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Watching Excited-State Symmetry Breaking in Multibranched Push-Pull Molecules

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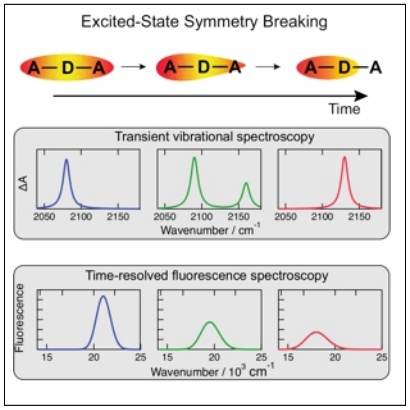
Abstract

The emissive properties of symmetric molecules containing several donor-acceptor branches are often similar to those of the single-branched analogues. This is due to the localisation, at least partial, of the excitation on one branch. Detailed understanding of this excited-state symmetry breaking (ES-SB) requires the ability to monitor this process in real time. Over the past few years, several spectroscopic approaches were shown to enable visualisation of ES-SB and of its dynamics. They include the detection of new vibrational or electronic absorption bands associated with transitions that are forbidden in the symmetric excited state. Alternatively, ES-SB can be detected by observing transitions that become weaker or vanish upon localisation of the excitation. Here, we discuss these different approaches as well as their merits and weaknesses.

Graphical TOC Entry



Keywords

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Over the past few years, symmetric molecules containing two or more electron donor-acceptor (D-A) branches have been attracting considerable attention. These molecules are being increasingly used as two-photon absorbers, electron acceptors or new luminescent materials in applications as diverse as fluorescence microscopy,[1,2] photopolymerisation,[3,4] organic photovoltaics,[5,6] or organic light-emitting diodes.[7,8] Although these compounds do not possess a permanent electric dipole moment, their fluorescence usually exhibits a strong solvatochromism that is, in same cases, as large as that measured with the single-branched D-A analogue.[9–14] This behaviour was explained in terms of excited-state symmetry breaking (ES-SB), i.e. a transition from a symmetric and multipolar state to an asymmetric and dipolar state.[10,15] In principle, emission solvatochromism cannot be considered as an unambiguous evidence of ES-SB, unless it is as large as that of the single-branch analogue. Indeed, quadrupole-dipole and octupole-dipole interactions do also contribute to the solvation energy and, hence, give rise to a solvatochromism. In the point quadrupole/octupole approximation, these interactions are much weaker than the dipole-dipole interaction as their energy is inversely proportional to the fifth and seventh power of the cavity radius, respectively.[16] However, considering that the length of a D-A branch is usually much larger than the size of a solvent molecule, the field perceived by the surrounding medium is certainly not that from a quadrupole or an octupole but rather the field generated by the dipole of the nearby branch. Based on this, the solvation energy of a molecule in a delocalised quadrupolar state was estimated to range from one eighth to one half of the solvation energy of the same molecule in a localised dipolar state, depending on the cavity model used.[17] Although a fluorescence solvatochromism as large as that of the single-branched analogue can be considered as evidence of ES-SB, not much can be concluded about the extent of ES-SB in non-polar or weakly polar environments.

Because of this, there is a need for methods giving a more reliable picture of the distribution of the excitation on the molecule and of its temporal changes. The first investigations of the ES-SB dynamics were carried out using transient electronic absorption spectroscopy in the UV-Vis region. However, no significant differences between the transient spectra of the multipolar dyes and those of their dipolar analogues could be found.[18–21] In the following, we discuss spectroscopic approaches that proved to allow for a direct, real-time, visualisation of ES-SB. We consider the pros and cons of each of them and show that the choice of the method depends strongly on the molecule under study.

Looking at symmetry-forbidden vibrational transitions. The vibrations of molecules with a centre of inversion are powerful reporters of the symmetry, because, as stated by the rule of mutual exclusion, a vibrational mode cannot be both IR and Raman active. Consequently, the loss of inversion symmetry leads to an increase in the number of vibrations visible in both the IR and Raman spectra. Since the detection of new bands in the IR absorption spectrum of polyacetylene films upon doping,[22] this idea has been advantageously exploited for investigating charge localisation in conjugated polymers.[23–26] This effect was explained by the loss of local symmetry of the polymer backbone as the injected charges self-localise.[26] As a consequence, Raman-active vibrational modes, that are normally IR silent, become IR-active vibrational (IRAV) modes.

Implementation of this approach to monitor ES-SB requires ultrafast vibrational spectroscopy. The first IR transient absorption (TA) study of the ES-SB dynamics was carried out with the D-π-A-π-D dye **1** illustrated in Chart 1.[27] It was selected for the presence of the -C≡C- ethyne groups, whose high-frequency stretching vibrations are localised in the D-A branches. Although dye **1** is not strictly centrosymmetric, its one- and two-photon electronic absorption spectra show the typical mutually exclusive selection rules for molecules with a centre of inversion. Additionally, it exhibits a very strong fluorescence solvatochromism, suggestive of ES-SB, at least in polar environments. As illustrated in Figure 1, the IR TA spectrum

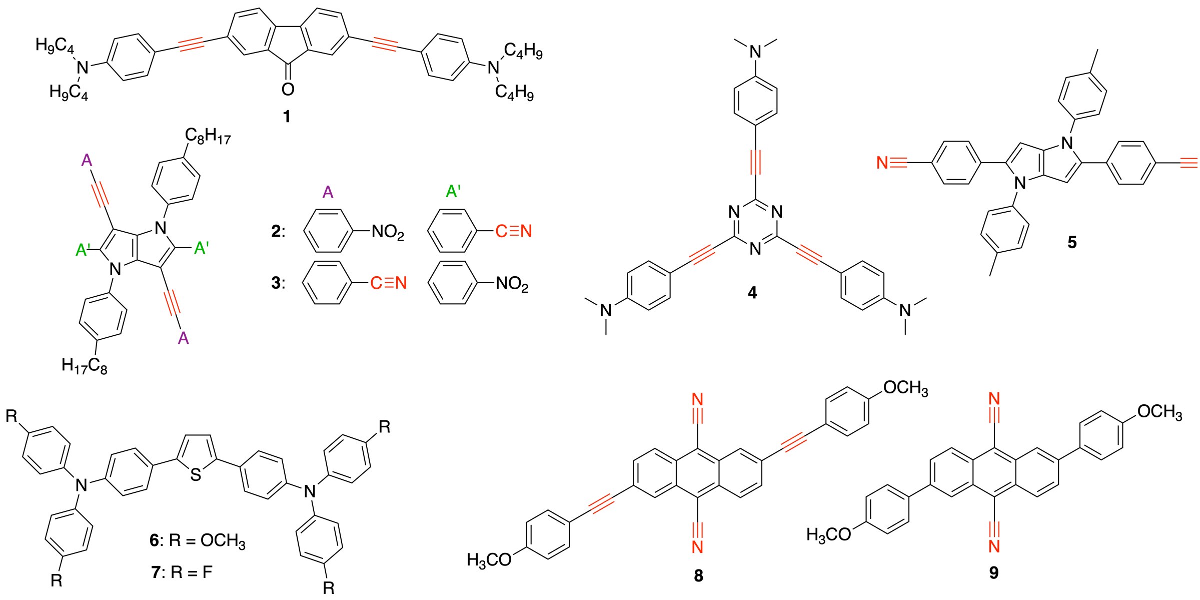

Chart 1: Structure of the multi-branched molecules discussed in this article. The vibrational markers are depicted in red.

of **1** in the -C≡C- stretching region measured directly after $S_1 \leftarrow S_0$ excitation in the non-polar cyclohexane exhibits a single excited-state absorption (ESA) band and remains unchanged during the whole 0-2 ns time window of the experiment. This band, assigned to the anti-symmetric -C≡C- stretch of **1** in the S_1 state, was interpreted as an indication of a symmetric and quadrupolar excited state.

A single band is also visible at early time in the medium polar chloroform, before the sub-ps rise of a second band around 2160 cm^{-1} (Figure 1). The presence of this second -C≡C- stretching band was attributed to the loss of centrosymmetry of the S_1 state. It is due to a vibration that is only IR active upon ES-SB and is, thus, equivalent to an IRAV mode. In highly polar solvents, the IR TA spectra evolve further and only a single band remains visible after a few ps. By comparison with the transient spectra of the single-branched analogue, this band could be attributed to the purely dipolar S_1 state, with the excitation entirely localised on one of the two branches. This example reveals that IR TA spectroscopy not only allows ES-SB to be visualised in real time but gives additionally rich insight into the location of the excitation, such as an uneven distribution on the two branches of **1** in medium polar solvents, or a full localisation in highly polar media. This is also supported by a theoretical model developed by Ivanov and co-workers, enabling the IR spectral dynamics upon ES-SB to be reproduced.[28,29]

This strategy was since applied to investigate ES-SB in other linear D-A$_2$ or A-D$_2$ molecules containing -C≡C- groups in their branches,[17,30,31] and/or -C≡N groups at their periphery.[32–34] Valuable information on the direction of the ES-SB in more complex multi-branched dyes like **2** and **3** (Chart1) could also be obtained using this spectroscopy.[35] In dye **2**, electronic excitation is evenly distributed over the two D-π-A branches in non-polar solvents and localises entirely on a single branch upon ES-SB in medium to polar solvents. However in dye **3**, where the A and A' acceptors are swapped, no -C≡C- ESA band could be observed in non-polar solvents indicating that the electronic excitation is mostly concentrated on the A'-D-A' core. In polar solvents, the excitation localises at least partially on one D-π-A branch as testified by the appearance of new -C≡C- ESA features.

In principle, similar information on ES-SB can be obtained using time-resolved Raman spectroscopy, the main difference being that now the anti-symmetric vibrations become Raman active upon ES-SB. Femtosecond stimu-

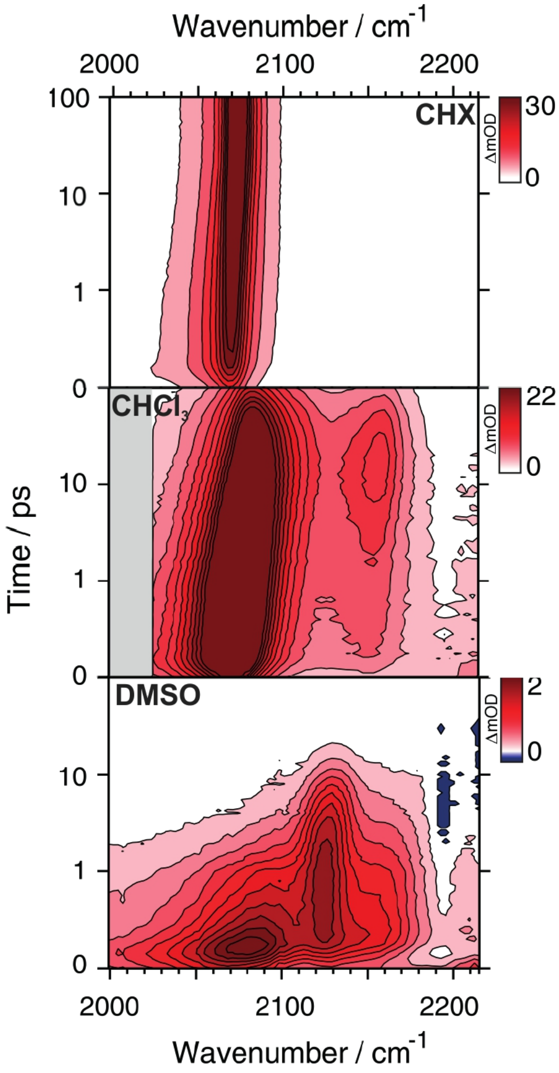

Figure 1: Observation of excited-state symmetry breaking using transient IR absorption upon 400 nm excitation of dye **1** in (A) cyclohexane (CHX), (B) chloroform ($CHCl_3$), and (C) dimethyl sulfoxide (DMSO). (Adapted with permission from ref. 27. Copyright 2016 American Chemical Society).

lated Raman spectroscopy was used to study A-D-A systems with a methylated oligosilane core and cyanovinyl-subtituted arene donors.[36] Relatively minor spectral dynamics could be observed in the -C=C- and -C=O stretching regions in polar solvents, suggesting that ES-SB was faster than the time resolution of the experiment.

Proper visualisation of ES-SB using time-resolved vibrational spectroscopy requires molecules with vibrational markers located within the D-A branches and/or at their end.

Detection of ES-SB in conjugated molecules without such specific markers, for example by looking at -C=C- vibrations, is much less straightforward and might be not totally unambiguous.[36,37]

Looking at electronic transitions in the mid-IR. Figure 2A shows transient IR spectra recorded at various delays after $S_1 \leftarrow S_0$ excitation of the three-branched dye **4** (Chart 1) in $CHCl_3$.[31] Sharp positive and negative spectral features can be seen on a broad positive background signal. After about 10 ps, the latter has entirely vanished, whereas vibrational bands are still visible. By contrast, in non-polar solvents, this broad band is present during the whole excited-state lifetime of the dye, > 1 ns. This feature can also be seen with the quadrupolar two-branched analogue of this dye, but is absent with the dipolar single branch.[31] Broad background absorption in the 2000-2500 cm^{-1} region with similar solvent-dependent dynamics was also observed with other multipolar dyes, such as dye **3**.[35] Its presence in the same spectral region as the vibrational markers bands complicates the detection of ES-SB via the rise of new vibrational transitions. In fact, this overlap leads to a distortion of the vibrational bandshape similar to those observed with Fano resonances.[38,39]

In the case of dye **5**, the red side of a broad band was observed above 3400 cm^{-1}, a frequency region which does not correspond to any molecular vibration.[40] Consequently, ES-SB in this dye could be clearly detected by monitoring its -C≡N stretching vibrations.[32] The decay of the broad absorption band was found to occur in parallel to ES-SB. This observation, together with those made with dye **4** and its quadrupolar and dipolar analogues, reveal that the broad mid-IR absorption is an intrinsic spectral signature of a delocalised excited state. The nature of this transition can be understood using a simple Frenckel exciton model, where each D-A branch is a chromophore with a charge-transfer (CT) excited state (Figure 2B). For a three-branched molecule like dye **4**, this model predicts the S_1 state to be doubly degenerated, and the Davidov splitting with the

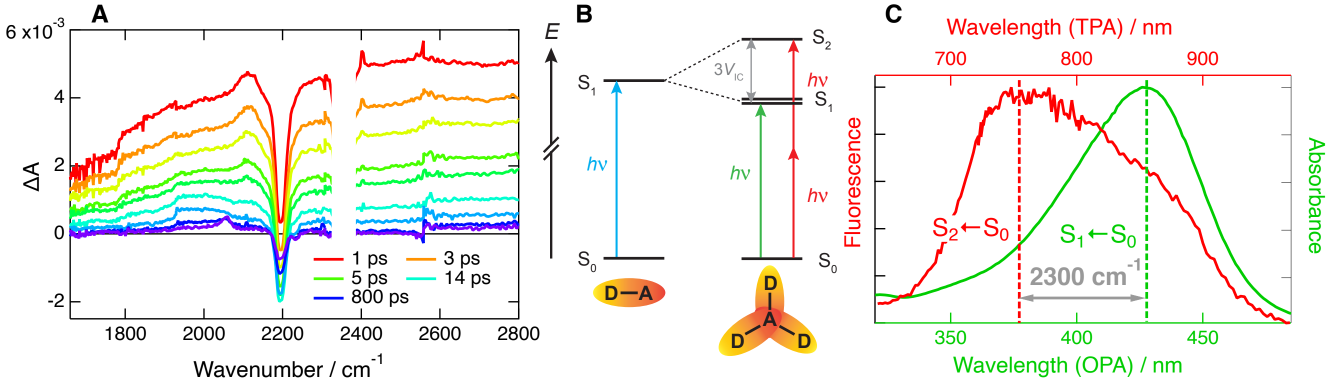

Figure 2: Mid-IR electronic absorption of the delocalised excited state. A) Transient IR absorption spectra recorded as various time delays after $S_1 \leftarrow S_0$ excitation of dye **4** in chloroform. B) Frenkel exciton model of the lowest electronic excited states of a three-branched dye. C) One-photon absorption spectrum (green) and two-photon excitation spectrum (red) measured with dye **4**. The energy difference between the band maxima corresponds to the Davidov splitting $3V_{IC}$. (Adapted from ref. 31).

S_2 state to amount to $3V_{IC}$, where V_{IC} is the inter-branch excitonic coupling. The lowest and highest excitonic states result from the additive and subtractive interactions between the transition dipoles on each D-A branch. As a consequence, the $S_1 \leftarrow S_0$ transition is one-photon allowed but weakly two-photon active, whereas the $S_2 \leftarrow S_0$ transition is one-photon forbidden and two-photon allowed.[41] For a linear two-branched molecule, the two excitonic states are splitted by $2V_{IC}$. As these molecules are centrosymmetric, the selection rules for one- and two-photon absorption are mutually exclusive: the $S_1 \leftarrow S_0$ transition is one-photon allowed and two-photon forbidden, while the opposite holds for the $S_2 \leftarrow S_0$ transition.

The Davidov splitting can, thus, be estimated by comparing the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transition energies extracted from the one- and two-photon absorption spectra illustrated in Figure 2C. For dyes **4** and **5**, it was found to amount to about 2300 and 4000 cm^{-1}, respectively.[31,40] These energies coincide with the positions of the broad absorption band observed in the mid IR. Consequently, these features were attributed to the $S_2 \leftarrow S_1$ electronic transition of the delocalised excited state of **4** and **5**, which, according to the exciton model, is one-photon allowed. As ES-SB takes place, excitation localises increasingly on one branch. Consequently, the Davidov splitting decreases and vanishes completely upon full localisation. In parallel to this, the dipole for the transition between these excitonic states decreases as well and vanishes for full localisation. This decay of the oscillator strength is probably the reason why no band shift could be observed so far upon ES-SB. However, giving the generally narrow spectral window of most IR TA setup, reliable measurement of the shape of such electronic absorption band is not straightforward.

This IR spectral signature of the delocalised state is a valuable alternative to time-resolved vibrational spectroscopy, especially for molecules which lack properly located vibrational markers. In principle, the position of this transition can be estimated beforehand from the Davidov splitting and therefore no lengthy scan throughout the mid IR is required. For some molecules where V_{IC} is very large, this transition may be situated in a spectral region difficult to access experimentally. In those cases, visualisation of ES-SB requires another approach.

Monitoring the oscillator strength for emission. Although powerful for monitoring ES-SB, the two above approaches require IR TA, which is not as widely available as time-resolved fluorescence or UV-Vis TA. As discussed in this section and the next one, these two techniques can also be exploited to investigate ES-SB dynamics in a wide variety of molecules. Figure 3A shows time-resolved emission spectra recorded by broadband fluorescence up-conversion spectroscopy with the two-branched molecules **6** and **7** in the polar DMSO.[42] These two dyes are characterised by similar fluorescence quantum yields (around 0.6-0.7) and lifetimes (1-2 ns) in this solvent. However, only dye **6** exhibits a strong fluorescence solvatochromism, pointing to ES-SB in **6** but not in **7**, in agreement with the different electron-donating strength of the methoxy- and fluoro-phenyl substituents.

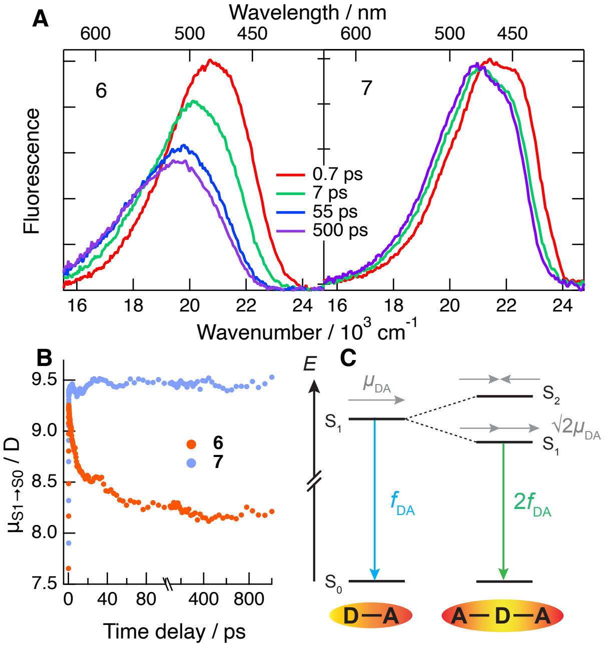

Figure 3: Excited-state symmetry breaking detected by time-resolved fluorescence: A) Transient fluorescence spectra recorded as various times after $S_1 \leftarrow S_0$ excitation of dyes **6** and **7** in dimethyl sulfoxide. B) Time evolution of the $S_1 \to S_0$ transition dipole. C) Frenkel exciton model illustrating the difference of emission dipole moment, μ, and oscillator strength, f, when excitation is localised on a single branch or on two branches. (Adapted with permission from ref. 42. Copyright 2017 American Chemical Society).

Figure 3A reveals that the fluorescence of **6** undergoes a significant red shift and intensity decrease during the first 60 ps, whereas the spectrum of **7** remains almost unchanged. However, neither **6** nor **7** show such early dynamics in non-polar media. This partial decay of the emission band integral on a much shorter timescale than the fluorescence lifetime was attributed to a decrease of the $S_1 \to S_0$ transition dipole upon ES-SB (Figure 3B).[42] This effect, which was also observed subsequently with other multi-branched D-A molecules,[35,43] can again be explained using a Frenckel exciton model, as illustrated in Figure 3C. When excitation is evenly delocalised over all branches, fluorescence occurs from the lowest excitonic state, which bears the whole oscillator strength. In the case of a linear two-branched molecule, the magnitude of the emission dipole amounts to $\sqrt{2}\mu_{\mathrm{DA}}$, where μ_{DA} is the $S_1 \to S_0$ transition dipole moment of the single D-A branch. Consequently, this model predicts a halving of the oscillator strength, hence of the fluorescence intensity, upon ES-SB and full localisation of the excitation on one branch. For a three-branched dye like **4**, the oscillator strength should only decrease by one third. Using a more advanced model of ES-SB, Antipov and Ivanov confirmed such a reduction of the emission dipole moment as electronic excitation localises.[44]

This approach does not necessitate any quantitative determination of the emission dipole moment. As the emission band integral is proportional to the square modulus of the transition dipole, the ES-SB dynamics can be determined from its decay. However, to be reliable, this method requires the excited-state lifetime to be significantly longer than the timescale of ES-SB. Otherwise, disentangling the contribution of ES-SB to the intensity decay from that of population dynamics becomes problematic.

As discussed above, the presence of fluorescence solvatochromism is not univocal evidence of ES-SB. For the same reason, the dynamic fluorescence Stokes shift does not necessarily reflect ES-SB. Indeed, it was shown that, whereas ES-SB in polar solvents is always accompanied by a time-dependent shift of the emission band, the opposite is not true.[42] Dipolar solvent relaxation upon a change of quadrupolar moment is also expected to be appear as a dynamic Stokes shift.

Although powerful to measure energy hopping between identical chromophores, time-resolved fluorescence anisotropy is not helpful for looking at ES-SB. Indeed, no change of emission anisotropy is expected in either linear two-branched dyes or symmetric planar dyes with three branches or more. However, fluorescence anisotropy is useful to detect ground-state symmetry breaking in non-linear multi-branched molecules,[45,46] whereas, for formally centro-symmetric compounds, this information can be deduced from the two-photon absorption spectrum.[47–49] On the other hand, defocused single molecule fluorescence imaging allows distinction between linear and planar emitters.[50] Using this method, Mitsui and coworkers could show that the emission from a planar six-branched molecule in a polymer film was taking place via a linear transition dipole, i.e., from a single branch or two opposite branches, pointing to the occurrence of ES-SB.[51] The time resolution of this technique is, however, not sufficient to follow the localisation of the excitation in real time.

ES-SB in a chiral D-A-D molecule with a helicene acceptor core was recently detected using circular-polarised luminescence (CPL).[52] The luminescence dissymmetry factor, g_{lum}, was found to decrease by a factor ten upon going from non-polar to polar solvents. This was explained by the localisation of the excitation on one D-A side, suppressing the interbranch excitonic coupling and leading to a decrease of the rotatory strength of the $S_1 \rightarrow S_0$ transition. This elegant approach could in principle be applied to measure the ES-SB dynamics. However, this remains a very challenging task as this requires major developments in time-resolved CPL spectroscopy.[53]

Exploiting the relaxation of the Laporte rule. As mentioned above, the attempts to visualise ES-SB using UV-Vis TA were generally not really successful, because no clear spectral signature could be detected.[18–21,54] The spectral dynamics observed in the UV-Vis region is often dominated by the red shift of the stimulated emission band. This shift together with the frequent overlap of the stimulated emission band with positive ESA features seriously complicate the determination of its area and, thus, the detection of ES-SB.

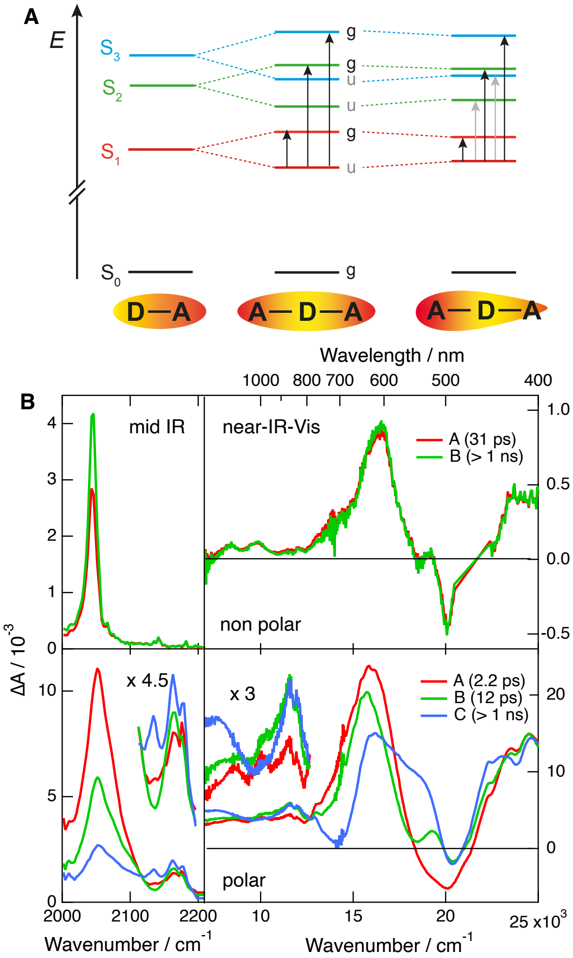

Figure 4: Relaxation of the Laporte rule upon symmetry breaking: A) Frenkel exciton model for the lowest singulet excited states of a two-branched D-A dye, assuming that the S_1 to S_3 states of the single branch have a charge-transfer character. B) Evolution-associated difference absorption spectra and time constants obtained from a global analysis of the mid-IR and near-IR-Vis transient spectra measured with dye **8** in cyclohexane (top) and benzonitrile (bottom) assuming a series of successive exponential steps. (Adapted with permission from ref. 55. Copyright 2021 Royal Society of Chemistry).

However, extension of the excitonic model to upper excited states suggests that substantial changes in the electronic TA spectrum can be expected upon ES-SB. In the case of linear two-branched molecules, only ESA bands due transitions from the S_1 state to upper excited states of gerade symmetry should appear in the TA spectrum of the quadrupolar excited state (Figure 4A). The first of them, the $S_2 \leftarrow S_1$ transition, is at an energy equal to the Davidov splitting and, as shown above, is often in the mid-IR region. As ES-SB takes place, the splitting and the oscillator strength of this transition decrease. At the same time, the electronic structure of the molecule is no longer centrosymmetric and the electronic transitions are not any more restricted by the Laporte rule. Consequently, new electronic transitions that were forbidden in the symmetric quadrupolar S_1 state are expected to appear in the TA spectrum upon partial localisation of the excitation (Figure 4A right).[55]

The validity of this idea was demonstrated with the two-branched dyes **8** and **9**.[17,55] Occurrence of ES-SB with **8** in polar solvents was inferred from the IR TA spectra in the -C≡C- stretching region showing the rise of a second -C≡C- band around 2150 cm^{-1}, that is absent in non-polar solvents (Figure 4B left). ESA bands due to the -C≡N stretching modes are also visible but do not report on ES-SB along the D-A-D axis as the cyano groups are on an orthogonal axis. The electronic TA spectra in the visible region exhibit significant dynamics in polar solvents that can be mostly attributed to the Stokes shift of the stimulated emission overlapping with ESA bands. In the near-IR region, where these complications are absent, a new ESA band peaking around 1350 nm appears in polar solvents on the same timescale as ES-SB. This band, not visible in non-polar solvents, can be attributed to an $S_{n>1} \leftarrow S_1$ transition that is Laporte forbidden in the quadrupolar excited state. Occurrence of ES-SB in polar media with dye **9**, that lacks the -C≡C- vibrational markers, could also be deduced from the rise of a new ESA band in the near IR.

In principle, higher energy ESA bands can also be expected in the visible region. However, their detection is more difficult as the UV-Vis region is already crowded by negative bands due to stimulated emission and ground-state bleach as well by more numerous ESA bands. Moreover, these new transitions are intrinsically weak. On the one hand, if the extent of ES-SB is small, they are almost forbidden because the electronic structure is quasi centrosymmetric. On the other hand, if the extent of ES-SB is large, their oscillator strength is small as well because the molecular orbitals involved in these transitions have most of their amplitude on different branches of the molecule. Therefore, their overlap decreases as ES-SB increases. The near-IR region is, thus, best suited to detect the rise of these new bands upon ES-SB.

As this approach is not restricted to molecules with vibrational markers or long-lived fluorescence, it is, in principle, generally applicable. However, the spectral response of the near-IR InGaAs detectors used in most TA setups drops to zero around 1700 nm. Therefore, the accessible near-IR spectral range is not sufficiently broad for detecting all low-energy ESA bands. Quantum-chemistry calculations can be helpful to predict the presence of ESA bands below 1700 nm. However, considering that an energy difference of 0.1 eV corresponds to about 200 nm in this range, this requires an accuracy that is not obvious for electronic excited-state calculations.

At present, a whole palette of spectroscopic approaches is available for monitoring ES-SB dynamics in multi-branched D-A dyes. The decrease of emission transition dipole as well as the decay or the appearance of electronic absorption bands enable straightforward visualisation of symmetry breaking. However, these methods, as used until now, give only limited quantitative information on the distribution of the excitation. By contrast, better insight into the extent of ES-SB and the localisation of the excitation can be obtained using time-resolved vibrational spectroscopy. The combination of both transient IR and Raman spectroscopies, which, to the best of our knowledge, has not been applied so far, should give deeper insight. Furthermore, investigations at the single molecule level, using a combination of scanning tunnelling microscopy and optical spectroscopy, can be expected to give a most detailed picture of ES-SB.[56,57] Additionally, the interpretation of the spectroscopic data would greatly benefit from simulations based on quantum-chemical calculations. Such calculations, involving electronic excited-states with charge-transfer character and requiring the explicit description of the environment and of its dynamics, represent a major challenge as they combine a large number of complications. However, efforts in this direction as well as further systematic experimental investigations should ultimately allow for a comprehensive understanding of the distribution of the electronic excitation in these multi-branched molecules and in larger conjugated systems, as well as its temporal evolution, and its possible control using, for example, selective vibrational excitation.[58]

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Biography

Eric Vauthey obtained his chemistry diploma and Ph.D. from the University of Fribourg. After postdoctoral research at Imperial College London and ETH Zurich, he started independent research in Fribourg. He has been a professor at the University of Geneva since 2001. His main research interest is the dynamics of molecular photoinduced processes in the condensed phase and at interfaces.

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