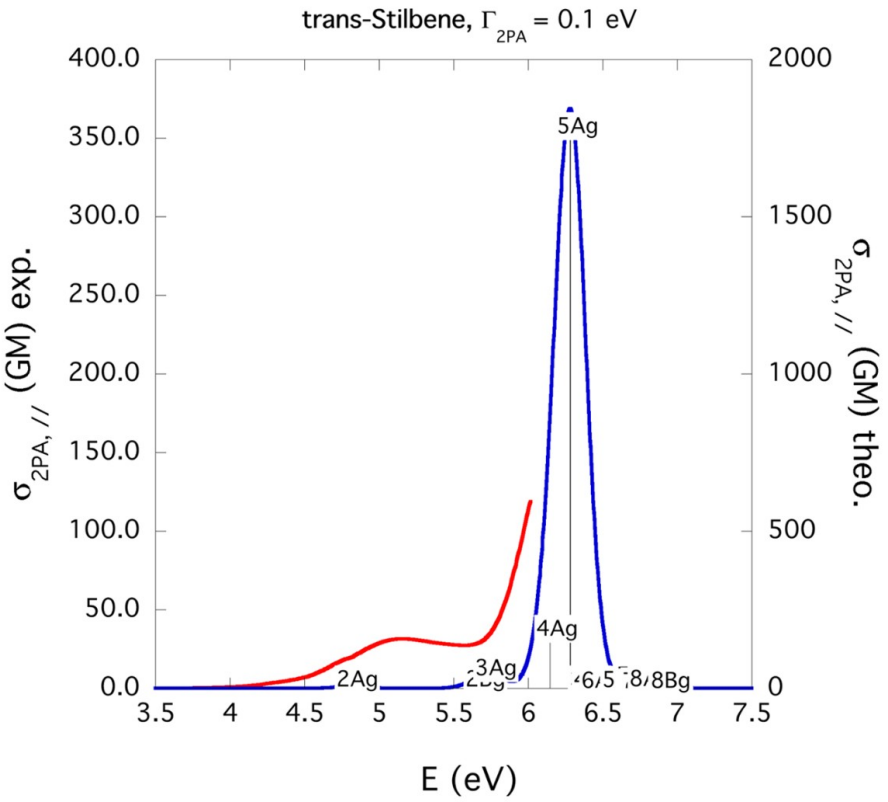
– **Excess energy does not efficiently couple into torsional coordinate!**

– *Minimum energy path of S_1 is key!*

Houk, *et al.*, *JPC-B*, **119**, 9335 (2015)

Two-photon absorption spectroscopy

Can we rationalize the spectrum with gas-phase calculations?



EOM-EE-CCSD/
d-aug(-d)-cc-pVDZ

***Anna Krylov** (USC)*

Marc de Wergifosse

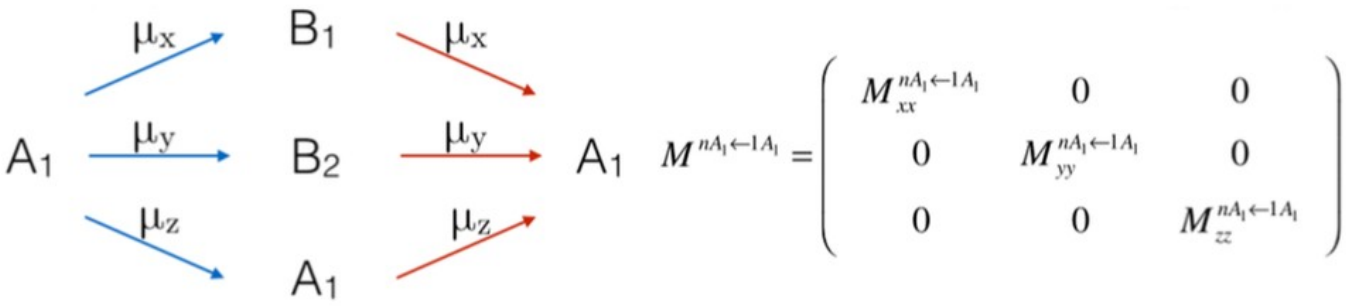
De Wergifosse, *et al.*, *JCP*, **146**, 144305 (2017)
De Wergifosse, *et al.*, *JCP*, **146**, 174102 (2017)

Two-photon absorption spectroscopy

Can we rationalize the spectrum with gas-phase calculations?

Sum over states (transition to *k*):

$$M_{bc}^{k\leftarrow 0} = -\sum_{n}\left(\frac{\langle k|\hat{\mu}^{c}|n\rangle\langle n|\hat{\mu}^{b}|0\rangle}{\Omega_{n0}-\omega_{1}}+\frac{\langle k|\hat{\mu}^{b}|n\rangle\langle n|\hat{\mu}^{c}|0\rangle}{\Omega_{n0}-\omega_{2}}\right)$$

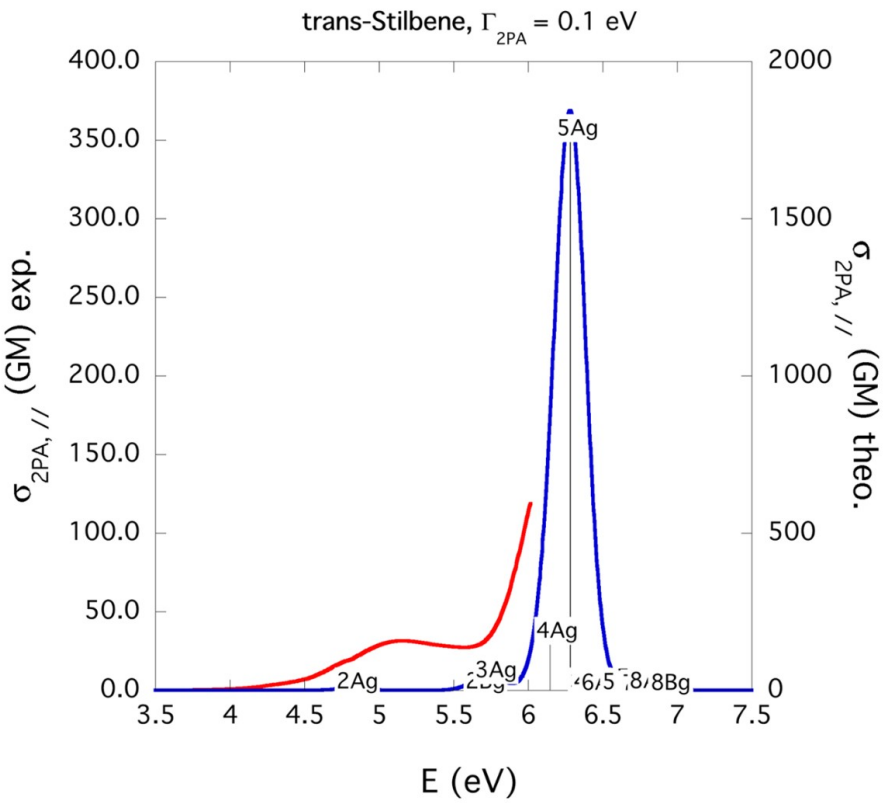


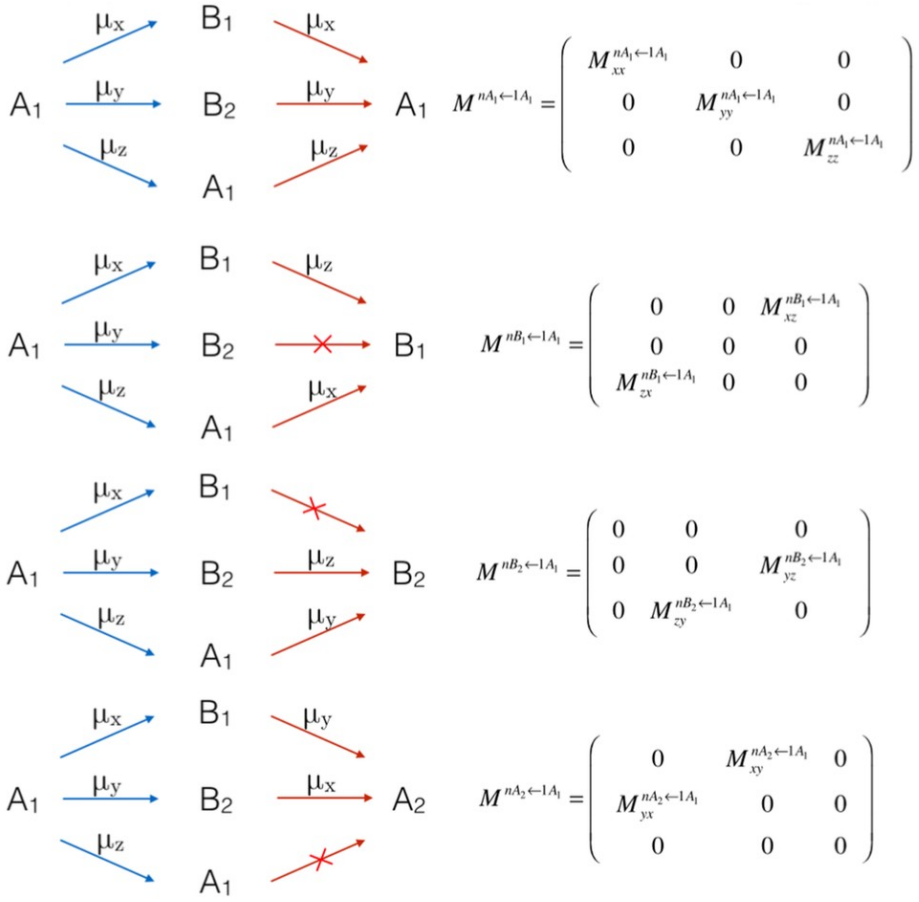
$$M^{nA_1\leftarrow 1A_1} = \begin{pmatrix} M_{xx}^{nA_1\leftarrow 1A_1} & 0 & 0 \\ 0 & M_{yy}^{nA_1\leftarrow 1A_1} & 0 \\ 0 & 0 & M_{zz}^{nA_1\leftarrow 1A_1} \end{pmatrix}$$

Two-photon absorption spectroscopy

Can we rationalize the spectrum with gas-phase calculations?

Spectrum is dominated by totally symmetric (A_1) transitions:





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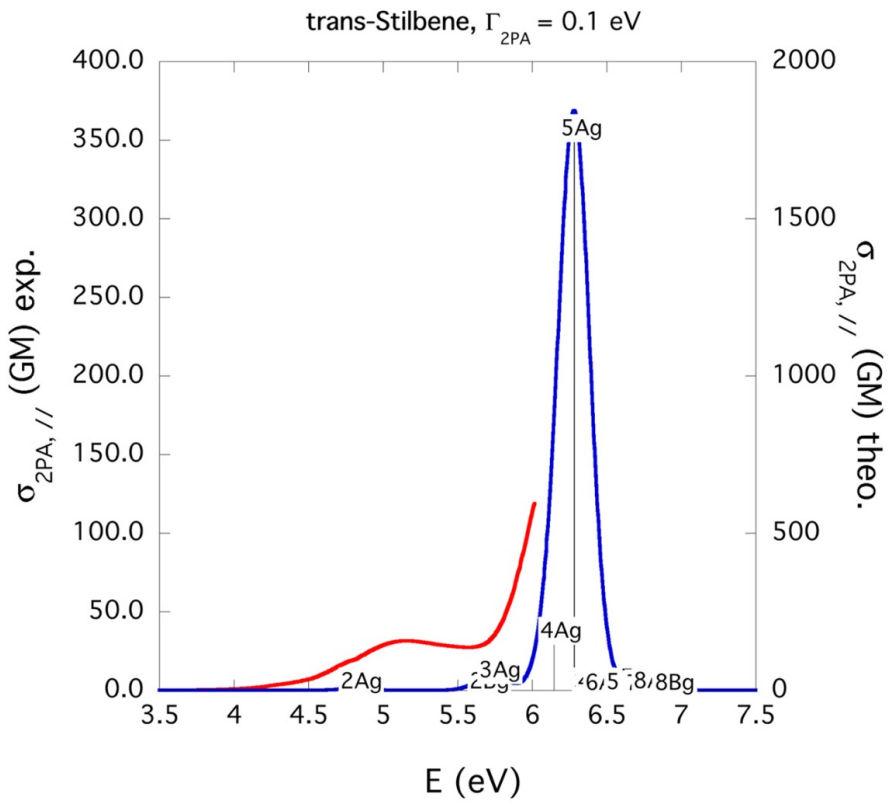
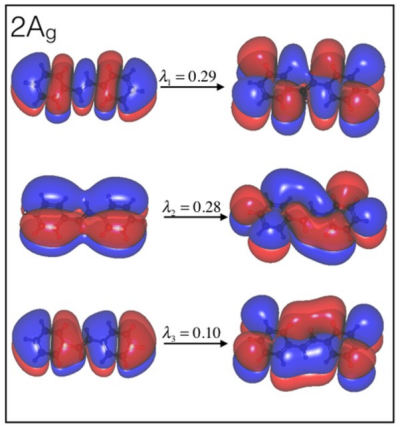
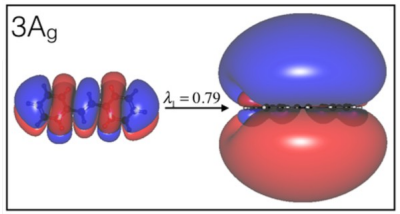
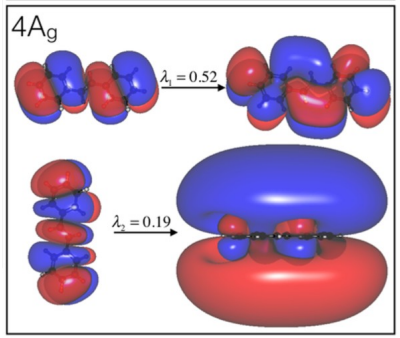
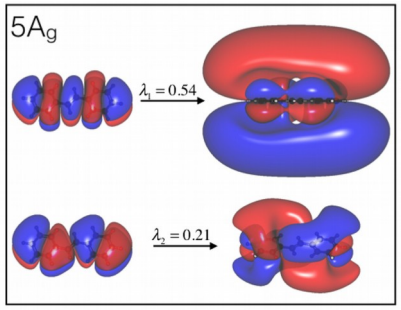


Rydberg transitions have highest intensity…





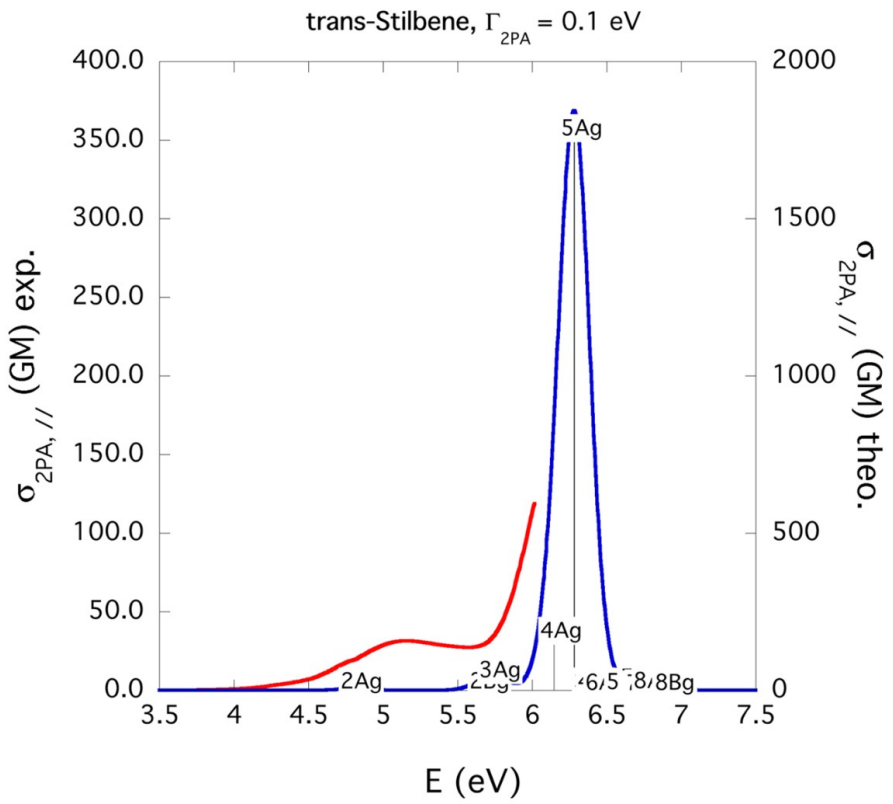




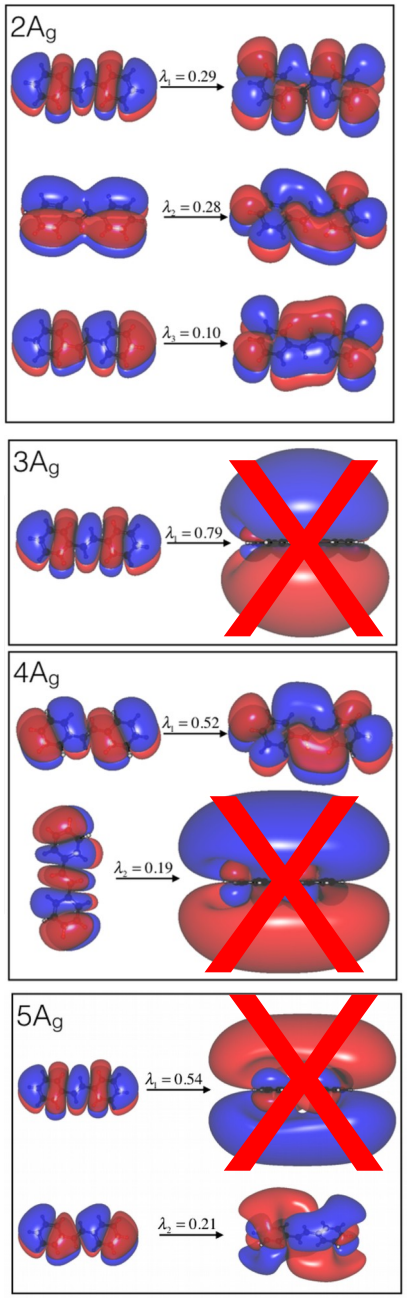
Two-photon absorption spectroscopy

Can we rationalize the spectrum with gas-phase calculations?

Spectrum is dominated by totally symmetric (A_1) transitions:



Rydberg transitions have highest intensity…
but no relevance in solution!



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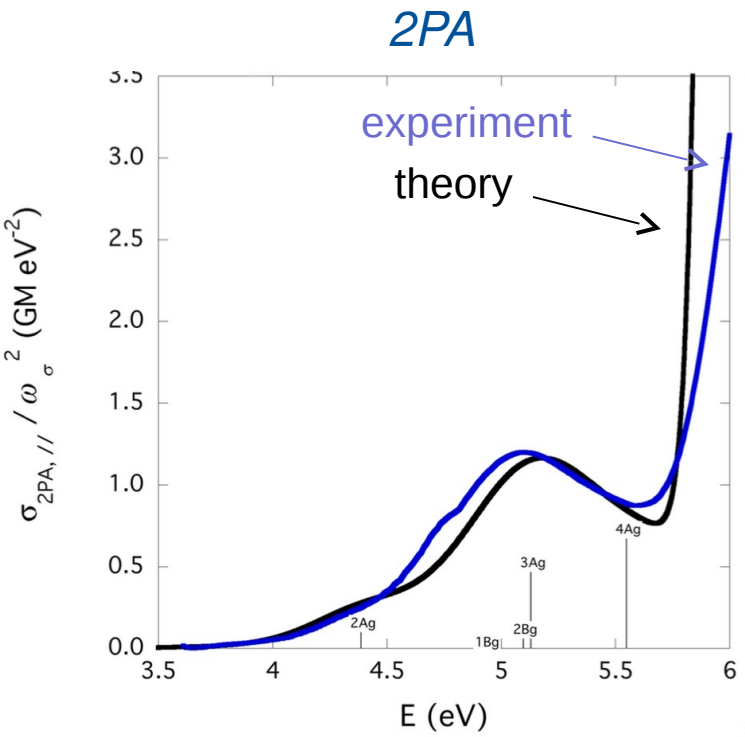
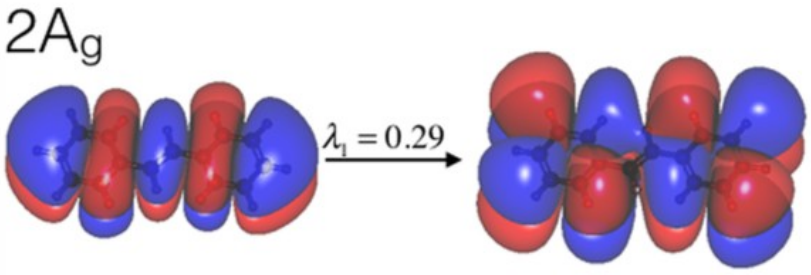




Valence transitions only:

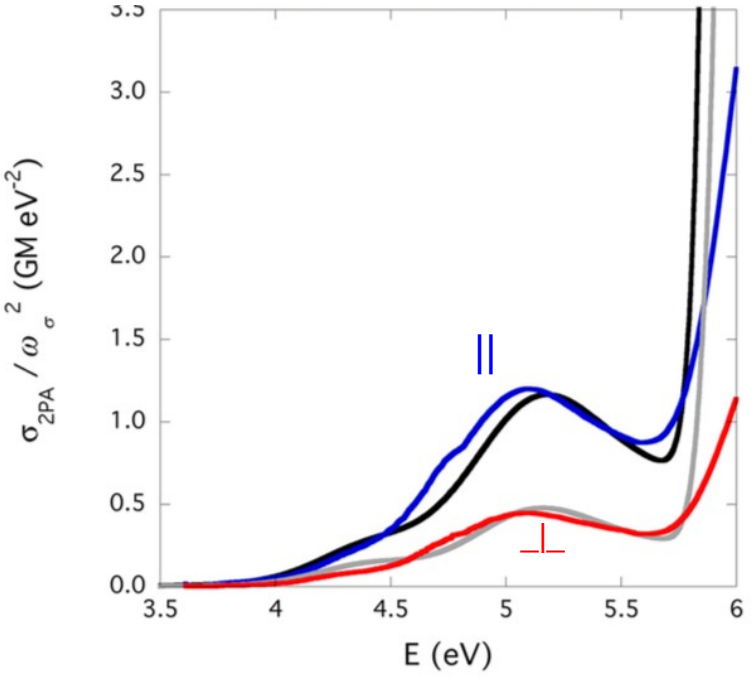
– shift by –0.4 eV

– broaden by 0.2 eV (or more)

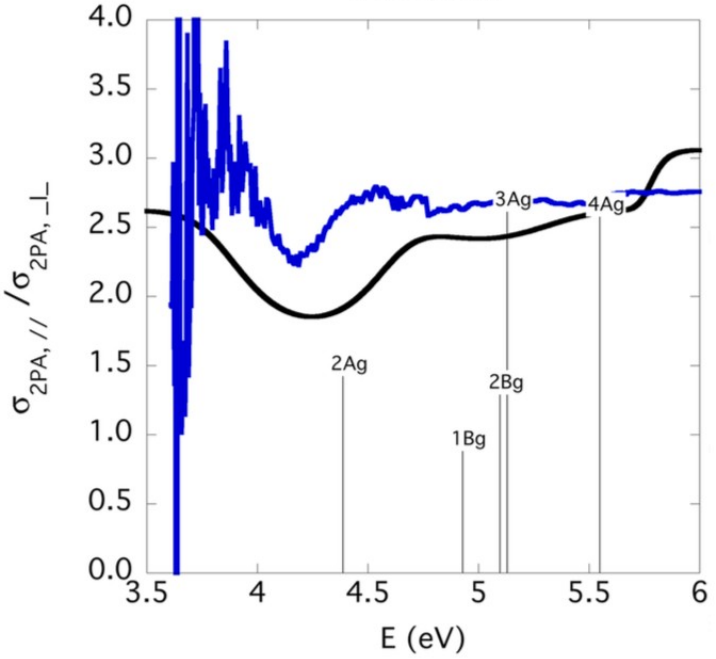
Two-photon absorption spectroscopy

Can we rationalize the spectrum with gas-phase calculations?

2PA



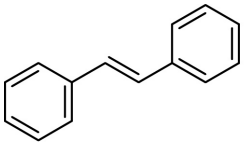
Polarization ratio



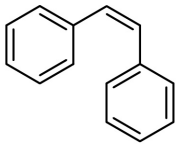
Calculations also reproduce polarization dependence!

Two-photon absorption spectroscopy

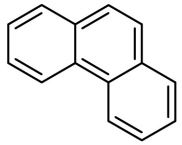
Other “stilbene” species: *different symmetry…*



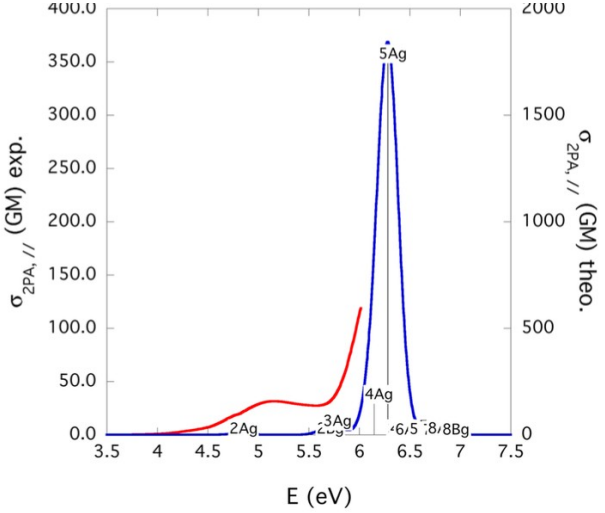
trans-stilbene

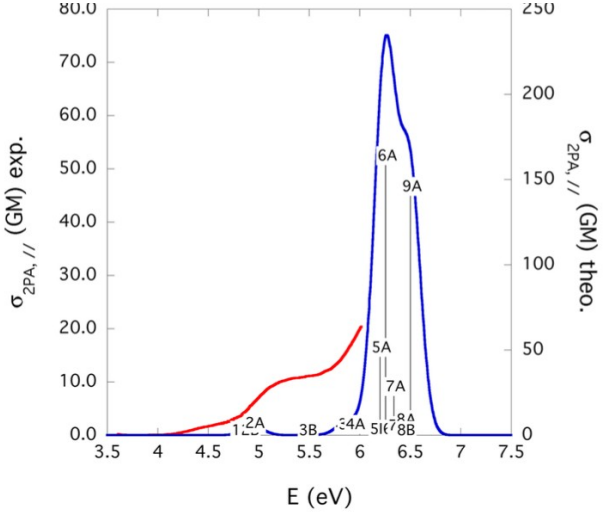


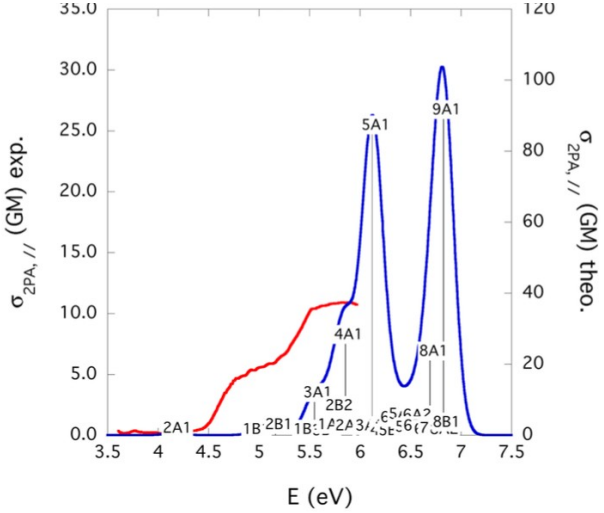
cis-stilbene



phenanthrene







Similar results: dominated by totally symmetric states

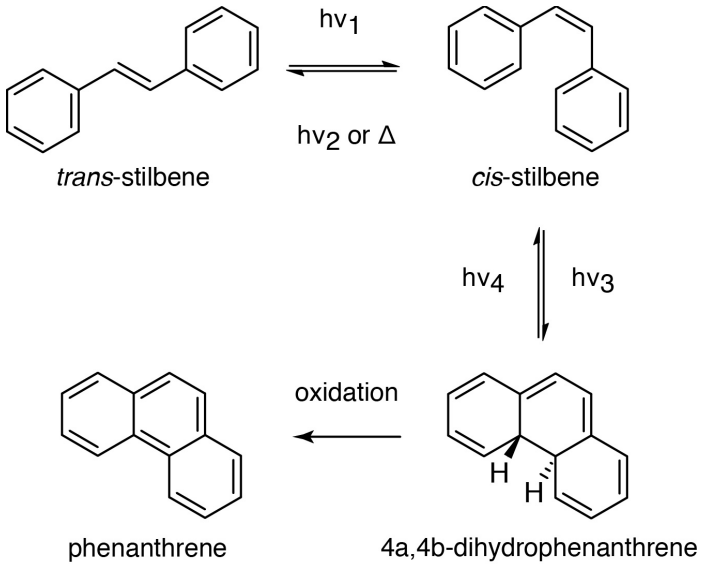
valence states reproduce low-energy spectrum

Conclusions

Spectroscopy and dynamics of higher-lying electronic excited states

- Two-photon excitation accesses new excited states
- Dynamics depend on S_1 minimum energy path
- 2PA spectroscopy reveals identity of excited-states

What happens to Rydberg states in solution???



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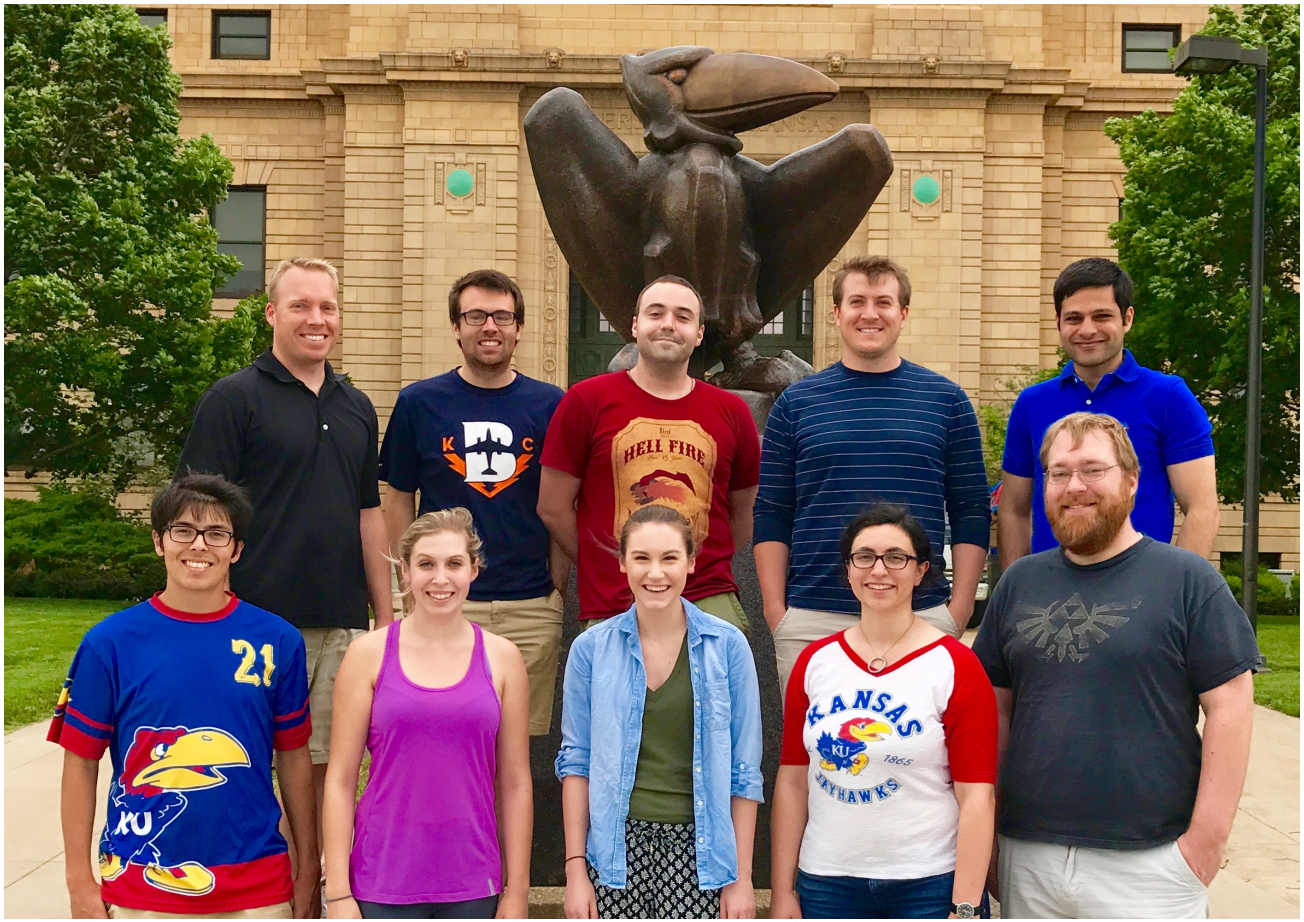

Collaborators:

***Anna Krylov** (USC)*

Marc de Wergifosse

Amanda Houk
(Savannah River National Lab)

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