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ABSTRACT

Tetracene (Tc) is a prototype material undergoing singlet fission (SF), the formation of a pair of triplet excitons from a singlet exciton. The tetracene dimer Tc_2 is supposed to be a structural unit providing SF behavior. This work is devoted to the study of the mechanism of singlet exciton decay in van der Waals dimers of Tc_2. A nanosecond pump-probe approach is used, tuning both pumping and probing wavelengths. It is shown that the photoexcitation of both the Tc monomer and dimer gives rise to a triplet $Tc(T_1)$ with very similar photoionization spectra, indicating an intersystem crossing (ISC) as the source of $Tc(T_1)$ in both cases. This finding, together with the very short lifetime of the singlet exciton in van der Waals Tc_2 dimers as reported earlier in the literature, indicates that the ISC process is much faster in the dimer than in bare Tc. The factors that increase the rate of ISC in donor–acceptor complexes are the low-lying charge-transfer state in the Tc_2 dimer and the proximity in the energy between the singlet S_1 and triplet T_2 states in tetracene. This fast ISC process is assigned to the temperature-independent process reported earlier in the literature, leading to a "dark" state in tetracene. The results obtained indicate that the dimer of tetracene can be considered to be a structural unit responsible for both fast ISC and SF processes.

I. INTRODUCTION

Dimers of polyacenes are considered to be structural units in which processes occur, which leads to the fission of singlet excitons in these materials. Singlet fission (SF) is a process of the conversion of singlet excitons giving rise to a pair of triplet states. Huge interest in this phenomenon is provided by the perspectives of its use in organic photovoltaics for the conversion of solar energy into electric energy. According to the estimates by Hanna and Nozik,[1] the use of this phenomenon can shift the so-called Shockley–Queisser limit[2] for conversion efficiency in one gap photovoltaic devices from 34% to 44%. This effect is ensured by excluding the thermalization of a large part of the absorbed energy due to the fact that all or almost all of the absorbed energy passes into the energy of two triplet excitons. Furthermore, each triplet exciton gives rise to an electron–hole pair. SF is also used for sensitizing silicon solar cells, providing the enhancement of solar energy conversion efficiency.[3] Organic semiconductor SF materials are considered to be used in hybrid materials with inorganic quantum dots to provide highly efficient broadband down-conversion materials.[4] SF is also considered as a method of generating spin states, which exhibit promising spin qubit properties.[5] This wide range of application dictates fundamental interest to SF. SF was first revealed in crystal anthracene in 1965.[6] The physical processes underlying the SF behavior are considered in a series of reviews.[7–15] Traditionally, singlet fission is presented as a process,

$$S_1 \Leftrightarrow {}^1(T_1T_1) \Leftrightarrow T_1 + T_1, \tag{1}$$

where ${}^1(T_1T_1)$ is a correlated triplet pair, which is supposed to be provided by a pair of adjacent triplet molecules in the coupled state, with the total spin of the pair equal to 0.[7]

The higher acenes tetracene and pentacene are among the most studied SF materials. These acenes fit the condition for SF behavior, $E(S_1) \gtrsim 2E(T_1)$, where $E(S_1)$ and $E(T_1)$ are the energy values of the first excited singlet and triplet states. The experimental study is usually carried out with the films or polycrystalline samples of

acenes. There is a big problem with the complex morphology of these samples, which is necessary but difficult to take into account for a complete description of the photophysics in these systems.[16,17] In an early work, Katul and Zahlan revealed the similarity in the absorption and fluorescence spectra of crystal tetracene (Tc) with its dimer (Tc_2) in solution.[18] Hence, in the theoretical description of singlet fission in polyacenes, the dimer of acene molecules is usually considered to be a structural unit of the material providing SF behavior.[9,19] This dictates the interest to provide the conditions for the experimental study of the isolated dimers of acenes. The progress in this direction was achieved with the use of synthesized dimers[13,20–27] or oligomers,[28] where polyacene molecules are connected by a covalent linker. This approach allows one to control the structure of the dimer unit, but this advantage turns out to be a problem from the point of SF efficiency. The fixed structure of the dimer does not allow the appearing triplets to fly away. The fusion of triplet states located nearby with final radiative and non-radiative relaxation of the system into the ground state can reduce SF efficiency. Another approach for the study of the basic processes of SF is the study of van der Waals dimers of acenes. These dimers have no rigid structure, and for them, there is no structural limitation for the formation of free triplets. The first experimental study of these dimers was reported by Schouder *et al.*[29] These authors studied the structure of tetracene dimers Tc_2 obtained at a very low temperature of helium nanodroplets. The authors spatially aligned these dimers by a moderately intense laser pulse and then provided a Coulomb explosion of aligned Tc_2 by the femtosecond laser pulse. The angular distribution of the recoiling photoions Tc^+ indicates the structure of the precursor Tc_2 to be a parallelly displaced or parallelly slightly rotated structure.[29] These two structures correspond to the most stable gas-phase conformations as it was found with quantum chemical calculations carried out in the same paper.[29] Recently, the experimental study of van der Waals dimers Tc_2 generated in the molecular beam was reported by Hoche *et al.*[30] These authors applied picosecond pump-probe REMPI [1 + 1′] detection of the parent photoions of Tc_2. This approach allowed the authors to record the absorption spectra of Tc_2 corresponding to the transitions into the lowest excited singlet states and to observe the dynamics in these states in a ps time-domain.[30] Three bands centered at 455, 427, and 403.5 nm were revealed in the absorption spectrum of the dimer, which were assigned to correspond to the vibrational structure of the $(S_0S_0) \rightarrow (S_1S_0)$ transition in the dimer. The REMPI signal of the parent ion looks like a fast-rising pulse with a decay formally described by a sequential two-step process. The characteristic times of these two sequential steps varied with the excitation wavelength and expansion conditions, which govern the vibrational temperature of dimers. The pair of times was longer (62 and 123 ps) for excitation at 455 nm and decreased to 18 and 54 ps for excitation at 403.5 nm. To interpret the observed time-resolved behavior, the authors of Ref. 30 simulated the dynamics in the excited state with the use of calculated intermolecular potentials and nonadiabatic couplings. According to the results of this simulation, Hoche *et al.* concluded that the observed REMPI signal belongs to the excimer state of the dimer, with the decay of the signal provided by relaxation into the ground state of the dimer.[30] To estimate the total decay time as a sum of the measured characteristic times of two sequential steps, the lifetime of a singlet exciton is derived to be near 200 ps when excited at 455 nm and near 70 ps at 403.5 nm.

In the current paper, the nanosecond pump-probe REMPI [1 + 1′] approach is applied with the wavelength tuning for both pumping and probing nanosecond lasers. This tuning allows us to identify the nature of the electronic states involved in the excited state dynamics provided by the excitation of the Tc_2 dimer.

II. EXPERIMENTAL

The molecular beam setup is described elsewhere.[31] The home-built heated electromagnetic valve with a 0.3 mm nozzle is used. A cap with tetracene (Sigma-Aldrich) is mounted inside the valve for the saturation of the carrier gas helium with tetracene vapor. During the experiments, the valve temperature has been fixed at 220 °C, which provides partial pressure of tetracene equal to about 20 Pa.[32] The backing pressure of helium is fixed at 1.1 bar.

Two nanosecond lasers have been used in the present work. The tunable dye laser [coumarin 47, spectral range 445–462 nm (hv = 2.79–2.68 eV), spectral FWHM = 0.01 nm (0.5 cm^{-1}), pulse energy 5 mJ, and pulse duration 7 ns] is pumped by a third harmonic of Nd:YAG laser (Lotis TII). The fifth harmonic of Nd:YAG [213 nm (hv = 5.82 eV), 15 ns, and 20 μJ], produced in a high-harmonic generator HG-Five pumped by an LS-2145-Optical Parametric Oscillator (OPO) (both from Lotis TII), has been used as the probing radiation, providing the photoionization of pre-excited molecules. The photoionization spectra were recorded with the radiation of the second harmonic (213–300 nm, pulse energy 7–20 μJ depending on wavelength, and 15 ns) of the tuned OPO laser (LS-2145-OPO). This second harmonic is created in a Lotis-TII SHG-OPO. The wavelength of the dye laser and OPO radiation is measured with an Angstrom WS-6 wavelength meter. The setting of the time-delay between the laser pulses has been provided with a delay generator (BNC 505). Laser energy was controlled by a Gentec-EO with a QE25SP-S-MT-D0 pulse energy meter. Signals were accumulated with a repetition rate of 5 Hz.

The spatially overlapped non-focused laser beams of about 2 mm in diameter cross the molecular beam at a distance of 150 mm from the nozzle. Photoions are produced by both pumping and probing laser pulses. All time-of-life (TOF) mass-spectra consist mainly of a broad peak centered at 228 amu, which corresponds to the parent tetracene ion $C_{18}H_{12}^+$. The photoions provided by a pump-probe signal coincide in time with a signal provided by the probing pulse itself, which was subtracted. The pump-probe signals obtained with the spectral tuning of the probing laser with wavelength-dependent pulse energy have been normalized to the fixed probing pulse energy.

III. RESULTS AND DISCUSSION

A. REMPI spectra

In Fig. 1, the spectral profiles of the appearance of the Tc^+ TOF-signal are presented as a function of pumping laser wavelength. In both REMPI spectra, we see the sharp lines centered at 446.5 and 447.2 nm. These lines, superimposed on a decreasing background dropping to 0 at a wavelength of about 450 nm, coincide with the REMPI spectra observed for Tc seeded in a supersonic expansion of He in paper.[33] The line at 446.5 nm (22 396.4 cm^{-1}[33]) was assigned to the 0_0^0 transition of the $S_1 \leftarrow S_0$ band in bare Tc. The narrow line at 447.2 nm together with a decreasing background was found

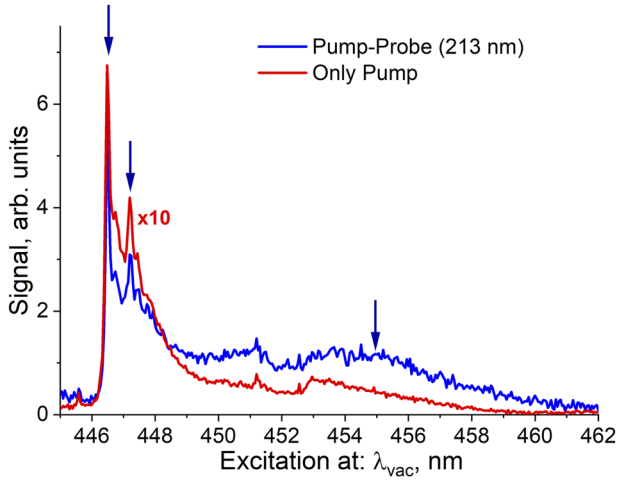

FIG. 1. One-color (red) and two-color (blue) REMPI spectra measured at a mass of the Tc^+ ion. The red line corresponds to the one laser experiment, and the blue line corresponds to the two laser experiment with the pulse of the probing laser being delayed by 300 ns. The expanded carrier gas He contained Tc vapor pressure being in equilibrium with the Tc solid sample at 220 °C. Arrows indicate wavelengths where the time-delay dependence of the pump-probe signal was measured (see text).

to depend on the backing pressure of the carrier gas He and was assigned to be provided by the clusters of the Tc monomer with helium Tc-$(He)_N$.[33] The narrow line at 447.2 nm (22 361.3 cm^{-1}) was assigned to the absorption by the cluster Tc-$(He)_8$.[33] In addition to the spectra observed in the paper,[33] the experiments of this work reveal the contribution of the red-shifted broad spectrum starting at about 448 nm, which looks similar to the spectrum of the van der Waals dimer Tc_2 recorded by Hoche *et al.*[30]

B. Pump-probe time-profiles

In Fig. 2, the dependence of the pump-probe TOF signal of the tetracene parent ion on the time-delay between pumping and probing pulses is presented. Three presented profiles correspond to the pumping wavelengths of 446.5, 447.2, and 455 nm, which are indicated by blue arrows in Fig. 1.

1. Tc molecule

A wavelength of 446.5 nm corresponds to the 0_0^0 transition of the $S_1 \leftarrow S_0$ band in the monomer of Tc (22 396.4 cm^{-1})[33]. In the pump-probe profile shown in Fig. 2(a), corresponding to the pumping of the Tc monomer via the 0_0^0 transition, we see a spike several tens of nanoseconds wide. We attribute the shape of this spike to a competition between the accumulation of Tc molecules in the excited S_1 state by pumping and the decay of the excited state population due to luminescence and intramolecular relaxation. The ionization of Tc in a pump-probe process is the REMPI [1 + 1′] process. The sum of pumping (2.78 eV) and probing (hν = 5.82 eV) photons' energy is equal to 8.6 eV, which is higher than the ionization potential of tetracene (IP = 6.933 eV[34]).

The width of the spike is governed by the widths of pumping (7 ns) and probing (15 ns) laser pulses and the lifetime of vibrationless Tc in the S_1 state. This last lifetime was measured by Amirav *et al.* to be equal to 20 ns.[35] After decay, the signal shown in Fig. 2(a) goes to a nearly constant level. The slow decay visible on the right side of the temporal profile in Fig. 2(a) is governed by a spatial shift of the cloud of Tc molecules pre-excited by the pumping pulse. The molecular beam moves in the direction perpendicular to the laser beams with a velocity of about 10^5 cm/s. Hence, the bigger the delay time, the larger the part of the cloud of pre-excited Tc comes out from the location probed by ionizing the UV-pulse. We assign this constant level of Tc^+ signal to the photoionization of the long-lived triplet monomer of the tetracene ^3Tc appearing due to ISC in the excited singlet $^1Tc(S_1)$ molecule,

$$^1Tc(S_1) \xrightarrow{ISC} {}^3Tc(T_1). \quad (2)$$

The sum of the probing photon energy and energy of the T_1 state in tetracene $E(T_1)$ = 1.30 eV[36] is equal to 7.12 eV, which is still higher than the IP of Tc. The difference between the measured lifetime of the vibrationless S_1 state τ = 20 ns and pure radiative lifetime τ_r = 30–35 ns allowed Amirav *et al.* to conclude that the luminescent decay of this state competes with the non-radiative electronic relaxation.[35] This electronic relaxation was interpreted by these authors to be due to the $S_1 \rightarrow T_1$ conversion intermediated with the T_2 electronic state lying closely to the electronic origin of the S_1 state and effectively coupled with the T_1 quasicontinuum. This mechanism was proposed by Amirav *et al.* to explain the observed retardation in the electronic relaxation rate for vibrationally excited Tc in the S_1 state. The importance of the T_2 state for ISC in Tc was shown also by Burgdorff *et al.*[37] The above-mentioned difference in the observed and pure radiative lifetimes results in the estimate of the characteristic time of ISC in vibrationless $Tc(S_1)$ to be $\tau_{ISC} \approx 50$ ns. This ISC in monomeric Tc was also detected in solution in the spectra of transient absorption, where the system of $S_N \leftarrow S_1$ absorption bands measured at a short delay was changed by a system of $T_N \leftarrow T_1$ bands on a longer time-scale.[38]

2. Cluster Tc-$(He)_8$

The pumping wavelength of 447.2 nm corresponds to the 0_0^0 transition of the $S_1 \leftarrow S_0$ band in the cluster Tc-$(He)_8$ (22 361.3 cm^{-1}[33]). The temporal pump-probe profile shown in Fig. 2(b) corresponds to the excitation of the cluster Tc-$(He)_8$ at this wavelength. The similarity of the temporal profile to the one observed in Fig. 2(a) for bare Tc is due to the negligible effect of the He environment on photophysical parameters of $Tc(S_1)$. According to the literature data, the radiative lifetime and ISC rate in the $Tc(S_1)$ state become affected by the noble gas (Ng) environment only in the case of heavy atoms Ng = Kr and Xe.[39]

3. Dimer Tc_2

The pumping wavelength of 455 nm corresponds to the maximum of the absorption by the dimer $(Tc)_2$. The time-profile obtained with this pumping is shown in Fig. 2(c). In this profile, there is no well-defined spike similar to that observed in Figs. 2(a) and 2(b). There is only a noisy scatter of the signal. The absence of the spike indicates that the conversion of the excited singlet state into the long-lived state proceeds on a time-scale much shorter than that observed for bare Tc in Figs. 2(a) and 2(b). The nature of this long-lived state arising from the Tc dimer is questionable. The nature of

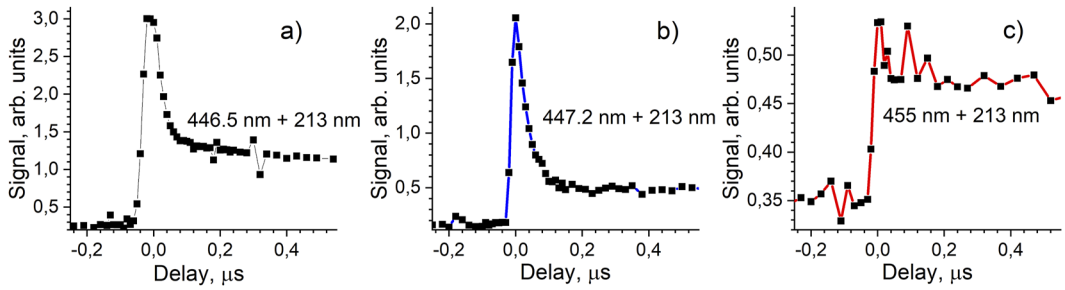

FIG. 2. Pump-probe TOF signal of the tetracene parent ion given in the dependence on the delay-time between pumping and probing pulses. The pump laser wavelength is 446.5, 447.2 and 455 nm in experiments presented in figures (a)–(c), respectively. The probe laser wavelength is 213 nm.

the electronic states of Tc responsible for the shape of the temporal pump-probe profiles is further investigated with the measurement of the photoionization spectra for different parts of the temporal profiles from Fig. 2.

C. Photoionization spectra and mechanism of singlet exciton decay

1. Short-lived state

In Fig. 3, the dependence of the pump (446.5 nm)-probe signal on the wavelength of probing radiation is presented. The signal is measured at zero delay-time between the pulses, which corresponds to the maximum of the spike in the temporal profile given in Fig. 2(a).

This signal corresponds to the REMPI [1 + 1′] process. The signal goes down to zero at the wavelength of probing radiation near 300 nm. At this wavelength, the sum of pumping (2.78 eV) and probing (hν = 4.13 eV) photon energies is equal to 6.91 eV, which is close to IP of Tc. This limit corresponds very well to the photoionization of the vibrationless S_1 state excited at 446.5 nm. In Fig. 3(b), the spectrum of the photoionization of Tc by radiation of the probing laser is shown. The intense line with a maximum at 255.5 nm (hν = 4.85 eV) corresponds to the brightest transition $S_8(B_{3u}) \leftarrow S_0$, which was observed earlier in the absorption spectrum of Tc in heptane solution with the maximum at 275 nm (hν = 4.51 eV).[40]

2. Long-lived state

The spectrum of the photoionization signal measured at a delay-time of 300 ns has the photoionization limit at a much shorter wavelength, as we see in Fig. 4.

The delay-time 300 ns corresponding to the part of the temporal profile shown in Fig. 2(a) is provided by photoionization of the long-lived state arising from the conversion of the vibrationless S_1 state excited at 446.5 nm. The photoionization yield drops down to very small numbers at about 230 nm (hν = 5.39 eV). The shift of the limiting photon energy to higher values than the photoionization of Tc(S_1) indicates the formation of the lower electronic state, which we assign to the triplet tetracene Tc(T_1). This state is long-lived with submillisecond lifetime (τ_T = 630 μs in benzene solution[37]). The energy of the T_1 state in solution is equal to 1.3 eV.[36] This energy is lower than IP(Tc) by 5.63 eV. The energy of a photon at 230 nm (hν = 5.39 eV) is lower than this value by about 0.2 eV. We see two possible reasons for this shift. First, the energy of Tc(T_1) in vacuum can be somewhat higher than that in a solution. For example, the spectral maximum of the 0_0^0 transition of the $S_1 \leftarrow S_0$ band in vacuum (2.78 eV) is shifted to a higher energy value than the number for the solution in cyclohexane (2.60 eV[41]) by about 0.2 eV. Here, we should also mention that ISC (2) in the Tc molecule, isolated in the molecular beam, proceeds with conservation of total energy. Therefore, the appearing Tc(T_1) is vibrationally excited. This excitation can provide a minor red shift of the photoionization threshold as

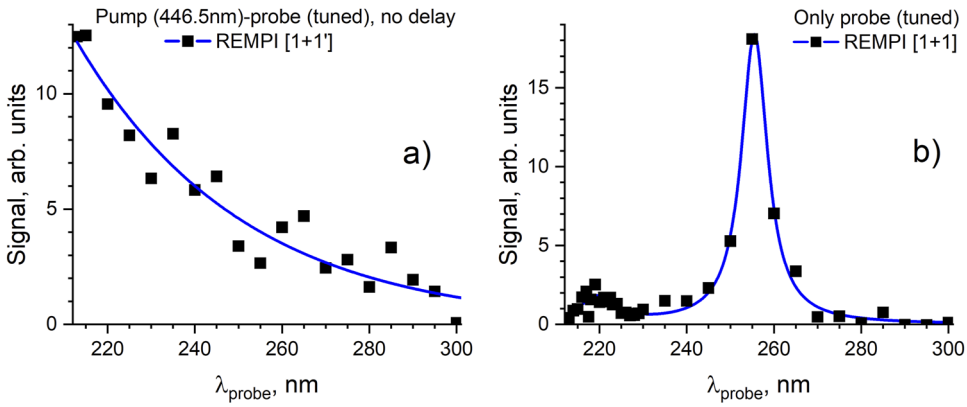

FIG. 3. (a) REMPI [1 + 1′] signal of Tc recorded in pump (446.5 nm)-probe experiments with tuning wavelength of the probing radiation and with time-delay between pulses equal to 0 ns. The presented signal is a result of normalization to the fixed probing pulse energy; (b) REMPI [1 + 1] signal of Tc recorded in one laser experiments with only tuned probing radiation. In the data presented in (a), the contribution of the REMPI [1 + 1] signal presented in (b) is absent due to its subtraction. Blue lines are given for visualization of the dependency.

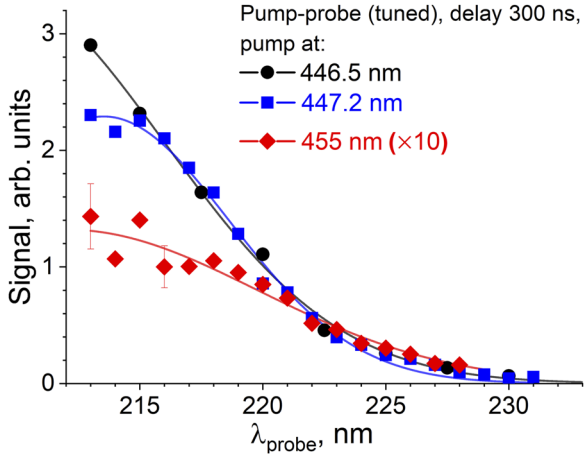

FIG. 4. REMPI [1 + 1′] signal of Tc recorded in the pump-probe experiments with tuning wavelength of the probing radiation and with time-delay between pulses equal to 300 ns. The three presented curves correspond to the pumping wavelengths shown by arrows in Fig. 1 and are used for generation of data presented in Figs. 2(a)–2(c). The presented signal is a result of normalization to the fixed pulse energy. The lines are given for visualization of the dependencies. Error bars correspond to the scatter of the data of several measurements.

well. A very similar wavelength limit for photoionization is observed when the pumping wavelength of 447.5 nm coincides with the 0_0^0 transition in Tc embedded in the cluster Tc-$(He)_8$. This again confirms the conclusion that the He environment does not affect the photophysical processes in Tc. A similar photoionization pattern, presented in Fig. 4 for the long-lived state appearing after excitation of the tetracene dimer Tc_2, indicates the formation of free Tc(T_1) as well. The comments given below allow us to think that the characteristic time of singlet exciton decay measured for the dimer in Ref. 30 belongs to the process giving rise to Tc(T_1).

In the pump-probe experiment with picosecond time resolution, Hoche *et al.* measured the decay of the population of the singlet exciton in the dimer $(Tc)_2$ pumped at 455 nm.[30] After excitation at this wavelength, the dimer was ionized by probing UV-radiation (263.5 nm) with a variation in the delay time. The authors of Ref. 30 fixed the REMPI [1 + 1′] TOF-signal at the mass of the dimer and revealed that its decay with the total characteristic time τ is shorter than 200 ps into the final state (P), which is not ionized by probing radiation,

$$Tc_2(S_0S_0) \xrightarrow{h\nu} Tc_2(S_1S_0) \xrightarrow{\frac{1}{\tau}} P. \quad (3)$$

Based on the results of theoretical simulations, Hoche *et al.* concluded that the photoexcited state $Tc_2(S_1S_0)$ converts finally into the ground state of the dimer. Our results definitely indicate the formation of the long-lived free triplet tetracene as a product of singlet exciton decay. Therefore, we conclude that the time of singlet exciton decay (shorter than 200 ps), measured by Hoche *et al.* in Ref. 30, corresponds to its conversion to the free triplet tetracene Tc(T_1). It is not surprising that Hoche *et al.* did not see the ionization signal of the triplet tetracene. In Ref. 30, the radiation with a wavelength of 263.5 nm was used for probing with the photon energy hν = 4.7 eV, which is not sufficient for one-photon ionization of the triplet Tc(T_1) state (threshold wavelength near 230 nm, see Fig. 4).

We can consider two processes of dimer conversion as a source of free Tc(T_1),

$$^1Tc_2(S_0S_0) \xrightarrow{h\nu} {}^1Tc_2(S_1S_0) \xrightarrow{ISC} {}^3Tc_2(T_1S_0) \rightarrow Tc(T_1) + Tc(S_0) \quad (4)$$
$$\Delta E \approx 2 \text{ eV},$$

$$\xrightarrow{SF} {}^1Tc_2(T_1T_1) \rightarrow Tc(T_1) + Tc(T_1) \quad \Delta E \approx 3.3 \text{ eV}. \quad (5)$$

Process (4) is the ISC in the dimer, and (5) is the singlet fission. The given energy threshold (ΔE) values are defined in the next paragraph. The comments given below allow us to exclude process (5) as a source of free Tc(T_1) detected in our experiments.

Valente *et al.* carried out extended quantum chemical calculations for dimers of tetracene.[42] They have found that the most stable structure corresponds to the slightly rotated stacked arrangement. The binding energy of Tc molecules in these structures was calculated by several methods, and the results obtained vary within the limits 16.93 (0.73 eV)–20.42 kcal/mol.[42] The lowest number of this interval together with the value for energy of the triplet state E(T_1) = 1.3 eV is used to estimate the energetic threshold values (ΔE) for processes (4) and (5). The energy of the pumping photon at 455 nm (hν = 2.72 eV) is lower than the threshold (3.3 eV) for process (5). In order to estimate the possible contribution of process (5), we should estimate the vibrational energy of the dimer Tc_2 in the molecular beam. In our experiments, the dimers Tc_2 are formed in the expanding gas jet via collisions of free cooled Tc molecules Tc + Tc + He → Tc_2 + He. In our previous experiments described in Ref. 33, the REMPI spectra of Tc molecules were measured under similar conditions. Absence of any "hot" bands in the spectra allowed us to conclude that free Tc molecules are vibrationally cold. The binding energy Tc–Tc (≈0.7 eV[42]) released, when Tc molecules are associated with a dimer, provides excitation of low-frequency intermolecular vibrations of the dimer. Low-frequency vibrations can be further quenched in the collisions of the dimer with carrier gas He atoms. Even the quenching of the minor part of this released binding energy makes the SF process (5) energetically impossible. Here, we should notice that another pathway can provide vibrationally cold dimers in our experimental conditions as well. According to our previous experimental data,[33] the long-wavelength decaying tail of the line at 446.5 nm (see Fig. 1) is provided by absorption of generated clusters $Tc(He)_n$. The formation of dimers via recombination of these clusters $Tc(He)_n$ + $Tc(He)_m$ → Tc_2 + (n + m)He provides carrying away of some part of the binding energy by the released He atoms. The energy of even a partially relaxed dimer is not sufficient to provide the SF process (5) with excitation at 455 nm (hν = 2.72 eV). Hence, the SF process (5) can be excluded as a source of free Tc(T_1) in our experiments.

The above-discussion allows us to conclude that the fast decay of the singlet exciton in the van der Waals dimer Tc_2 is governed by ISC followed by the dissociation of the dimer.

D. The mechanism of fast ISC in dimers Tc_2

The next question is whether ISC in the dimer can be so fast (~200 ps) when it is substantially slower (~50 ns) in bare Tc. Existing experimental data on the rate of ISC in some molecular complexes

of tetracene Tc-X demonstrate this rate enhancement. Amirav *et al.* revealed the heavy atom effect on the rate of ISC in the van der Waals complex of Tc with heavy inert gases.[39] The lifetime of the vibrationless S_1 state of Tc in complexes Tc–Kr and Tc–Xe is shortened to about 6.4 and <3 ns, respectively, as compared to the 20 ns for bare Tc.[39] Given the lack of dependence of this effect on the number of noble gas atoms, Amirav *et al.* concluded that a specific pairwise interaction is responsible for this effect. The authors of Ref. 39 supposed that this interaction is due to the enhancement of the intramolecular spin–orbit coupling provided by mixing with the charge-transfer (CT) state of the complex. The experimental data indicating the enhancement of the rate of ISC in molecular donor–acceptor (D-A) complexes are known since long ago.[43] Lim *et al.* considered the nature of this rate enhancement.[44] They showed that ISC in the CT state of the complex (^{1}CT–^{3}CT coupling) cannot be efficient because the corresponding matrix element of spin–orbit coupling vanishes in the one-electron approximation.[44] These authors also showed that there is a non-vanishing spin–orbit coupling between the CT state of the complex and the local triplet state of the acceptor (^{1}CT–^{3}A*).[44] Recently, Gibson *et al.* showed that this spin–orbit coupling (SOC) is not sufficient for explanation of the experimentally observed very fast rate of the processes of reverse intersystem crossing (rISC) in donor–acceptor complexes.[45] Gibson *et al.* showed that this fast rate of rISC is provided by a mechanism involving simultaneous contributions of the upper SOC and vibronic (nonadiabatic) coupling between the local triplet state (^{3}LE) of D or A and the charge-transfer triplet state (^{3}CT) of the complex.[45] This last coupling is provided by low-frequency vibrations twisting the donor–acceptor dihedral angle. Gibson *et al.* carried out the calculations of the dynamics of rISC and direct ISC and found the enhancement of ISC and rISC rates due to this mechanism by orders of magnitude. These calculations showed high sensitivity of ISC and rISC rates to the energy gap between CT and local triplet states of the complex. Etherington *et al.* carried out experiments with the tuning of this gap and found maximal effect when the energy of CT and the ^{3}LE state coincide.[46]

When applied to our case of S_1–T conversion in the isolated D-A complex, the above-mentioned mechanism of the ISC rate enhancement is expected to proceed when two conditions are fulfilled. The first is that the excited state S_1 contains a significant contribution of CT nature, which can be ensured if the complex has a low-lying CT state close in energy to the S_1 state. The second condition is the existence of a local triplet state, which is close in energy to the excited state S_1. We can say that the dimer Tc_2 is a complex where both conditions are realized.

The process of ISC in the dimer Tc_2 is shown in Fig. 5. The gap in energy between the 0-0 transition of the band $S_1 \leftarrow S_0$ and the lowest CT state (located on the pair of the nearest Tc molecules) was measured in electro-absorption measurements with tetracene by Sebastian *et al.*, who found it to be equal to 0.37 eV.[47] Yamagata *et al.* carried out the calculations of the CT state contribution into the lowest spectral component of the 0-0 transition into the S_1 state in crystalline tetracene and found this contribution to be close to 0.3.[48] The closeness in the energy of excited S_1 and local T states also takes place in the Tc_2 dimer. The energy of the triplet state T_2 in the Tc molecule can be estimated to be about 2.6 eV, which is the sum of the experimentally determined values of the T_1 state energy of 1.3 eV[36] and the energy of the $T_2 \leftarrow T_1$ transition

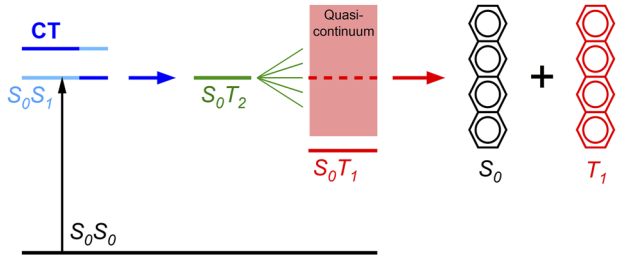

FIG. 5. Scheme of ISC in the dimer Tc_2. The deep-blue part of the line corresponding to the pumped singlet state indicates the contribution of the CT character in the pumped state (see text), and light-blue indicates the contribution of the S_1S_0 exciton character.

of 1.29 eV.[49] This value of 2.6 eV is only slightly less than the photon energy hν = 2.72 eV used for S_1 state excitation in Tc_2 in our experiments. Coupling of T_2 with quasicontinuum of T_1 vibronic states makes $Tc(T_1)$ to be the final state of ISC. Vibrational excitation in the S_0T_1 state of the dimer is sufficient for its further dissociation, giving rise to free $Tc(T_1)$ [process (4)], which is detected in our experiments.

E. Fast ISC in the tetracene dimer as a source of a "dark" state in tetracene

Some comments are necessary before comparing our results with literature data on photo-induced dynamics of singlet excitons in tetracene. The experiments by Burdett *et al.* showed that the variation in the excitation wavelength within the interval of 400–510 nm and temperature variation from 298 to 4 K do not affect the fast dynamics of singlet exciton decay (~100 ps) in tetracene.[50] This indicates that the fast vibrational relaxation takes place in the excited singlet state and experimentally observed dynamics can be assigned to the vibrationally relaxed S_1 exciton. This allows us to expect the relevance of our results, obtained for the conversion of the vibrationless S_1 exciton in dimer Tc_2, to the literature data for tetracene. Wan *et al.* supposed a contribution of nanosecond ISC to the appearance of T_1 in single crystal tetracene.[51] This ISC was supposed to be provided by the singlet exciton trapped in a crystal defect.[51] The contribution of intersystem crossing giving rise to free $Tc(T_1)$ was also detected by Bayliss *et al.*[52] The authors of Ref. 52 measured the transient spin polarization with the use of the time-resolved electron spin resonance technique. They found that in a cold (T = 200 K) Tc crystal, the observed polarization corresponds to ISC, which is assigned to be a contribution of Tc molecules non-coupled with the environment. At higher temperature (T = 300 K), the polarization changed sign, which indicated the SF process to be the dominating source of $Tc(T_1)$ with some contribution of ISC detected as well.[52] This result indicates that the SF process is thermally activated, which is in agreement with the slightly endoergic nature of the SF process in tetracene.[7] The existence of the contribution of the thermally activated process was also demonstrated by Bardeen and co-workers in Refs. 17 and 53. In the temperature range of 300–400, K Piland and Bardeen found clear Arrhenius behavior in the decay rate of picosecond fluorescence with the activation energy dependent on the sample morphology.[17] In a recent

work, Cruz *et al.* studied the temperature-dependent fluorescence spectrum, decay rate, and spin quantum-beats in single tetracene crystals.[53] These authors found that all the data for temperature T > 250 K are consistent with the thermally activated process of singlet exciton decay, which is interpreted to be the direct production of a spatially separated pair of triplets in a state $^1(T_1 \ldots T_1)$.[53] At the same time, Bardeen and co-workers revealed that even at a lower temperature, the singlet exciton continues to undergo fast decay.[50,53] Cruz *et al.* found the decay of singlet excitons with a characteristic time of ~200 ps, which is not affected by temperature in the interval 20–250 K in a single crystal.[53] A close in value characteristic time of ~100 ps was observed in the work by Burdett *et al.* for the decay of picosecond fluorescence in polycrystalline tetracene, which was not affected in the temperature range 300–4 K.[50] Moreover, the observation of the delayed fluorescence provided by a fusion of triplet states even at 20 K allowed Cruz *et al.* to conclude that this temperature-independent process gives rise to triplets as well, but via a mechanism different from the thermally activated process contributing at high temperature.[53] In Ref. 50, this process of unknown nature was assigned to be a channel giving rise to the so-called "dark" state. Here, we can fix that the fast ISC revealed in our experiments demonstrates all the properties of upper fast temperature-independent decay. First, ISC provides $Tc(T_1)$, which does not fluoresce, so it is "dark." Second, its characteristic time of $\lesssim$200 ps is similar to that (100–200 ps) observed by Bardeen and co-workers[50,53] for temperature-independent decay of singlet excitons. Third, the ISC process has no energy threshold because the intermediate T_2 state and final T_1 state are lower in energy than the initial S_1 state. This conclusion indicates that the fast ISC process in solid tetracene is an intrinsic property of the dimer of tetracene. Thus, the tetracene dimer can be considered to be a common structural unit for both fast ISC and SF processes.

IV. CONCLUSIONS

This paper is devoted to the study of the processes responsible for the decay of singlet excitons in the van der Waals dimer of tetracene Tc_2. The pump-probe REMPI [1 + 1′] approach is applied with the wavelength tuning of both pumping and probing nanosecond lasers. The variation in the pumping and probing photon energy allows us to identify the nature of the electronic states involved in the excited state dynamics provided by the excitation of the dimer Tc_2. The pump-probe spectrum with a delayed probing pulse allowed us to reveal the REMPI spectrum of the van der Waals dimer Tc_2 with the maximum at about 455 nm, which is red-shifted from the 0_0^0 transition of the $S_1 \leftarrow S_0$ band in bare tetracene (Tc). This red-shifted spectrum is similar to that recently revealed by Hoche *et al.* in Ref. 30. The temporal profiles obtained with the variation in the time-delay between pumping and probing pulses together with the photoionization spectrum allow us to identify the electronic states in the observed dynamics of singlet exciton decay. When the bare Tc molecule is excited, the decay of the short-lived state to the long-lived state is observed. Photoionization spectra of the short-lived state and appearing long-lived states correspond to S_1 and T_1 states, respectively. When the dimer is excited, the short-lived component in the temporal profile is absent with prompt appearance of the long-lived state that indicates the lifetime of the S_1 exciton to be much shorter than that in bare Tc. The photoionization spectrum of the long-lived component, in this case, is similar to that observed for the free triplet $Tc(T_1)$ arising from bare Tc. This allows us to make a conclusion that the S_1 exciton in dimer decays gives rise to the pair $Tc(T_1) + Tc(S_0)$ corresponding to the intersystem crossing (ISC). Recently, the kinetics of singlet exciton decay in the van der Waals dimer Tc_2 excited at the same wavelength were measured by Hoche *et al.*[30] and found to be $\lesssim$200 ps. We conclude that ISC proceeds much faster in the dimer Tc_2 than in individual Tc. We explain this fast conversion by taking into account the factors that are known to enhance the intersystem crossing rate via the contribution of a low-lying charge transfer state in the donor–acceptor molecular complex. These factors are (1) proximity in the energy of S_1 and the low-lying CT state in the dimer Tc_2 and (2) closeness in the energy between singlet S_1 and triplet T_2 states in tetracene.

We assign the observed fast ISC process in the dimer Tc_2 to the temperature-independent process of singlet exciton decay in solid tetracene of various morphologies, giving rise to the earlier unidentified "dark" state (Bardeen and co-workers[50,53]). This allows us to identify this "dark" state to be a triplet state of tetracene arising in the fast ISC process in the dimer Tc_2. The results obtained allow us to conclude that the dimer of tetracene can be considered to be a common structural unit for both fast ISC and SF processes in tetracene.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Alexandr S. Bogomolov: Investigation (equal). **Vladislav M. Rogoveshko**: Investigation (equal). **Alexey V. Baklanov**: Investigation (equal); Supervision (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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