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Excited-State Symmetry Breaking and the Laporte Rule

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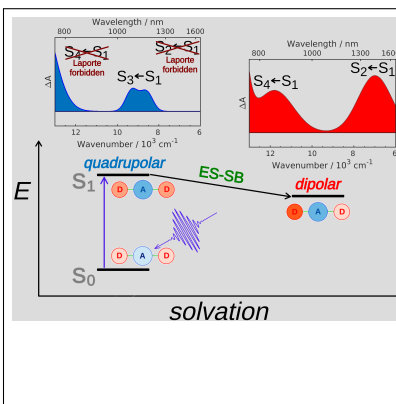
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Abstract

Excited-state symmetry breaking (ES-SB) is common to a large number of multi-branched electron donor acceptor (DA) molecules in polar environments. During this process, the electronic excitation, originally evenly distributed over the molecule, localizes, at least partially, on one branch. Due to the absence of an unambiguous spectroscopic signature in the UV-Vis region, electronic transient absorption (TA) has not been the method of choice for real-time observation of this phenomenon. Herein we demonstrate that the Laporte rule, which states that one-photon transitions conserving parity are forbidden in centrosymmetric molecules, provides such clear signature of ES-SB in electronic TA spectroscopy. Using a dicyanoanthracene-based D-A-D dye, we show that transitions from the S_1 state of this molecule, which are initially Laporte forbidden, become allowed upon ES-SB. This leads to the rise of new TA bands, whose intensity provides a direct measure of the extent of asymmetry in the excited state.

Graphical TOC Entry



Excited-state symmetry breaking (ES-SB) in multibranched electron donor-acceptor (D- A_n or A- D_n) conjugates has focussed considerable attention over the past few years.¹⁻²² One major interest for these molecules stems from their large cross-section for two-photon absorption (TPA),^{23,24} which makes them attractive for a broad variety of applications, ranging from fluorescence imaging to microfabrication.²⁵⁻³⁶ However, the strong solvent dependence of their excited-state properties makes them intriguing per se. Upon optical excitation in a non-polar medium, their electronic structure is generally symmetric, whilst in polar environments, the symmetry of the electronic distribution breaks, resulting in the partial or complete localization of the excitation on one of the D-A branches. This ES-SB has been shown to be triggered by the fluctuations of the surrounding solvent field and to occur on the time scale of solvent motion.^{5,6,37-39} Time-resolved IR (TRIR) absorption spectroscopy has proven to be particularly powerful for monitoring ES-SB, as the selection rules for vibrational absorption are closely related to symmetry.^{4-7,17,40} The excited-state properties of these multipolar dyes can be rationalized with a simple excitonic model, where each D-A branch can be viewed as an individual chromophore.^{10,37,41} Therefore, the S_1 state of a single D-A branch is split in two, S_1 and S_1' , in its two-branched D-A-D or A-D-A analogue by an amount that depends on the excitonic coupling. Upon ES-SB, excitation localises on one arm and the splitting vanishes. This has been observed experimentally by monitoring the disappearance of the $S_1' \leftarrow S_1$ absorption band in the mid-IR,^{8,9,42} or the decrease of the emission transition dipole by time-resolved fluorescence.^{9,10,16,18} However, apart from the decrease of the excitonic $S_1' \leftarrow S_1$ band measured by TRIR spectroscopy, direct observation of ES-SB using electronic transient absorption (TA) spectroscopy has not been successful so far, because of the lack of clear signature of this process in the UV-Vis region.^{11,12,15} Nevertheless, like for vibrations, the selection rules for electronic absorption are sensitive to symmetry. This is reflected by the Laporte rule,⁴³ which states that one-photon electronic transitions conserving the parity of the wavefunction (i.e., gerade transitions, $g \leftrightarrow g$ or $u \leftrightarrow u$) are forbidden in centrosymmetric molecules. However, this rule no longer holds for asym-

metric systems. Therefore, Laporte-forbidden electronic transitions should become allowed upon ES-SB.

Here, we report on the first observation of ES-SB based on the Laporte rule using electronic TA spectroscopy. We demonstrate this using a centrosymmetric dicyanoanthracene-based D-A-D dye, **Q**, and its dipolar D-A analogue, **D**, as reference (Figure 1). We show that, although **Q** has vibrational marker modes localised in the D-A branches, the spectroscopic signature of ES-SB in the TRIR spectra is ambiguous, whereas it is unequivocal in the electronic TA spectra.

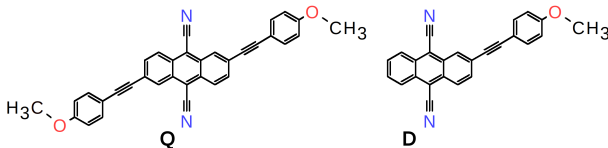


Figure 1: Structure of the dyes **Q** and **D**

The synthesis and basic photophysical properties of **Q** and **D** were reported previously.⁴⁴ In brief, both dyes show a negligible solvatochromism in absorption (Figures S3-S4) but a strong and non-linear solvatochromism in fluorescence (Figures S5-S11). In medium and highly polar solvents, the emission spectra of **Q** and **D** are almost identical (Figures S8-S10) pointing to a similar nature of their excited state and, thus, to ES-SB in **Q**. A non-linear solvatochromism is expected for **Q**, because the excited state changes from quadrupolar to dipolar upon ES-SB. Such behaviour is however less common for a dipolar dye like **D** and suggests that the charge-transfer character of its S_1 state increases significantly with solvent polarity.

The TRIR spectra measured with **Q** in the $-C\equiv C-$ and $-C\equiv N$ stretching region conform with those expected for a quadrupolar S_1 state in non-polar solvents and with ES-SB in polar environments (Figures S16-S18). In cyclohexane (CHX), the spectra are dominated by an intense excited-state absorption (ESA) band, ESA1, at 2045 cm^{-1} , which decays on the ns time scale (Figure 2). Based on previous studies, ESA1 can be assigned to the antisymmetric $-C\equiv C-$ stretching mode of the symmetric and quadrupolar S_1 state.^{5,6,45} At early time in

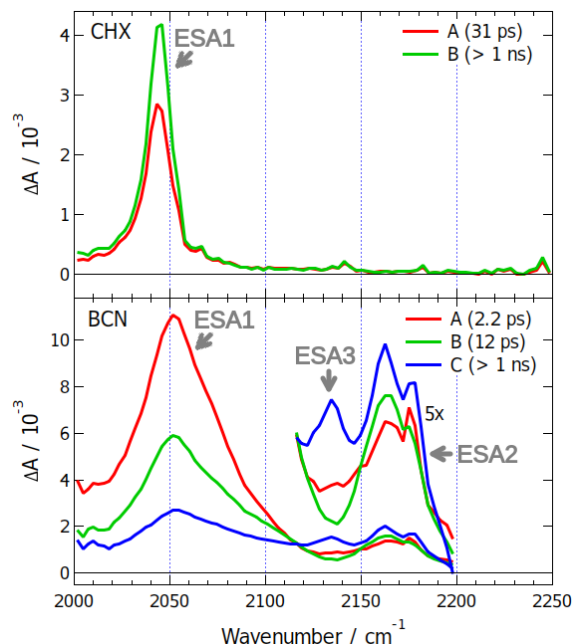


Figure 2: Evolution-associated difference spectra in the triple bond stretching region and time constants obtained from the global analysis of the merged TRIR–electronic TA spectra measured with **Q** in cyclohexane (CHX) and in benzonitrile (BCN) assuming a series of successive exponential steps (A→B→...). The spectra in BCN are cut above 2200 cm^{-1} because of the intense $-\text{C}\equiv\text{N}$ stretch absorption band of the solvent.

polar solvents, ESA1 is broader, and weaker features, ESA2, that can be attributed to the $-\text{C}\equiv\text{N}$ stretching modes, are also visible around $2165\text{--}70\text{ cm}^{-1}$.⁴⁶ ESA1 weakens within a few ps and a new band, ESA3, rises at 2135 cm^{-1} . According to time-resolved anisotropy measurements, ESA3 can be attributed to the $-\text{C}\equiv\text{C}-$ stretching mode of the symmetry-broken state (see SI, Section S3.1 for details).

In principle, one would expect the TRIR spectra measured with **D** to be similar to those of the symmetry-broken state of **Q**.⁵ Unexpectedly, they exhibit a solvent dependence that resembles those of **Q** (Figure 3). Such an effect can be attributed to the weakness of the anisole donor group and, hence to a strong dependence of the charge-transfer character of the $S_1\leftarrow S_0$ transition on the solvent polarity (see Section S3.2 for further discussion). This is consistent with the non-linear fluorescence solvatochromism of **D** and with an increase of the dipole moment of the S_1 state with solvent polarity. Because of this significant solvent dependence of the electronic structure of **D** itself, the IR spectral dynamics measured with

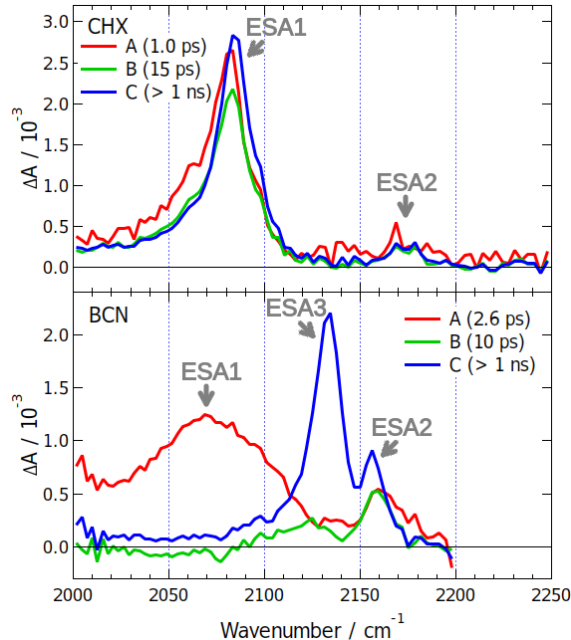


Figure 3: Evolution-associated difference spectra in the triple bond stretching region and time constants obtained from the global analysis of the merged TRIR–electronic TA spectra measured with **D** in cyclohexane (CHX) and in benzonitrile (BCN) assuming a series of successive exponential steps ($A \rightarrow B \rightarrow \dots$). The spectra in BCN are cut above 2200 cm^{-1} because of the intense $-\text{C}\equiv\text{N}$ stretch absorption band of the solvent.

Q cannot be really considered as unambiguous evidence of ES-SB.

We now turn to electronic TA spectroscopy to demonstrate how such evidence can be obtained by considering the Laporte rule. We first examine the electronic transitions occurring from the S_1 state of **Q** and **D** on the basis of quantum-chemical calculations at the time-dependent density functional level of theory (Figure 4 and SI Section S4.1 for details).

In accordance with the excitonic model, the calculations predict that several excited states of **D** split when going to **Q**. For example, the S_1 state of **D** splits into S_1+S_3 in **Q** (see SI, Section S4.1). Moreover, in agreement with the Laporte rule, the one-photon transitions of **Q**, which are forbidden from the gerade S_0 state are allowed from the ungerade S_1 state. This rule does no longer apply for **D** and none of the transitions from the S_0 and S_1 states are parity forbidden. Therefore, the electronic TA spectrum of **Q** in the symmetric excited state should only exhibit the $S_3 \leftarrow S_1$ and $S_5 \leftarrow S_1$ ESA bands. However, upon ES-SB and uneven distribution of the excitation over the two D-A branches, additional ESA bands

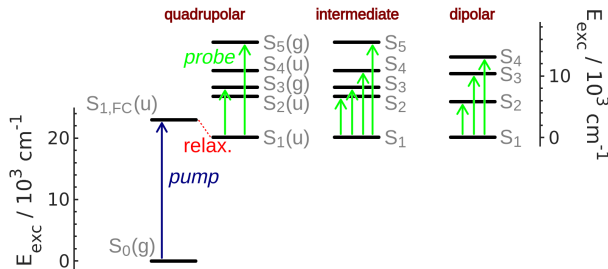


Figure 4: Calculated (ω B97X-D/6-31+G*, vacuum) excitation energies and parities of the singlet states of **Q**. The $S_{2-5} \leftarrow S_1$ excitations were estimated as $E(S_{2-5} \leftarrow S_1) = E(S_{2-5} \leftarrow S_0) - E(S_1 \leftarrow S_0)$ calculated at the optimized S_1 geometry for the quadrupolar and intermediate states, and at the optimized S_1 geometry of **D** for the dipolar state. Gerade and ungerade symmetries are designated as (g) and (u), respectively.

corresponding to the $S_2 \leftarrow S_1$ and $S_4 \leftarrow S_1$ transitions should become visible. Finally, upon complete localization of the excitation on one D-A arm, the electronic TA spectrum of **Q** should resemble that of **D**. These ESA bands are predicted to be at relatively low energy, i.e. in the red and near IR regions of the spectrum (SI, Section S4.1).

Based on these calculations, we extended the spectroscopic window of the electronic TA measurements up to 1500 nm (SI, Section S3.5). Figures 5, S28 and S33 depict the evolution-associated difference spectra (EADS) in the UV-Vis-NIR region resulting from the global analysis of the merged TRIR–electronic TA data measured with **Q** and **D** in solvents of different polarity.⁴⁷ The region above 600 nm contains only positive bands that can be attributed to $S_{2-5} \leftarrow S_1$ transitions. ESA bands due to transitions to higher excited states are present below 600 nm but overlap with negative bands originating from ground-state bleach and stimulated emission (SE). The presence of these negative bands together with the dynamic Stokes shift of the SE band upon solvent relaxation complicate the interpretation of the TA spectra below 600 nm.

The TA spectra measured with **Q** in CHX exhibit a single ESA band with a vibronic structure in the NIR region, which can be assigned to the $S_3 \leftarrow S_1$ transition. The presence of a single ESA band points to a symmetric electronic structure of the S_1 state, with Laporte forbidden $S_2 \leftarrow S_1$ and $S_4 \leftarrow S_1$ transitions. In contrast, all the computed transitions of **D**

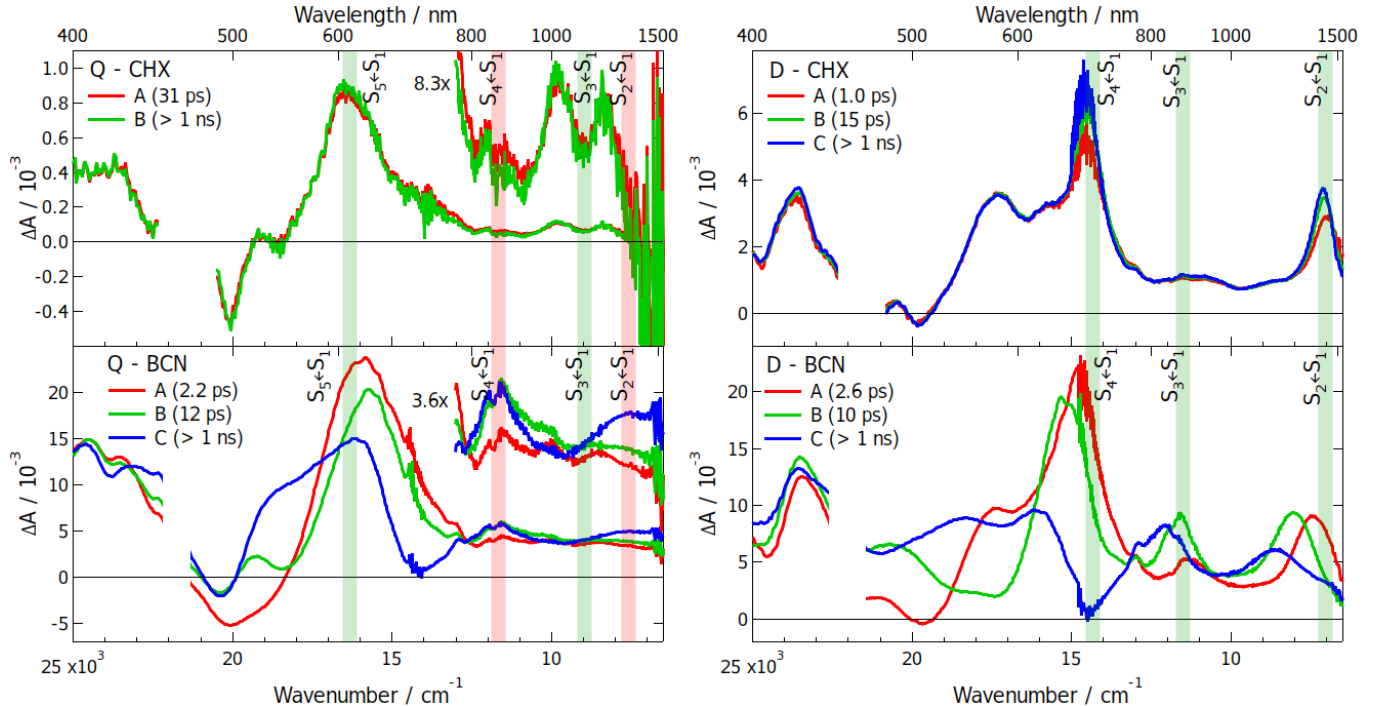


Figure 5: Evolution-associated difference spectra in the UV-Vis-NIR region and time constants obtained from the global analysis of the merged TRIR–electronic TA spectra measured with **Q** (left) and **D** (right), in cyclohexane (CHX) and in benzonitrile (BCN), assuming a series of successive exponential steps ($A \rightarrow B \rightarrow \dots$). The green (allowed) and red (Laporte forbidden) vertical lines represent the calculated $S_{2-5} \leftarrow S_1$ transitions shifted by 800 cm^{-1} for **Q** and by 1100 cm^{-1} for **D**.

are observable in this solvent. Only minor spectral dynamics take place during the whole temporal window, as also found in the mid-IR (Figures 2 and 3).

More pronounced spectral changes are visible in polar solvents. The early spectra measured with **Q** in benzonitrile (BCN) are similar to those in CHX. However, two new ESA bands rise around 1350 and 850 nm (7500 and 11700 cm^{-1}) on a timescale similar to that of solvent motion.⁴⁸ These wavelengths are in excellent agreement with those predicted for the $S_2 \leftarrow S_1$ and $S_4 \leftarrow S_1$ transitions, respectively. The rise of these bands associated with Laporte forbidden transitions can be considered as direct evidence of ES-SB in BCN. Similar spectral dynamics can be observed in the more polar N-methyl-formamide (NMF), where these bands are even more pronounced (Figure S28), indicative of a larger extent of asymmetry of the relaxed S_1 state. Furthermore, the weakening of the $S_3 \leftarrow S_1$ band in the late spectra,

particularly in NMF, suggests an electronic structure of the excited state of **Q** similar to that of **D**, i.e. a close to full localization of the excitation on one branch. On the other hand, the TA spectra measured with **D** in polar solvents resemble those in CHX, with additionally a significant spectral dynamics due mostly to the dynamic Stokes shift of the SE band (Figure S31).

These findings support our hypothesis that the intensity of initially Laporte-forbidden transitions is closely related to the dissymmetry of the excited-state wavefunction and can be used as a direct measure of ES-SB.

In conclusion, we have presented a new approach based on the Laporte rule for monitoring ES-SB in centrosymmetric molecules using electronic TA spectroscopy. As the electronic structure of the excited state becomes asymmetric, new absorption bands become visible in the TA spectrum. This strategy is more general than that based on TRIR spectroscopy as it can be applied to A-D_n and D-A_n dyes that do not have vibrational marker modes localised in their branches. Moreover, the presence of such vibrational modes does not warrant unambiguous evidence of ES-SB by TRIR spectroscopy, if the excited-state properties of the single branch analogue itself depend on the solvent polarity, as shown here with **D**. The approach presented here is also more direct than the measurement of the emission transition dipole by time-resolved fluorescence, that becomes problematic with short-lived excited states. It works best in the near IR region, where the density of ESA bands is the lowest and where complications due to e.g. an overlapping SE band are absent. This new addition to our spectroscopic toolbox should contribute to a better understanding of the charge-transfer dynamics in symmetric molecular systems.

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Supporting Information Available

Experimental details, stationary absorption and emission, TRIR dynamics, TRIR anisotropy, global analysis, additional TRIR and TA spectra, quantum chemical calculations.

All data can be downloaded from <https://doi.org/10.26037/yareta:ll6hei2zbbzbqveaqhli4pcyqgi>

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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