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Looking at Photoinduced Charge Transfer Processes in the IR: Answers to Several Long-Standing Questions

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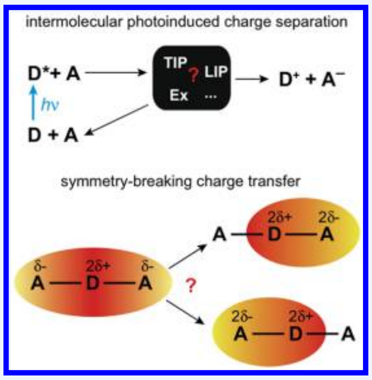

CONSPECTUS: Because of its crucial role in many areas of science and technology, photoinduced electron transfer is the most investigated photochemical reaction. Despite this, several important questions remain open. We present recent efforts to answer some of them, which concern both inter- and intramolecular processes. The decisive factor that allowed these issues to be successfully addressed was the use of time-resolved infrared (TRIR) spectroscopy.

Many different transient species, such as tight and loose ion pairs (TIPs and LIPs) and exciplexes, have been invoked to explain the dynamics of intermolecular photoinduced charge separation reactions (i.e., electron transfer between two neutral species) and the production of free ions. However, their structures are essentially unknown, and their exact roles in the reaction mechanism are unclear. Indeed, the commonly used transient electronic absorption spectroscopy does not give much structural insight and cannot clearly distinguish ion pairs from free ions, at least in the visible region. Unambiguous spectral signatures of TIPs, LIPs, and exciplexes could be observed in the IR using electron donor/acceptor (D/A) pairs with adequate vibrational marker modes. The ability to spectrally distinguish these intermediates allowed their dynamics to be disentangled and their roles to be determined. Structural information could be obtained using polarization-resolved TRIR spectroscopy. Our investigations reveal that moderately to highly exergonic reactions result in the formation of both TIPs and LIPs. TIPs are not only generated upon direct charge-transfer excitation of DA complexes, as usually assumed, but are also formed upon static quenching with reactant pairs at distances and orientations enabling charge separation without diffusion. On the other hand, dynamic quenching produces primarily LIPs. In the case of highly exergonic reactions, strong indirect evidence for the generation of ion pairs in an electronic excited state was found, accounting for the absence of an inverted region. Finally, weakly exergonic reactions produce predominantly exciplexes, which can evolve further into ion pairs or recombine to the neutral ground state.

The high sensitivity of specific vibrational modes to the local electronic density was exploited to visualize the photoinduced charge flow in symmetric $A-(\pi-D)_2$- and $D-(\pi-A)_2$-type molecules developed for their two-photon absorption properties. The electronic ground state and Franck−Condon S_1 state of these molecules are purely quadrupolar, but the strong solvatochromism of their fluorescence points to a highly dipolar relaxed S_1 state. This has been explained in terms of excited-state symmetry breaking induced by solvent and/or structural fluctuations. However, real-time observation of this process was missing. Direct visualization of symmetry-breaking charge transfer was achieved using TRIR spectroscopy by monitoring vibrations localized in the two arms of these molecules. A transition from a purely quadrupolar state to a symmetry-broken state on the timescale of solvent relaxation could be clearly observed in polar solvents, indicating that symmetry breaking occurs primarily via solvent fluctuations. In the case of the $D-(\pi-A)_2$ molecule, this breaking results in different basicities at the two A ends and consequently in different affinities for H-bonds, which in turn leads to the formation of an asymmetric tight H-bonded complex in highly protic solvents.

■ INTRODUCTION

Electron transfer (ET) is the simplest and most ubiquitous chemical reaction, and despite several decades of intensive research, it is still attracting major interest from both the theoretical and experimental sides.[1,2] Photoinduced ET reactions are being particularly thoroughly investigated because of their key roles in many areas of science and technology. Additionally, their ability to be triggered by light confers on them the possibility to be scrutinized with a temporal resolution of a few femtoseconds. Although we have achieved generally good understanding of these processes, there are still several aspects that deserve further attention. We will discuss here recent efforts to address some of these questions, which include the absence of an inverted region for bimolecular photoinduced charge separation (CS), the structure of exciplexes, and the origin of symmetry-breaking charge transfer in quadrupolar molecules. Major advances could be achieved thanks to the application of ultrafast time-resolved infrared (TRIR) spectroscopy. Although the distinct advantages of TRIR spectroscopy[3] have already been exploited in several studies of photoinduced ET in organic, inorganic, and biological systems,[4−11] the vast majority of investigations have been carried out using time-resolved fluorescence and transient electronic absorption spectroscopies, which do not yield

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significant structural information on the various states/intermediates involved in these processes.

■ THE PRIMARY PRODUCT OF BIMOLECULAR PHOTOINDUCED CHARGE SEPARATION

One of the main applications of bimolecular photoinduced CS (i.e., ET between two neutral species) is the generation of free ions. Ions are first produced as geminate pairs with a structure that depends on the mutual distance and orientation of the reactants at which CS takes place.[12] On the basis of picosecond investigations and free-ion yield measurements,[13−15] two forms of ion pairs were proposed: (i) tight ion pairs (TIPs) generated by charge-transfer excitation of ground-state donor−acceptor complexes (DACs) and (ii) loose ion pairs (LIPs) produced upon bimolecular photoinduced CS. TIPs and LIPs have essentially the same electronic absorption spectra as free ions, at least in the visible region. Therefore, apart from different recombination dynamics, which is faster for TIPs than for LIPs, not much was known about the natures of these pairs.

An exciplex can be viewed as the product of an incomplete CS process. Exciplexes are usually observed in apolar or moderately polar solvents and more rarely in highly polar solvents, but only when CS is weakly exergonic ($\Delta G_{CS} \gtrsim -0.4$ eV). Despite numerous studies,[16−19] their structure and exact role in the formation of free ions in polar solvents are still not fully understood. Apart from their fluorescence, exciplexes lack clear spectroscopic signatures, at least in the visible region. Moreover, as their emission often overlaps with that of the excited reactant and their radiative rate constant is small, ultrafast time-resolved fluorescence studies of exciplexes are hardly feasible.

Tight and Loose Ion Pairs

In an early time-resolved resonance Raman (TR^3) investigation of the quenching of anthraquinone in the T_1 state by 1,2,4-trimethoxybenzene (TMB) in tetrachloroethane, a distinct frequency downshift of a TMB$^{\bullet+}$ band was observed on a 100 ns timescale and attributed to the dissociation of the ion pair into free ions.[20,21] In acetonitrile, however, dissociation was faster than the ∼15 ns resolution of the experiment.

TRIR investigations of singlet ion pair dynamics in acetonitrile were performed more recently with the fluorescence quenching of perylene by 1,4-dicyanobenzene (DCB) using the antisymmetric C≡N stretching vibration of DCB$^{\bullet-}$ as a marker.[22] A partial decay and ∼20% narrowing of the IR band were observed on a 300 ps timescale and were attributed to the recombination and dissociation of the ion pair into free ions. Although no conclusion about the nature of the pair (TIP or LIP) could be drawn, this result revealed the high sensitivity of the C≡N stretching frequency to small changes in electronic density such as those accompanying the dissociation of an ion pair.

Unambiguous spectral discrimination between TIPs and LIPs was demonstrated with the quenching of methylperylene (MPe) by the strong acceptor tetracyanoethylene (TCNE).[23] As illustrated in Figure 1A, the TRIR spectra in the C≡N stretch region of TCNE$^{\bullet-}$ point to the presence of two species: species I appearing within 1 ps, decaying in a few picoseconds, and characterized by two relatively broad bands, and species II generated on a timescale of ∼100 ps and associated with narrower bands upshifted by 4−5 cm^{-1}. Measurements at different TCNE concentrations showed that the relative population of species I is negligible at 0.05 M but dominates at 0.9 M and that the buildup of species II accelerates with increasing concentration. Additionally, the TRIR spectra recorded upon charge-transfer excitation of the MPe/TCNE DAC show the exclusive presence of species I (Figure 1B). Consequently, species I can be interpreted as a TIP generated upon static quenching, with reactants at a distance/orientation enabling CS without significant diffusion, whereas species II can be assigned to a LIP formed upon diffusional quenching. TIPs and LIPs should not be understood as species with well-defined geometries and lifetimes but rather as two limiting forms in a broad distribution of structures with different electronic coupling. These results reveal that, contrary to the general assumption, TIPs are not only generated upon charge-transfer excitation of DACs but also produced upon bimolecular CS quenching.[24]

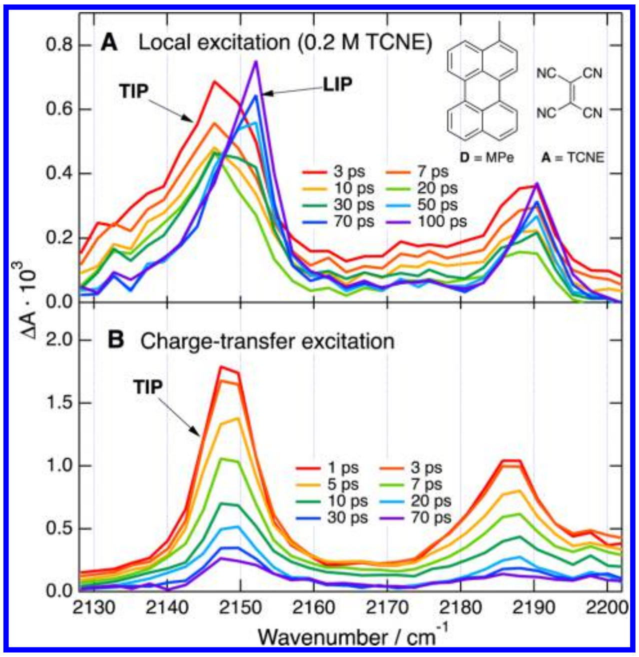


Figure 1. TRIR spectra recorded at different time delays in acetonitrile upon (A) local excitation of MPe at 400 nm with 0.2 M TCNE and (B) charge-transfer excitation of the MPe/TCNE complex at 800 nm. Adapted with permission from ref 23. Copyright 2008 Wiley-VCH Verlag.

Structural information could be deduced from polarization-resolved TRIR experiments. The initial anisotropy of 0.09 ± 0.03 measured for both C≡N bands of TCNE$^{\bullet-}$ is unambiguous evidence that the mutual orientation of the ions in a TIP is not random. Although several mutual orientations can account for this anisotropy, they all point to a sandwich-like geometry with the molecular planes of the ions being face-to-face.

Exciplexes

Although no specific Raman band of exciplexes could be observed in an early TR^3 investigation,[25] we decided, on the basis of the above-described results, to look for such exciplex signatures in the IR. We selected donor/acceptor (D/A) pairs with sensitive IR marker modes, such as the C≡N and C═O stretching vibrations, and with a weak driving force for CS. Clear exciplex IR bands were first observed with the 9-cyanoanthracene (CA)/phthalic anhydride (PA) pair in tetrahydrofuran (THF) (Figure 2) and, to a minor extent, in acetonitrile.[26] According to their frequencies, these bands were

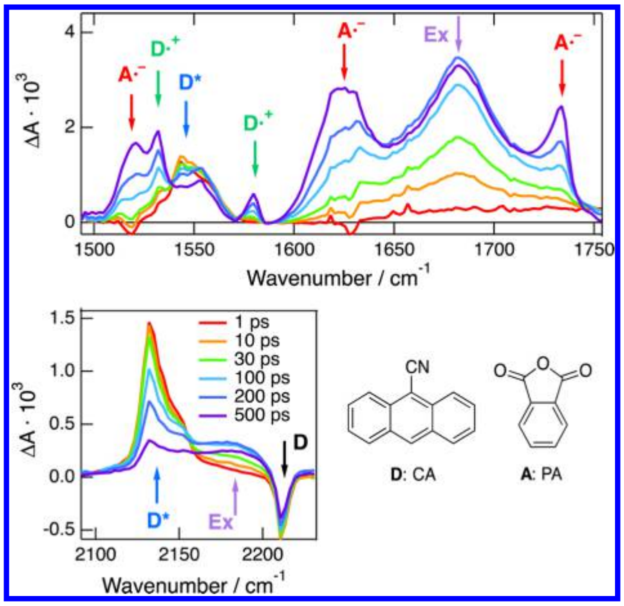


Figure 2. TRIR spectra in the (top) C═C and C═O and (bottom) C≡N stretching regions recorded upon excitation of CA with 1 M PA in tetrahydrofuran and band assignment (Ex, exciplex). Adapted from ref 26. Copyright 2014 American Chemical Society.

ascribed to the C≡N stretching mode of the partially oxidized donor, CA$^{\delta+}$, and to the antisymmetric C═O stretching mode of the partially reduced acceptor, PA$^{\delta-}$. Their large bandwidth relative to those of the other transients suggests a distribution of exciplex geometries and hence of the magnitude of the partial charges (δ+ and δ−) and of the vibrational frequencies. The time evolution of all of these bands in THF was analyzed globally assuming different reaction schemes. Although several models could reproduce the observed kinetics, only one (Figure 3A) correctly reproduced the difference absorption spectra of each species. This scheme evidences the crucial role of the exciplex for the formation and decay of the ion pairs.

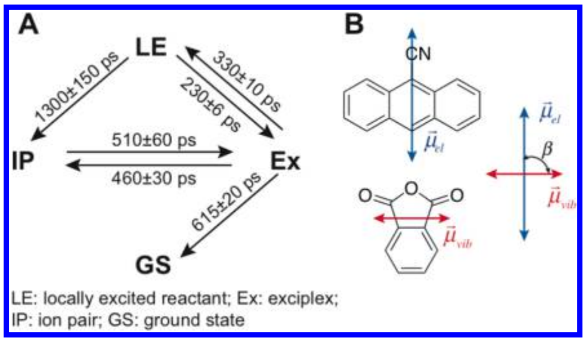


Figure 3. (A) Reaction scheme and time constants deduced from the global analysis of the TRIR data shown in Figure 2. (B) Orientations of the dipole moments associated with the $S_1 \leftarrow S_0$ transition of CA and the exciplex C═O band.

Structural information was obtained from polarization-resolved TRIR measurements. The anisotropy of the exciplex C═O band was found to vary from −0.08 ± 0.01 to zero in 31 ± 7 ps. This is about 3 times as slow as the anisotropy decay measured with CA alone and reflects the concerted motion of both CA$^{\delta+}$ and PA$^{\delta-}$ during the reorientation of the exciplex. The initial anisotropy depends on the angle β between the $S_1 \leftarrow S_0$ transition dipole of CA, $\vec{\mu}_{\mathrm{el}}$, and the transition dipole moment associated with the antisymmetric C═O stretch mode of PA$^{\delta-}$, $\vec{\mu}_{\mathrm{vib}}$ (Figure 3B). An anisotropy of −0.08 can correspond to several mutual orientations of CA$^{\delta+}$ and PA$^{\delta-}$. Assuming a face-to-face sandwich-like structure and taking into account the large width of the bands, this anisotropy is compatible with a 40°-wide Gaussian distribution of β centered at 90°.

For energetic reasons, the CA/PA pair cannot be studied in solvents less polar than THF. Exciplex dynamics in solvents ranging from diethyl ether to acetonitrile were investigated with the dimethylanthracene (DMA)/phthalonitrile (PN) pair (ΔG_{CS} = −0.50 eV in acetonitrile vs −0.13 eV for CA/PA).[27] A broad exciplex band attributed to the antisymmetric C≡N stretch of PN$^{\delta-}$ is observed in all of the solvents tested (Figure 4). Its amplitude relative to the two C≡N stretch bands of PN$^{\bullet-}$ decreases with increasing solvent polarity. Its width, which is larger by a factor 4−5 compared with that of the PN$^{\bullet-}$ bands, can also be attributed to a dynamic distribution of exciplex geometries and of the partial charge on PN$^{\delta-}$, in agreement with quantum-chemical calculations.[27] Except for diethyl ether, the exciplex band is already observed at the earliest time delays, pointing to its formation by static quenching (Figure 4). However, this initial population decays within the first 10−20 ps. This decay is complete in acetonitrile, but in the less polar solvents, the band rises again at a rate that increases with the quencher concentration, indicating exciplex formation by dynamic quenching. In the case of the above-discussed CA/PA exciplex, static quenching is not operative because the driving force is too weak.

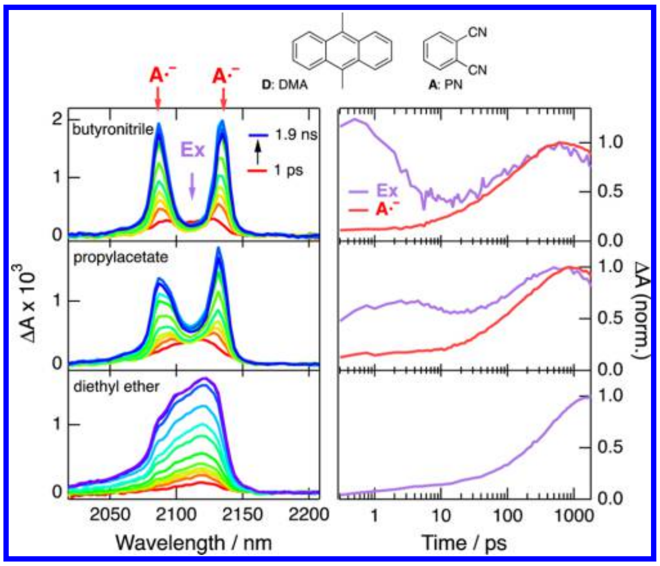


Figure 4. (left) TRIR spectra in the C≡N stretch region recorded upon excitation of DMA with 0.4 M PN (0.05 M in diethyl ether). (right) Time evolution of the anion (A$^{\bullet-}$, 2087 cm^{-1}) and exciplex (Ex, 2113 cm^{-1}) band intensities in the same solvents. Adapted from ref 27. Copyright 2015 American Chemical Society.

Because of the partial overlap of the broad exciplex band with the anion bands, differences between the spectra of the early and late exciplexes could not be determined. However, these two forms of exciplexes behave similarly to the above-discussed TIPs and LIPs, pointing to different coupling strengths between the two constituents. By analogy, they were named tight and loose exciplexes. The difference between ion pairs and exciplexes is that CS is almost complete in the former but

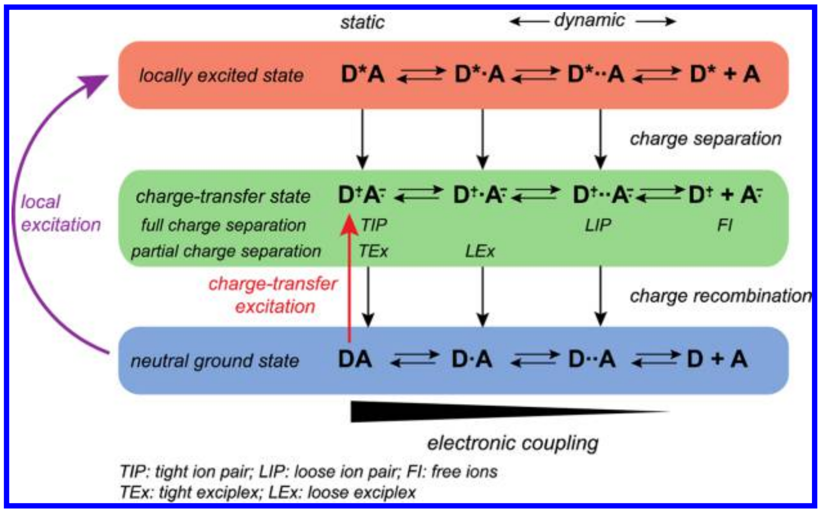


Figure 5. General scheme for bimolecular electron transfer in polar solvents illustrating the different types of quenching products depending on the driving force and the reactant pair distribution (the excited reactant was arbitrarily chosen to be the donor). Partial CS dominates for weak driving forces; static quenching is favored at high quencher concentrations.

only partial in the latter. Whether an ion pair or an exciplex is primarily formed depends on ΔG_{CS}: no exciplex is observed with MPe/TCNE because CS is energetically much more favorable for this pair than for CA/PA. Therefore, for large driving forces, the quenching product ranges from TIPs to LIPs, whereas for weak to moderate driving forces, it ranges from tight exciplexes to LIPs, with the loose exciplex corresponding most probably to an intermediate form (Figure 5).

Excited Ion Pairs

The formation of TIPs observed with the MPe/TCNE pair is unexpectedly fast considering that this process should take place in the inverted regime ($\Delta G_{CS} = -2.07$ eV), i.e., in the region where Marcus theory predicts a decrease in the ET rate constant with increasing driving force.[12] However, as shown more than 4 decades ago,[28] bimolecular CS quenching remains diffusion-controlled in acetonitrile at $\Delta G_{CS} \lesssim -0.5$ eV (see Figure 8). We recently determined the driving-force dependence of the intrinsic CS dynamics above the diffusion limit and found only a shallow inversion (see Figure 8).[29] Several hypotheses, including long-distance CS and the formation of ions in an electronic excited state, have been proposed to explain the absence of an inverted region.[28,30] However, none of them could be unambiguously confirmed or refuted. Excited radical ions are elusive species with generally ultrashort lifetimes due to very efficient nonradiative decay to the D_0 ground state.[31,32] Therefore, instead of searching for spectroscopic signatures of excited ions in a highly exergonic CS process, we chose to detect their presence by looking at the vibrational energy produced upon their nonradiative decay.[33] As shown in Figure 6, two CS pathways are energetically feasible: the highly exergonic path I to the ground-state product and the less exergonic path II to the excited product with $MPe^{\bullet+*}$ in the $D_{n\geq1}$ state. If CS follows path I, the energy released upon CS and CR is equally redistributed into the vibrational modes of MPe and TCNE, and both reach the same vibrational temperature (~600 K, assuming vibrational cooling to be slower than CS and CR). Alternatively, if CS occurs via path II, the energy released upon internal conversion of $MPe^{\bullet+*}$ is redistributed into the vibrational modes of $MPe^{\bullet+}$. Therefore, the vibrational temperature of MPe after CR is substantially higher (~800 K) than that of TCNE (~460 K). The vibrational temperatures of MPe and TCNE after the ultrafast CS/CR cycle in TIPs were estimated from the shape of the C═C and C≡N stretching bands of MPe and TCNE in the hot ground state.

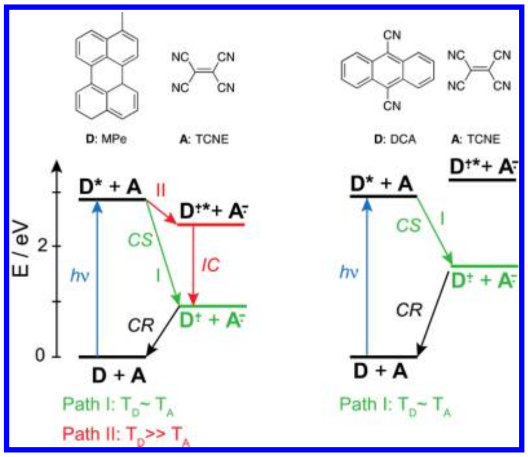


Figure 6. Energy-level schemes for the MPe/TCNE pair with two possible CS pathways and the DCA/TCNE pair with only one CS pathway (IC, internal conversion; T, vibrational temperature).

Figure 7A shows difference IR absorption spectra of TCNE calculated assuming various temperature jumps. Thermal population of low-frequency modes and anharmonic coupling lead to a negative bleach around the room-temperature C≡N stretch frequency and to the presence of a broad positive band at lower frequencies.

Figure 7B,C compares the TRIR spectra in the same spectral region measured with the MPe/TCNE pair and the DCA/TCNE pair, for which only path I is operative (Figure 6). These spectra show the two positive C≡N bands of $TCNE^{\bullet-}$ and the negative C≡N bleach of the neutral TCNE. The relative intensity of the bleach is much larger and the high-frequency $TCNE^{\bullet-}$ band is considerably broader with DCA/TCNE. These differences point to a markedly higher vibrational temperature of TCNE with DCA than with MPe, suggesting that path II is operative with the latter. This was confirmed by TRIR measurements of vibrational modes of MPe and DCA as

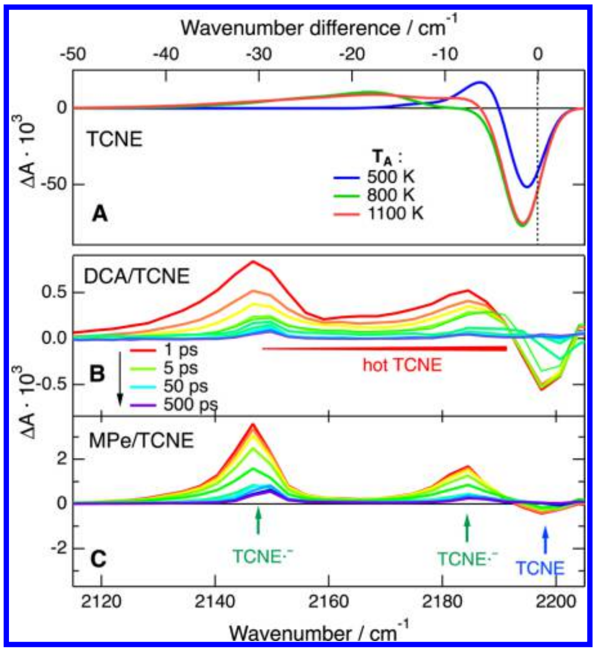


Figure 7. (A) Simulated difference IR absorption spectra of the antisymmetric $C\equiv N$ stretch of TCNE after different temperature jumps (from 293 K to T_A). The dashed vertical line represents the $C\equiv N$ stretch frequency at 293 K. (B, C) TRIR spectra recorded after excitation of (B) DCA and (C) MPe with 1 M TCNE in acetonitrile. Adapted from ref 33. Copyright 2013 American Chemical Society.

well as by transient electronic absorption measurements, which revealed a much higher vibrational temperature for MPe than for DCA.[33] This pronounced asymmetry in the energy redistribution observed with MPe/TCNE but not with DCA/TCNE is strong indirect evidence of the population of excited radical ions in a highly exergonic CS and can account for the absence of an inverted region. However, direct spectroscopic observation of excited ions, which would represent a definitive confirmation, is still missing.

The results obtained so far using TRIR spectroscopy reveal a picture that is more complex than usually assumed for bimolecular photoinduced CS. Indeed, CS quenching results in a broad variety of species, including exciplexes and ion pairs in the ground or excited state with different coupling strengths and charge-transfer characters depending on the environment and the driving force (Figures 5 and 8). In most cases, these intermediates cannot be considered as species with well-defined geometries and lifetimes but rather correspond to some representative forms of a broad distribution. Further systematic investigations are still necessary before a comprehensive picture of these apparently simple reactions is realized.

■ SYMMETRY-BREAKING CHARGE TRANSFER

We have exploited the sensitivity of various vibrational modes to the electronic density for visualizing the charge flow in symmetric $D-\pi-A-\pi-D$ and $A-\pi-D-\pi-A$ compounds. These quadrupolar molecules are attracting considerable attention as two-photon absorbers for a large variety of applications.[34,35] Contrary to expectations, their fluorescence often exhibits a substantial solvatochromism, indicative of a dipolar excited state, i.e., of a larger charge-transfer character in one branch than in the other.[36,37] This has been explained in terms of excited-state symmetry breaking driven by fluctuations of the structure of the molecule itself and/or of its environment.[38−40] However, real-time observation of this symmetry breaking, which could reveal its origin, was missing. Whereas time-resolved electronic spectroscopy does not give much insight into this process, an unambiguous signature of symmetry breaking can be obtained using time-revolved vibrational spectroscopy, provided that the molecules possess local vibrational marker modes at well-defined positions.

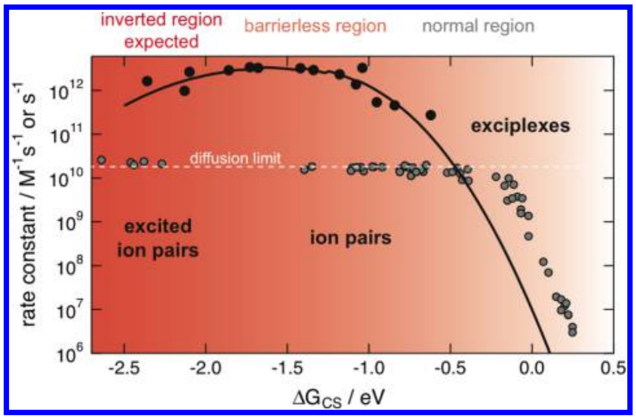


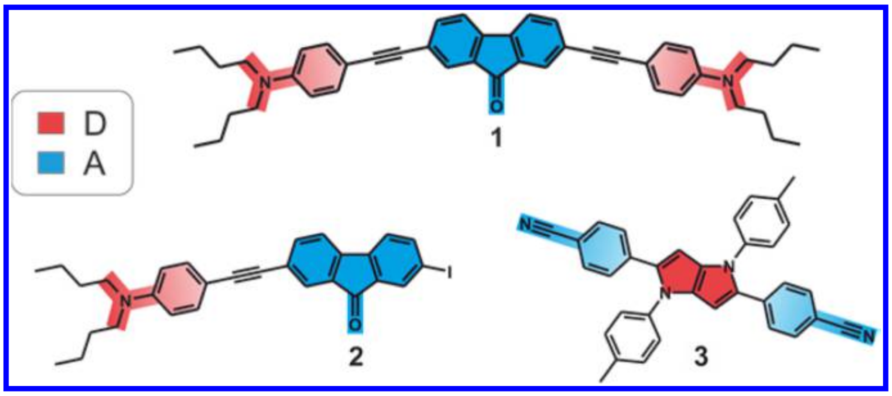
Figure 8. Driving-force dependence of the diffusional quenching rate constant (gray, from ref 28), the intrinsic static CS rate constant (black, from ref 29), and the nature of the primary product in acetonitrile (ion pairs include TIPs and LIPs).

Direct Visualization of Symmetry Breaking

Excited-state symmetry breaking was first visualized with the $D-\pi-A-\pi-D$ molecule **1** (Chart 1).[41] Its one-photon and two-photon absorption properties are consistent with a quasi-centrosymmetric quadrupolar ground state and Franck−Condon S_1 state. The solvatochromism of its fluorescence, which is almost as pronounced as that for its single-branch analogue **2**, points to a strongly dipolar character of its relaxed S_1 state and thus to symmetry breaking. Transient electronic absorption does not reveal significant spectral differences between **1** and **2** or any dynamics that could be ascribed to a transition from a quadrupolar to a dipolar excited state. However, spectacular solvent dependence and spectral dynamics are observed in the IR at frequencies corresponding to the $C\equiv C$ stretch of the π bridges (Figure 9). In nonpolar cyclohexane, the TRIR spectra exhibit a single intense absorption band assigned to the antisymmetric $C\equiv C$ stretching mode, ν_a, with a lifetime identical to that of the S_1 state. The S_1 state of **1** is thus symmetric and purely quadrupolar. Indeed, as the electronic density is the same in both arms, the two ethyne bonds vibrate at the same frequency, and a single vibrational band is visible. In weakly polar solvents (chloroform and diethyl ether), the same single ν_a band is present at early times. However, the spectrum evolves in a few picoseconds to one with two bands of different intensities, which remains unchanged during the S_1 state lifetime.

The second band is due to the symmetric $C\equiv C$ stretch, ν_s, and its IR activity reveals that the S_1 state of **1** is no longer symmetric. As the electronic densities on the two branches are not the same, the two ethyne bonds vibrate at different frequencies: the band located further away from the ground-state bleach and with the higher intensity corresponds to the branch with more excitation and higher charge-transfer character, whereas the other band can be related to the branch with less excitation and lower amount of charge transfer.

Chart 1. Two-Branch D−π−A−π−D (1) and A−D−A (3) Molecules and the Single-Branch D−π−A Analogue (2)



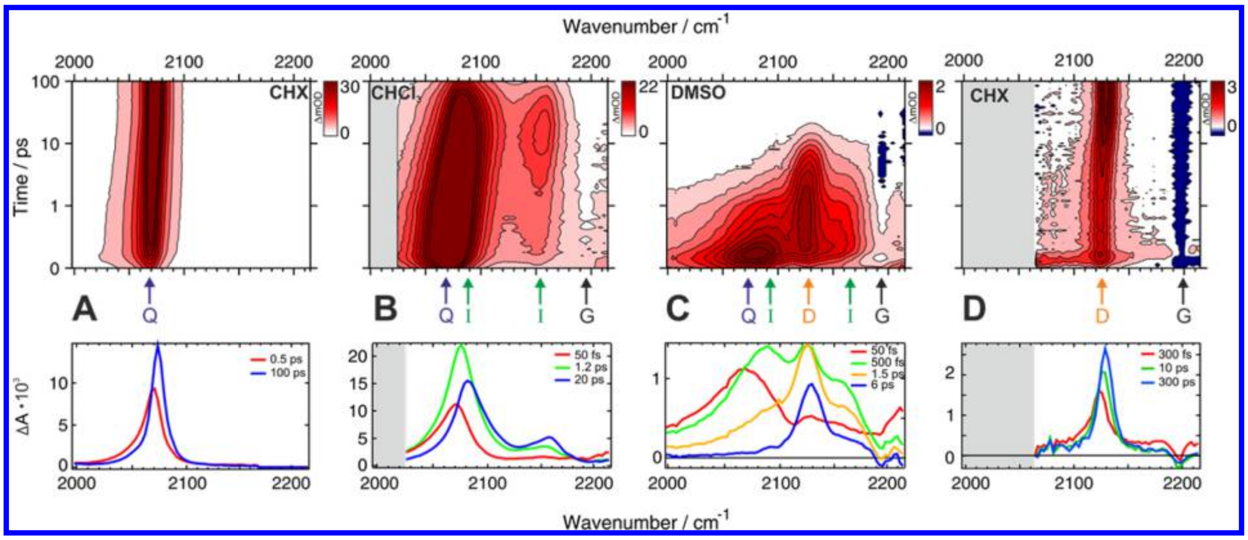


Figure 9. (top) Temporal evolution of the transient infrared absorption recorded upon 400 nm excitation of **1** in (A) cyclohexane, (B) chloroform, and (C) dimethyl sulfoxide and (D) of **2** in cyclohexane (D). (bottom) Transient spectra measured at selected time delays. (Q, quadrupolar state; I, intermediate state; D, dipolar state; G, ground state). Adapted from ref 41. Copyright 2016 American Chemical Society.

Consequently, the transformation of the TRIR spectrum from one to two bands reflects symmetry breaking in **1**.

The same early spectral dynamics are observed in highly polar solvents such as benzonitrile and dimethylsulfoxide. However, as shown in Figure 9, the two-band spectrum evolves further to a single-band spectrum, which decays with the S_1 lifetime. Unambiguous assignment of this single band can be made with the TRIR spectrum of the single-branch analogue **2**, which exhibits a single C≡C band at the same frequency in both apolar and polar solvents. Therefore, the late single-band spectrum of **1** corresponds to a purely dipolar S_1 state with the excitation fully localized on one branch. The timescales associated with these transitions from quadrupolar to partially and fully dipolar excited states are similar to those of solvent relaxation. This and the quadrupolar nature of the S_1 state in apolar solvents indicate that the symmetry breaking is due to the environment. Because of thermal fluctuations, the orientations of the solvent around the two arms of **1** just after excitation are not identical. In polar environments, this results in an asymmetry of the solvent field, and consequently, one arm of the quadrupolar Franck−Condon S_1 state is better solvated than the other. This in turn favors an asymmetric distribution of the excitation of **1** toward the better-solvated branch, which is further stabilized as solvent relaxation takes place, first via ultrafast inertial motion and then via diffusive motion on a timescale of a few picoseconds. In the most polar solvents, the asymmetry of the solvent field is large enough to fully localize the excitation on one branch.

Symmetry Breaking and H-Bonding Interactions

To figure out whether the symmetry-breaking dynamics found with **1** is general, similar measurements have been performed with the A−D−A molecule **3** (Chart 1), whose branches are shorter and contain weaker D/A pairs.[42] In nonpolar solvents, the TRIR spectrum of **3** in the C≡N stretch region also exhibits a single excited-state absorption band, indicative of a fully symmetric and quadrupolar S_1 state (Figure 10). In polar solvents, the spectrum consists of a strong band and a weak band, originating from the ν_a and ν_s C≡N stretching modes, respectively. Therefore, as for **1**, the symmetry is broken in polar solvents. However, several significant differences can be observed: (i) the two-band spectrum is observed even at the earliest time delays; (ii) this spectrum does not change significantly even in the most polar solvents; and (iii) the bandwidth, the band splitting, and the relative intensity of the ν_s band increase with solvent polarity. These observations indicate that (i) symmetry breaking occurs within the ~200 fs response time of the experiment, most probably because of the inherent asymmetry of the solvent field and inertial motion, and (ii) symmetry breaking to a fully dipolar S_1 state does not

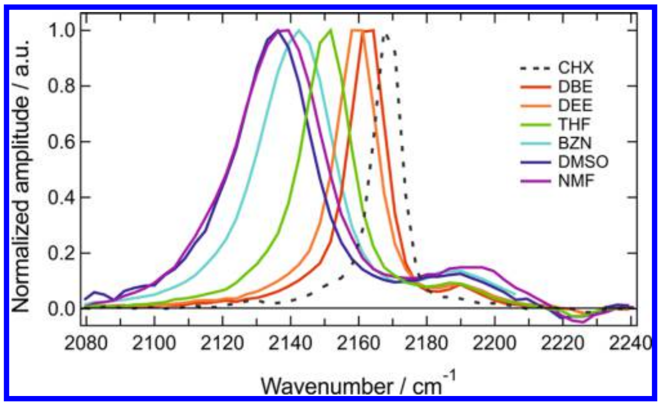


Figure 10. TRIR spectra measured after 400 nm excitation of **3** in solvents of varying polarity and corresponding to the difference absorption spectra of the relaxed S_1 state (CHX, cyclohexane; DBE, di-*n*-butyl ether; DEE, diethyl ether; THF, tetrahydrofuran; BZN, benzonitrile; DMSO, dimethyl sulfoxide; NMF, *N*-methylformamide). Adapted with permission from ref 42. Copyright 2016 Wiley-VCH Verlag.

occur, although (iii) the extent of asymmetry increases with the solvent polarity.

More pronounced spectral dynamics were observed in protic solvents.[42] In solvents with a Kamlet−Taft parameter α ranging between 0.2 (chloroform) and 1.28 (2-chloroethanol), the ν_a−ν_s band splitting exhibits a marked increase on a timescale similar to that of solvent relaxation (Figure 11). This is explained by the symmetry breaking brought about by dipolar solvation, which results in different basicities of the two C≡N ends of **3**. This in turn leads to a strengthening of the H-bonding interactions between the solvent and the more basic C≡N and to the concurrent weakening of these interactions at the other C≡N end. Therefore, the increasing band splitting reflects the amplification of symmetry breaking by H-bonding interactions. Afterward, all of the bands decay in ∼1.5 ns, in agreement with the fluorescence lifetime.

Going to more protic solvents (α > 1.5) leads to further asymmetry of the S_1 state (Figure 11). After an initial downshift, the intense ν_a band decreases and is replaced by a new band at lower frequency. An opposite but not as clear effect with a frequency upshift also takes place with the weak ν_s band. These two new bands decay in a few hundreds of picoseconds, pointing to a substantial reduction of the S_1 lifetime in these "superprotic" solvents. This can be explained by the formation of a tight asymmetric H-bonded complex consisting of **3** in the S_1 state and a solvent molecule H-bonded on the C≡N end with the higher electronic density. This process is accompanied by a decrease in the electronic density on the other C≡N group. The acceleration of the nonradiative decay upon H-bonding interactions has been observed with other molecules with a charge-transfer excited state[43,44] and is operative here. By comparison, only loose H-bond complexes are formed in the less protic solvents with too weak interactions to affect the S_1 lifetime.

By probing vibrational modes localized on specific fragments of the molecule, submolecular spatial resolution can be achieved and symmetry breaking can be clearly visualized. The TRIR results reveal the crucial role played by the environment through both specific and nonspecific interactions. This process should be quite general for any symmetric architecture with a higher-order multipolar electronic distribution, but more systematic investigations are required before definitive conclusions can be drawn. Symmetry breaking can be exploited to fine-tune the photophysical properties of the molecule with the solvent. This idea could be extended to fine-tuning of the photoreactivity. The results obtained with **3** in "superprotic" solvents represent a first step in this direction. Such effects could be strongly relevant for the photochemistry of initiators for two-photon polymerizations or for the development of sensors with high two-photon-absorption cross sections.

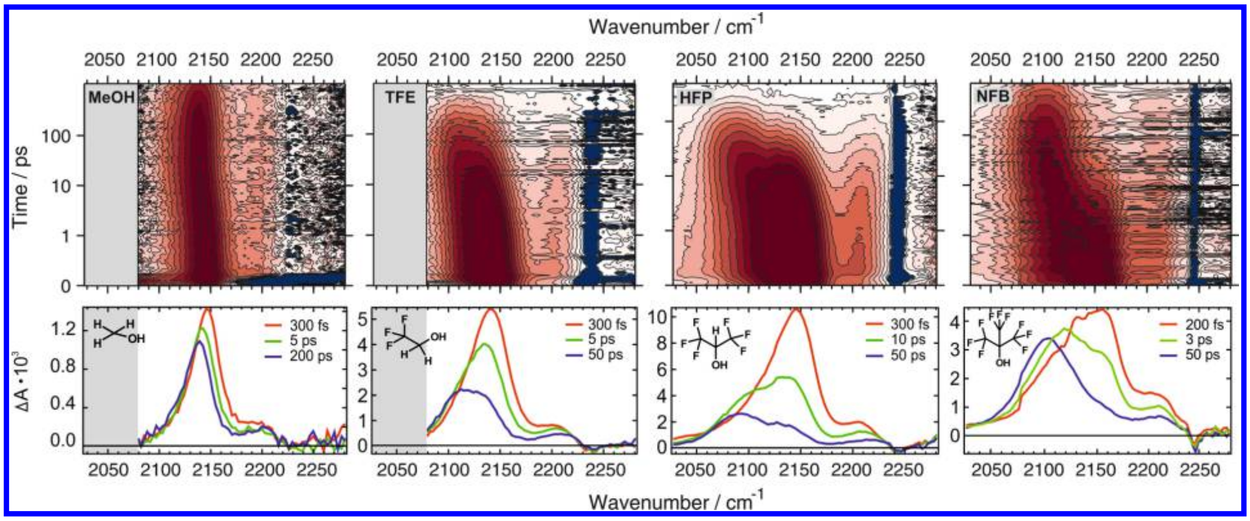


Figure 11. (top) Temporal evolution of the transient infrared absorption recorded upon 400 nm excitation of **3** in solvents of increasing H-bond-donating ability (the time axis is linear between 0 and 1 ps and is logarithmic from 1 ps to 1 ns; the transient absorption is plotted on an arcsinh scale to accentuate the weak spectral features). (bottom) TRIR spectra measured at selected time delays (MeOH, methanol (α = 0.98); TFE, trifluoroethanol (α = 1.51); HFP, hexafluoropropanol (α = 1.96); NFB, perfluoro-*tert*-butanol (α > 2)). Reprinted with permission from ref 42. Copyright 2016 Wiley-VCH Verlag.

CONCLUDING REMARKS AND OUTLOOK

TRIR spectroscopy was instrumental for obtaining rich insight into the nature of the products of bimolecular photoinduced CS processes and the origin and dynamics of symmetry-breaking charge transfer. This is due to the strong local character of some specific vibrational modes, which allows well-defined locations on a molecule to be probed selectively, as well as to the high sensitivity of their frequencies to the electronic density. Optimal exploitation of these features requires judicious selection of molecules with good vibrational markers at proper positions. In principle, similar information should also be accessible with femtosecond stimulated Raman spectroscopy.[45] The combined application of both techniques would be particularly powerful for investigating symmetry-breaking charge transfer because the relative intensities of the ν_s and ν_a bands would be opposite. Moreover, additional structural information on ion pairs and exciplexes should be obtainable with transient two-dimensional IR spectroscopy[46] by looking at the coupling between modes located on the two subunits. One can thus anticipate that our understanding of these processes should increase in the near future thanks to the further development and applications of these techniques.

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