Symmetry Breaking Hot Paper

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Symmetry-Breaking Charge Transfer and Hydrogen Bonding: Toward Asymmetrical Photochemistry

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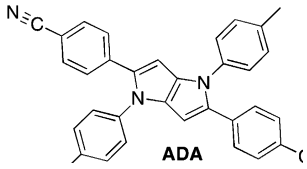
Abstract: *Symmetry-breaking charge transfer upon photoexcitation of a linear A-π-D-π-A molecule (D and A being electron donating and accepting groups) could be visualized using ultrafast time-resolved infrared spectroscopy by monitoring the CN stretching modes on the A units. Whereas in apolar solvents, the S_1 state remains symmetric and quadrupolar, symmetry breaking occurs within ca. 100 fs in polar solvents as shown by the presence of two CN bands, instead of one in apolar solvents, with a splitting that increases with polarity. In protic solvents, symmetry breaking is significantly amplified by H-bonding interactions, which are the strongest at the CN group with the highest basicity. In strongly protic solvents, the two CN bands transform in about 20 ps into new bands with a larger splitting, and the lifetime of the S_1 state is substantially reduced. This is attributed to the formation of an excited asymmetric tight H-bond complex.*

Symmetric quadrupolar molecules with D-π-A-π-D or A-π-D-π-A motifs, where D and A are electron donating and accepting units, respectively, are characterized by a large two-photon absorption (2PA) cross-section, σ_2,[1] and are thus highly advantageous for a broad range of applications.[2] Surprisingly, the fluorescence of most of these molecules exhibits a strong solvatochromism, indicative of a dipolar emissive state.[3] This has been explained in terms of symmetry breaking (SB) in the excited state induced by fluctuations of the orientation of the surrounding solvent and/or of the structure of the molecule itself.[4] However, a direct spectroscopic signature of the transition from a quadrupolar to a dipolar excited state was missing due to the lack of proper spectroscopic markers. We have recently been able to visualize this process with a D-π-A-π-D system using time-resolved IR (TRIR) spectroscopy.[5] This was achieved by monitoring vibrational modes localized on the ethyne π bridge. We found that in apolar solvents, the S_1 state is quadrupolar whereas, in polar solvents, the quadrupolar Franck–Condon (FC) S_1 state transforms into a symmetry-broken state where the density of electronic excitation on one branch is higher than on the other. In highly polar solvents, further evolution to a pure dipolar state with the excitation entirely localized on one branch occurs. The dynamics of these transitions were found to coincide with those of solvation, indicating that, in this case, symmetry breaking is driven by solvent fluctuations and relaxation.

Herein we present our results on the amplification of excited-state symmetry breaking via H-bond interactions, which can result in the formation of an asymmetric species. For this, we used a quadrupolar A-π-D-π-A molecular rod (ADA, Scheme 1), consisting of an electron-rich pyrrolo[3,2-*b*]pyrrole D core with cyanophenyl A sub-units at positions 2 and 5.[6] To visualize excited-state symmetry breaking, the CN stretch vibrations localized on both ends of ADA were monitored by TRIR spectroscopy. We will show that initial symmetry breaking occurs in all polar solvents via non-specific interactions, in agreement with our previous findings. In this case, symmetry breaking results in an increase of the basicity of one of the two CN units. Consequently, H-bonding occurs preferentially on this side, leading to further symmetry breaking. In the most protic solvents, a tight asymmetric H-bond complex, characterized by distinct spectral signatures and a strongly reduced S_1 lifetime, is formed. These results evidence the possibility to manipulate the balance of the photoreactivity of the two identical sides of quadrupolar molecules, opening new avenues for a fine-tuning of their photophysical and photochemical properties.



Scheme 1. Structure of ADA.

The electronic absorption spectrum of ADA is dominated by the $S_1 \leftarrow S_0$ band peaking around 400 nm with a weak shoulder at about 350 nm originating from the $S_2 \leftarrow S_0$ transition (Figure S1 in the Supporting Information). The inverse band intensity ratio can be observed in the 2PA spectrum (Figure S8).[7] This was shown to be in agreement with the selection rules for one- and two-photon transitions in centrosymmetric molecules.[7,8] This, together with the large 2PA cross-section ($\sigma_2 = 530$ GM at 690 nm),[7] and the negligible solvatochromism of the absorption (see Supporting Information and Figure S3), is consistent with symmetric quadrupolar S_0 and FC S_1 states. The fluorescence of ADA

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shows a substantial solvatochromism, which is not linear (Figures S2 and S3), indicating that the relaxed S_1 state has a dipolar character that increases with the solvent polarity. Overall, these data clearly point to the occurrence of symmetry breaking upon optical population of the S_1 state of ADA.

Transient electronic absorption measurements of ADA have been carried out in solvents of varying polarity (Figure S9). As discussed in more detail in the Supporting Information, the transient spectra do not exhibit a marked solvent dependence except for the dynamic Stokes shift of the stimulated emission band due to solvent relaxation. Global analysis reveals that the lifetime of the S_1 state increases from 1.0 to 1.5 ns with increasing solvent polarity, as also found by time-resolved fluorescence measurements (Table S4).

The TRIR spectra measured with ADA in the CN stretch region (2080–2240 cm^{-1}) upon $S_1 \leftarrow S_0$ excitation exhibit a much stronger solvent dependence (Figures 1 and Figure S13). In cyclohexane and other apolar solvents, the transient spectra consist of a single excited-state absorption (ESA) band around 2170 cm^{-1} and of a barely visible negative ground-state bleach (GSB) feature at 2230 cm^{-1}. Apart from a 1 cm^{-1} frequency up-shift and a 2–3 cm^{-1} narrowing in 7 ps, due to vibrational cooling,[9] no spectral change can be observed within the 0–2 ns time window. The band decreases with an approximately 1 ns time constant, in agreement with the S_1 lifetime of ADA in cyclohexane. In polar solvents, two

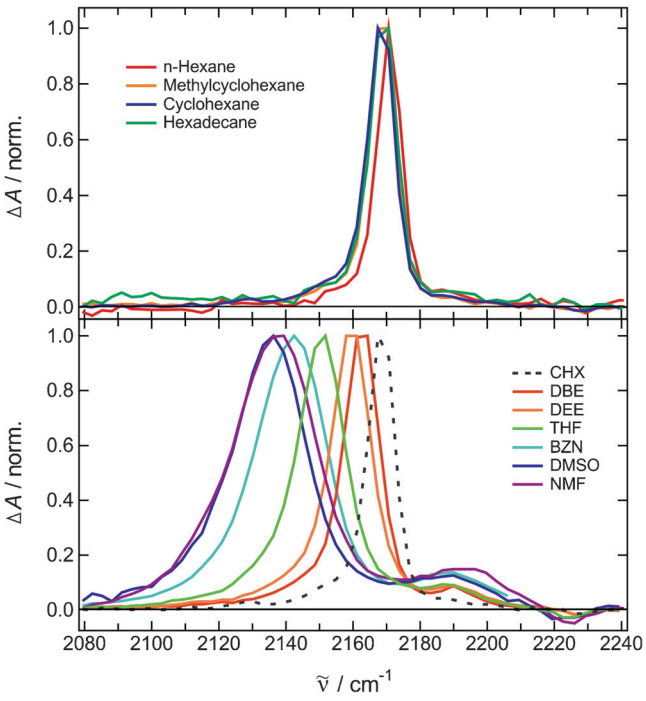

Figure 1. TRIR spectra measured after 400 nm excitation of ADA in apolar solvents of varying viscosity (top) and in solvents of varying polarity (bottom) and corresponding to the difference absorption spectra of the relaxed S_1 state (CHX: cyclohexane; DBE: di-*n*-butyl ether; DEE: diethyl ether; THF: tetrahydrofuran; BZN: benzonitrile; DMSO: dimethyl sulfoxide; NMF: *N*-methyl formamide).

ESA bands of very different intensity can be observed (Figure 1), with the most intense (ESA1) being at lower frequency than the weak one (ESA2). Both bands decay simultaneously on the ns timescale and are thus assigned to the S_1 state. Significant spectral dynamics can only be observed in benzonitrile and DMSO as a small temporal frequency downshift of ESA1 (4 and 2.5 cm^{-1}, respectively, as obtained from lineshape analysis). This shift is biphasic with time constants of 2.4 and 11 ps in benzonitrile and 0.3 and 1.9 ps in DMSO (Figure S14). Figure 1 and Figure S15 reveal that increasing the solvent polarity has several effects on the ESA bands: 1) ESA1 shifts to lower frequency, whereas ESA2 exhibits the opposite behavior; 2) the relative intensity of ESA2 increases; and 3) the width of ESA1 doubles. The transformation of the TRIR spectrum from one to two ESA bands upon going from apolar to polar solvents is an unambiguous evidence of symmetry breaking. ADA has two CN stretching modes: an IR inactive but Raman active symmetric stretch, ν_s(CN), and an IR active but Raman inactive antisymmetric stretch, ν_a(CN) (Table S6 Supporting Information). The single ESA band measured in apolar solvents can thus be assigned to the ν_a(CN) mode of ADA in the S_1 state. This state is totally symmetric with the same electronic density on both A sub-units and is purely quadrupolar. Upon symmetry breaking, the ν_s(CN) mode is no longer strictly IR inactive and, consequently, the IR spectrum exhibits a weak ν_s(CN) band beside the intense ν_a(CN) band. In other words, symmetry breaking leads to different electronic densities on both CN ends of ADA. Increasing the electronic density on a cyano A group results in a decrease of its stretch frequency.[10] Therefore, ESA1 can be attributed to the CN group located on the side of ADA with more excitation and thus with larger electronic density, whereas ESA2 can be assigned to the other CN group. The observed increase with solvent polarity of both the splitting of the bands and the relative intensity of ESA2 can be attributed to an increased asymmetry of the S_1 state, that is, to a higher dipolar character, in total agreement with the nonlinear solvatochromic plot of the fluorescence. The fact that the purely quadrupolar S_1 state cannot be observed in polar solvents at the earliest time delays indicates that the weak asymmetry of the solvent field experienced by ADA directly upon excitation might be sufficient to induce an ultrafast initial symmetry breaking without significant nuclear motion. Further symmetry breaking can then take place via inertial solvent relaxation on an approximately 100 fs timescale,[11] that is, faster than the resolution of the experiment. The temporal frequency downshift of ESA1 measured in benzonitrile and DMSO is not simply due to vibrational solvatochromism,[12] but can be assigned to additional symmetry breaking brought about by diffusive solvent relaxation as testified by the concurrent frequency upshift of ESA2. Finally, the increased width of ESA1 in highly polar solvents can be explained by the solvent fluctuations during the lifetime of the S_1 state, which lead to a distribution of the asymmetry of the solvent field and thus of the magnitude of the symmetry breaking.

Much stronger spectral dynamics were measured in protic solvents (Figure 2, Table S3). In solvents with a Kamlet–Taft

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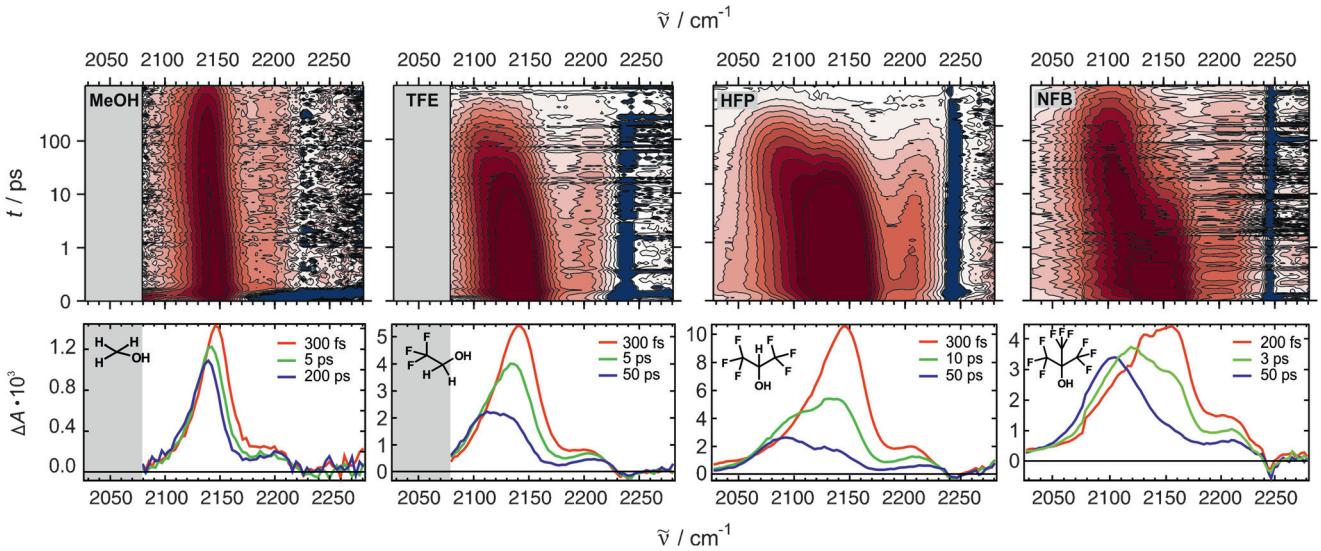

Figure 2. Top: Temporal evolution of the transient infrared absorption recorded upon 400 nm excitation of ADA in solvents of increasing H-bond donating ability (the time axis is linear between 0 and 1 ps and is logarithmic from 1 ps to 1 ns; the transient absorption is plotted on an arcsinh scale[13] to accentuate the weak spectral features). Bottom: TRIR spectra measured at selected time delays.

parameter α between 0.2 ($CHCl_3$) and 1.3 (2-chloroethanol), a distinct time-dependent splitting of the ESA bands can be seen, as illustrated with methanol in Figure 2. Quantitative analysis was mostly performed with ESA1, as a reliable determination of the maximum of ESA2 is difficult in view of its weak intensity. Whereas the initial position of ESA1 correlates with solvent polarity, as also found in the aprotic solvents, the magnitude of its temporal shift increases with α, ranging from 4.6 to 9.4 cm^{-1} when going from $CHCl_3$ to 2-chloroethanol (Figure S17). The time dependence of the peak position of ESA1 could be well reproduced using a sum of exponential functions (Figure S18) with the time constants and amplitudes listed in Table S7. These time constants are in good agreement with those of solvent relaxation reported in the literature.[11] Once the temporal shift of ESA1 and ESA2 is complete, both bands decay in around 1.5 ns, as in the aprotic solvents. More pronounced spectral dynamics were observed in the most protic solvents, trifluoroethanol (TFE, $\alpha = 1.51$), hexafluoroisopropanol (HFP, $\alpha = 1.96$,) and perfluoro-*tert*-butanol (NFB), with perfluoro-*tert*-butanol being the strongest H-bond donating solvent known.[14] Both bands shift even further than in the less-protic solvents (Figure 2). Global analysis reveals that this large shift is in fact due to the decay of ESA1 and the concurrent rise of a new band, ESA3, located at lower frequency (Figure S19). The same is apparently taking place with ESA2, that is, it transforms into a more blue-shifted band, ESA4. These changes are however less visible due to the weakness of ESA2 and its proximity with the negative GSB. The frequency of the latter also correlates with the α parameter of the solvent, pointing to H-bonding interactions in the ground state (Table S5). According to the global analysis, ESA1 and ESA2 undergo first an initial 5–10 cm^{-1} splitting in 2–3 ps before evolving to ESA3 and ESA4 in about 20 ps. Afterward, the whole TRIR spectrum decays to zero in 300, 110 and 950 ps in TFE, HFP, and NFB, respectively. These time constants coincide with the lifetime of the S_1 state of ADA measured by time-resolved fluorescence and transient electronic absorption (Table S9). Thus, the nature of the relaxed S_1 state of ADA in these three "superprotic" solvents differs markedly from that in the other solvents.

The spectral dynamics observed in all protic solvents can be explained in terms of H-bond interactions between the two CN ends of ADA and the solvent. Symmetry breaking brought about by dipolar solvation results in the excitation being more localized on one side of ADA (Figure 3). This leads to a higher electronic density on the corresponding CN group, hence to a downshift of its stretch frequency (ESA1), and to an increase of its basicity. Consequently, H-bond interactions strengthen at this CN group, favoring further polarization of the electronic density toward this side of ADA and increasing symmetry breaking. Such an enhancement of charge transfer upon H-bonding is similar to that occurring in proton-coupled electron-transfer processes.[15] The opposite takes place at the other CN end and, consequently, ESA2 shifts to higher frequency toward the GSB band, that is, the CN stretch frequency associated with ESA2 becomes closer to that in the ground state.

H-bonding in liquids is a dynamic interaction with ultrafast bond breaking and formation on a timescale of a few ps.[16] Therefore, the stoichiometry and the structure of H-bond complexes in protic solvents fluctuate rapidly. Consequently, the dynamic splitting of ESA1 and ESA2 observed in solvents with $\alpha < 1.3$ are attributed to the formation and equilibration of a loose asymmetric H-bond complex between ADA in the S_1 state and the solvent. This agrees with the good coincidence observed between the timescale of this splitting and that of solvent relaxation (Table S7). The more pronounced spectral dynamics observed in the three "superprotic" solvents is assigned to the formation of a tight H-bond complex. This is supported by the presence of distinct strongly shifted ESA bands (ESA3 and ESA4), by the unusually larger

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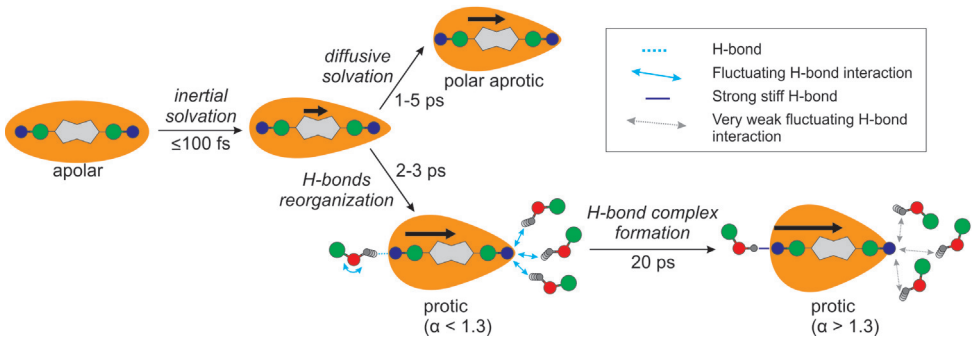

Figure 3. Schematic representation of the course of symmetry breaking of the S_1 state of ADA and approximate timescales (the orange area represents the distribution of the excitation and the black arrow the electric dipole moment). Green C of CN, blue N of CN, red O, small gray H.

H-bond donating ability of these solvents, and the shortened lifetime of the S_1 state. The acceleration of the non-radiative decay of excited molecules by H-bond interactions is well documented.[17] The mechanism of this radiationless deactivation in a tight H-bond complex will be discussed in detail elsewhere.

This assignment of ESA3 and ESA4 also agrees with the time-resolved fluorescence and transient electronic absorption spectra (see Supporting Information for a detailed discussion). Their global analysis results in time constants very similar to those found with the TRIR data (Table S9). The initial splitting of ESA1 and ESA2 occurs on the same timescale (2–3 ps) as the partial Stokes shift of the fluorescence and can be assigned to an initial stage of diffusive solvation and to the formation of a loose asymmetric H-bond complex. The transformation into ESA3 and ESA4 takes place with a similar time constant (ca. 20 ps) than further Stokes shift of the fluorescence. The relaxation dynamics of these three solvents is not known, but the formation of a tight complex requires some reorganization of the solvent around ADA. Therefore, this approximately 20 ps time constant is probably related to diffusive solvent motion. On the other hand, given the similarity of this time constant in these three different solvents, the rearrangement of intramolecular modes of ADA cannot be excluded.

The course of the symmetry breaking process in ADA upon photoexcitation is schematically summarized in Figure 3. Symmetry breaking could be clearly visualized thanks to the presence of appropriate vibrational markers located at the two ends of this molecular rod. The results presented here reveal the primordial influence of solute/solvent interactions on the distribution of the electronic excitation in symmetric molecules and on the magnitude of symmetry breaking. An important consequence of symmetry breaking is the ensuing asymmetry of the photoreactivity, the magnitude of which can be fine-tuned with the solvent. This was unambiguously illustrated here with the formation of an asymmetric H-bond complex. In principle, this effect could be extended to other reactions. We think that such detailed knowledge will be of use for understanding and possibly controlling the photochemistry of quadrupolar chromophores, such as the initiators for two-photon induced polymerization, as well as for the development of environment-sensitive probes with a high 2PA cross-section.

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