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Electroabsorption Spectra of Quadrupolar and Octupolar Dyes in Solution: Beyond the Liptay Formulation

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We present theoretical models for electroabsorption (EA) spectra of polar and multipolar (quadrupolar and octupolar) organic chromophores in solutions. Based on essential-state models for the electronic structure, we obtain closed expressions for the EA spectra of these dyes. For polar dyes, we regain the well-known Liptay result, which relates the EA spectrum to the linear absorption spectrum and its first and second derivatives. For multipolar dyes, an additional contribution is found, which is due to the field-induced absorption toward dark states: when the dark states are close in energy to allowed states, this term leads to spurious second-derivative-like structures in the EA spectrum. This is particularly well-apparent for quadrupolar dyes where second-derivative contributions to the EA signal are symmetry-forbidden. The extension of essential-state models to account for slow degrees of freedom, including molecular vibrations and polar solvation, leads to a more-realistic description of optical spectra but hinders the analytical treatment of EA. However, numerically exact EA spectra can be obtained along the same lines that have been recently developed for linear and two-photon absorption spectra of (multi)polar organic chromophores in solution. Essential-state models offer the possibility for a joint analysis of linear and nonlinear spectra (including EA) of (multi)polar dyes: reliable information can then be extracted also on molecular properties for systems where overlapping signals from allowed and dark states would hinder the standard analysis of EA spectra.

1. Introduction

Electroabsorption (EA) spectroscopy measures the effects of a static electric field on linear absorption spectra. It corresponds to a third-order nonlinear response, where one of the applied electric fields has vanishing frequency, and it is specifically described by $\chi^{(3)}(-\omega; \omega, 0, 0)$. As all nonlinear spectroscopic measurements, EA carries additional information, with respect to linear spectra, and, in view of the relatively simple instrumentation required, it is a widespread experimental technique.[1−3]

The early work of Liptay set the basis for retrieving microscopic information from EA spectra:[4,5] working with polar molecules in solution, Liptay demonstrated that EA spectra can be fitted as a linear combination of the linear absorption spectrum ($S(\omega)$) and its first and second derivatives ($S'(\omega)$ and $S''(\omega)$, respectively). The fitting coefficients give information on the mesomeric dipole moment $\Delta\mu$ that measures the variation of the molecular dipole moment upon photoexcitation (or, more precisely, its absolute value), and on $\Delta\alpha$, the variation of the molecular linear polarizability. Along these lines, Liptay was able to tabulate microscopic information on ground- and excited-state properties of a very large number of molecules.[5] As noted in the original papers,[4,5] the Liptay derivation holds true for molecules in frozen solutions (to avoid molecular reorientation along the field), with a single electronic excitation well-separated from other transitions, and in the absence of a vibronic structure. The requirements are tight, but the Liptay approach proved fairly robust and was successfully applied to many molecules, even in the presence of structured absorption bands.[1,6−8] EA measurements in frozen solution were also performed on mixed-valence complexes[2,9−12] and on quantum dots,[13] yielding important information on the charge distribution in the excited states.

EA was also applied to molecular crystals[14,15] and polymeric films.[3,16,17] In this context, it has been realized early that, being limited to well-isolated electronic absorptions, the Liptay approach becomes dangerous if forbidden (dark) states are not far in energy from apparently well-isolated linear absorption bands.[18−22] Specifically, pseudo-second-derivative contributions to the EA spectra can result from the electric-field-induced mixing of allowed and forbidden states. As a result, spurious large $\Delta\mu$ values may be estimated via a fit of EA spectra a la Liptay. The situation is particularly dangerous in the case of highly symmetric systems: in this case, in fact, the presence of dark states is not obvious from linear absorption spectra and, because of their different symmetry, dark states may be very close to the optically allowed state, leading to large effects in EA spectra.

Similar problems occur for EA spectra of highly symmetric quadrupolar and octupolar chromophores in solution. These molecules are interesting in several respects. They are extensively investigated for their large nonlinear optical (NLO) responses and, in particular, for their large two-photon absorption cross section;[23,24] moreover, the localization of the photoexcited state in one of the molecular arms, in some cases, leads to intriguing symmetry-breaking phenomena responsible for anomalous fluorescence solvatochromism.[25,26] EA spectra of highly symmetric structures, such as quadrupolar and octupolar dyes, may offer important information on molecular dark states that are not accessible via linear spectroscopy. However, the standard Liptay treatment hardly applies to these symmetric molecules, and new approaches must be devised to extract reliable microscopic information on the molecular properties from experimental EA data.

Essential-state models proved extremely useful to understand the basic physics of conjugated polymers[27] and have recently

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been adopted to describe in a unique and internally consistent picture linear and nonlinear spectra (including EA) of a PPV-based polymer, also accounting for electron-vibration coupling.[28] Essential-state models proved also useful to describe optical spectra of organic chromophores for NLO applications.[25,26,29−33] In these molecules, electron donor (D) and acceptor (A) groups are connected by π-conjugated bridges to give different types of structures, including dipolar (DA) structures, quadrupolar (DAD or ADA) structures, or more-complex octupolar (DA_3 or AD_3) systems. The low-energy physics of these molecules is governed by charge-transfer processes and the essential electronic states just correspond to the main charge-resonating structures. Two, three, and four electronic states are then required to model dipolar, quadrupolar, and octupolar dyes, respectively, and their intriguing spectroscopic behavior can be quantitatively rationalized in a description that explicitly accounts for electron-vibration coupling and for the interaction with the surrounding solvent.[25,26,29,31−33]

Here, we adopt essential-state models to describe the EA spectra of quadrupolar and octupolar chromophores. In the first part of the paper, we limit attention to the electronic degrees of freedom, and obtain analytical expressions relating the EA signal to the linear spectrum: for polar chromophores, the well-known Liptay expression is regained,[1,4,5] but new relations are found for quadrupolar and octupolar dyes. The different symmetry of the systems, and, specifically, the presence of dark states that become allowed in the presence of a static field, makes the analysis of EA spectra more complex but, in many respects, more informative. In the second part of the paper, we extend the discussion to account for molecular vibrations and polar solvation. As already suggested by Liptay for dipolar molecules, the interpretation of EA spectra becomes more delicate when slow degrees of freedom are involved: Liptay's expression for the EA spectra does not apply to molecules whose linear absorption spectra show prominent vibronic structure and/or in the presence of inhomogeneous broadening. Reliable microscopic information can be obtained under these conditions from a detailed analysis of solution spectra based on essential-state models that explicitly include electron-vibration coupling and polar solvation effects. The approach allows for the joint analysis of many different spectral properties, including, in addition to the EA spectra, linear (absorption and fluorescence) spectra as well as two-photon absorption (TPA) and other spectra (including vibrational ones), which, on one hand, leads to a more reliable definition of the molecular properties, and, on the other hand, leads to a better understanding of the spectroscopic behavior of the molecule of interest.

2. The Electronic Problem: Perturbative Approach to EA Spectra

2.1. Dipolar DA Dyes. Two-state models offer the simplest description of the electronic structure of dipolar DA chromophores.[29] The two basis states, $|DA\rangle$ and $|D^+A^-\rangle$, corresponding to the neutral and zwitterionic resonating structures, are separated by an energy gap $2z$ and are mixed by a matrix element $-\sqrt{2}t$. The resulting eigenstates,

$$|g\rangle = (1-\rho)^{1/2}|DA\rangle + \rho^{1/2}|D^+A^-\rangle \tag{1a}$$

$$|c\rangle = \rho^{1/2}|DA\rangle - (1-\rho)^{1/2}|D^+A^-\rangle \tag{1b}$$

are fully characterized by a single parameter $\rho = 0.5[1 - z/(z^2 + 2t^2)^{1/2}]$ that measures the weight of the zwitterionic state into the ground state, i.e., the amount of charge transferred from D to A ($D^{+\rho}A^{-\rho}$). The ground-state dipole moment is then $\mu_0\rho$, where μ_0 is the dipole moment of the $|D^+A^-\rangle$ state. Similarly, the excited-state dipole moment is $\mu_0(1-\rho)$. All quantities of spectroscopic interest can be written as functions of ρ: the optical transition from g to c has a charge-transfer character and the relevant squared transition dipole moment, $\mu_{gc}^2 = \mu_0^2\rho(1-\rho)$, vanishes in the two limits of a fully neutral ($\rho \to 0$) or fully zwitterionic ($\rho \to 1$) molecule, where the transition energy, $\hbar\omega_{cg} = \sqrt{2}t/[\rho(1-\rho)]^{1/2}$, diverges. The model describes a single absorption band whose transition dipole moment, lying along the molecular DA axis, is also parallel to the permanent dipole moment. Under these conditions, the Liptay treatment becomes exact.

For a solid solution, i.e., for molecules in a random frozen distribution, the EA spectrum (EA(ω)) only has quadratic contributions in the static field and is defined as[1]

$$\mathrm{EA}(\omega) = \frac{S(\omega, F) - S(\omega)}{F^2} \tag{2}$$

where $S(\omega)$ is the linear absorption spectrum and $S(\omega, F)$ is the linear absorption spectrum in the presence of an applied static field F. A perturbative expansion of molecular energies and wave functions on F leads to a closed expression for the EA spectrum that was first obtained by Liptay:[4,5]

$$\mathrm{EA}(\omega) = AS(\omega) + \omega B\frac{d}{d\omega}\left(\frac{S(\omega)}{\omega}\right) + \omega C\frac{d^2}{d\omega^2}\left(\frac{S(\omega)}{\omega}\right) \tag{3}$$

The coefficients A, B, and C are related to the molecular properties as follows:

$$A = 3M\left(\frac{3\Delta\mu_{c,g}^{\ 2} - 4\mu_{gc}^{\ 2}}{\omega_{gc}^{\ 2}}\right) \tag{4a}$$

$$B = 3M\left(\frac{2\Delta\mu_{c,g}^{\ 2} - 2\mu_{gc}^{\ 2}}{\omega_{gc}}\right) = 3M\left(\frac{2\Delta\mu_{c,g}^{\ 2}}{\omega_{gc}} + \frac{1}{2}\Delta\alpha_{c,g}\right) \tag{4b}$$

$$C = \frac{3}{2}M\Delta\mu_{c,g}^{\ 2} \tag{4c}$$

where $\Delta\mu_{c,g}$ and $\Delta\alpha_{c,g}$ are the changes in dipole moment and polarizability, respectively, upon excitation and M is a numerical factor accounting for orientational averaging. For linear molecules, $M = 1/5$ ($1/15$) when the oscillating electrical field is polarized parallel (perpendicular) to F. In the two-state model previously discussed, we can express all molecular properties entering eqs 4a−4c in terms of the model parameters, z, $\sqrt{2}t$, and μ_0, or, more efficiently, in terms of ρ.[29,33] We notice that μ_0 only enters the definition of the total EA intensity that grows as μ_0^4.

2.2. Quadrupolar D-A-D or A-D-A Dyes. Prototypical quadrupolar dyes are centrosymmetric chromophores with a D-A-D or A-D-A motif. The essential-state model for quadrupolar dyes accounts for three basis states, corresponding to the neutral structure ($|N\rangle = |DAD\rangle$) and to two degenerate structures ($|Z_1\rangle = |D^+A^-D\rangle$ and $|Z_2\rangle = |DA^-D^+\rangle$) (of course, analogous structures can be written for ADA chromophores).[25] The two charge-separated states Z_1 and Z_2 are degenerate and are separated by an energy gap $2z$ from the neutral state. A matrix element $-\sqrt{2}t$ mixes N to Z_1 and Z_2, whereas the direct mixing between Z_1 and Z_2 is neglected. To better understand the physics of quadrupolar dyes, we exploit symmetry and combine the two zwitterionic states in phase and out of phase: $Z_{+/-} = (Z_1 \pm Z_2)/\sqrt{2}$. The antisymmetric state, Z_-, stays unmixed and, as depicted in Figure 1, it corresponds to the lowest excited state, c, allowed in one-photon absorption processes. The two symmetric states, $|N\rangle$ and $|Z_+\rangle$ define a two state Hamiltonian similar

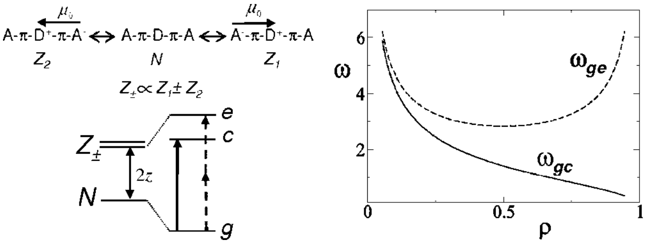

Figure 1. Left panel: a sketch of the three-state electronic model for quadrupolar chromophores. Right panel: the ρ dependence of the energy of the one-photon and two-photon allowed transitions (units of $\sqrt{2}t$).

to that described in the previous section. Specifically, the two states mix into a ground and an excited state:

$$|g\rangle = (1-\rho)^{1/2}|N\rangle + \rho^{1/2}|Z_+\rangle \tag{5a}$$

$$|e\rangle = \rho^{1/2}|N\rangle - (1-\rho)^{1/2}|Z_+\rangle \tag{5b}$$

where $\rho = 0.5[1 - z/(z^2 + 4t^2)^{1/2}]$ measures the weight of the Z_+ state into the ground state or, equivalently, the average charge on the central site, and is proportional to the quadrupolar molecular moment. We define μ_0 as the dipole moment of the charge-separated Z_1 state (an equal and opposite dipole moment is, of course, assigned to Z_2), so that all quantities of spectroscopic interest may be expressed as a function of ρ.[25,33] The ρ-dependence of the frequencies of the one-photon ($g \rightarrow c$) and of the two-photon allowed transition ($g \rightarrow e$) are shown in the right panel of Figure 1.

Similar to that observed with polar DA dyes, a perturbative treatment of the static electric field leads to a closed expression for the EA spectrum of quadrupolar dyes. However, because of the presence of a dark (one-photon forbidden) state, the expression for the EA signal obtained for quadrupolar dyes has a new term with no counterpart in the expression obtained previously for dipolar chromophores. Moreover, the prefactor of the second-derivative term, C in eq 3, proportional to the mesomeric dipole moment $\Delta\mu$, exactly vanishes in quadrupolar dyes, so that

$$\mathrm{EA}(\omega) = AS(\omega) + \omega B\frac{\mathrm{d}}{\mathrm{d}\omega}\left(\frac{S(\omega)}{\omega}\right) + D\omega T(\omega) \tag{6}$$

where the last term is due to the forbidden $g \rightarrow e$ transition that becomes allowed in the presence of the static electric field. Being related to a dark state, this term cannot be expressed in terms of the linear absorption spectrum $S(\omega)$ and its derivatives, and $T(\omega)$ represents a normalized band shape function (that we arbitrarily set equal to a Lorentzian). The prefactors A, B, and D in eq 6 are related to molecular properties. The first prefactor,

$$A = 3M\left(-4\frac{{\mu_{gc}}^2}{{\omega_{gc}}^2} - \frac{{\mu_{ce}}^2}{{\omega_{ce}}^2} + 2\frac{{\mu_{ce}}^2}{\omega_{ce}\omega_{gc}} + 2\frac{{\mu_{ce}}^2}{\omega_{ge}\omega_{gc}}\right) \tag{7}$$

is a cumbersome linear combination of dipole moments and energies, but the expression for B ($B = 3M\Delta\alpha_{g,c}/2$) coincides with the Liptay result, as applied to quadrupolar molecules with vanishing $\Delta\mu$ (cf eqs 4a–4c). Finally,

$$D = MK{\mu_{ce}}^2{\mu_{gc}}^2\left(\frac{1}{\omega_{gc}} - \frac{1}{\omega_{ce}}\right)^2 \tag{8}$$

involves the $c \rightarrow e$ transition dipole moment and frequency. K is the dimensional factor that transforms the dimensionless normalized band shape $T(\omega)$ into an absorbance.

As with polar chromophores, one can use the EA spectra of quadrupolar dyes to estimate molecular properties, relevant to the ground and excited states. However, a complication arises: in fact, in dipolar dyes, the EA signal is expressed as a linear combination of the experimentally accessible linear absorption spectrum and of its derivatives. On the opposite, for quadrupolar dyes, one of the contributions to the EA signal stems from forbidden states and the last term in the expansion previously presented cannot be related to the linear absorption spectrum. The position of the relevant feature in the EA spectrum can be inferred from the position of the TPA band, but the $T(\omega)$ shape cannot be deduced from any experimentally accessible quantity.

The analysis of EA spectra of quadrupolar dyes is particularly interesting, because it offers information on dark states that is not accessible by one-photon absorption (OPA); on the other hand, the analysis is hindered by the appearance of features that cannot be related to the linear spectrum or its derivatives. The actual possibility to obtain reliable information on the properties of quadrupolar molecules from EA spectra then is critically dependent on the energy gap between the two excited states and, hence, on ρ. As shown in Figure 1, largely neutral ($\rho \approx 0$) quadrupolar dyes have almost degenerate OPA ($g \rightarrow c$) and TPA ($g \rightarrow e$) excitations, so that, in the EA spectra, the features related to the two transitions overlap, hindering the analysis of the spectra. The situation improves as ρ increases and the two excitations move apart. However, as $\rho \rightarrow 1$ the frequency of the $g \rightarrow c$ transition vanishes, suggesting an instability of quadrupolar molecules with large ρ. As discussed in ref 25, so far, quadrupolar molecules with $\rho \approx 1$ have not been synthesized.

Figure 2 shows the spectra calculated for a largely neutral quadrupolar dye. Specifically, we adopt the same model parameters obtained in ref 25 for chromophore I. At this stage, we do not account for electron–phonon coupling nor for solvation effects, but we tune z to reproduce the estimated $\rho \approx 0.07$ value. The top panel of Figure 2 shows OPA and TPA spectra, both reported as a function of the transition energy (twice the absorbed photon energy for TPA). As expected for a largely neutral dye, the OPA and TPA bands are not far in energy. As a consequence, in the EA spectrum (the middle panel of Figure 2), the features related to $S(\omega)$ and $S'(\omega)$ are partly superimposed with the $T(\omega)$ signal, because of the field-induced absorption to the dark state (cf. the bottom panel of Figure 2, where the three contributions are shown separately). Discriminating among the different contributions only on the basis of the shape of the EA signal is almost impossible, and, what is even worst, the overall EA spectrum closely resembles a typical EA spectrum with a large second-derivative contribution. Under these conditions, attempting a fit of the EA spectrum following the standard Liptay procedure would be extremely dangerous, because spurious second-derivative contributions would be extracted, which would suggest sizable value for the mesomeric dipole moment $\Delta\mu$, that instead vanishes by symmetry.

The situation improves for dyes with larger values of ρ, as exemplified in Figure 3 for a dye with $\rho \approx 0.13$ and whose parameters correspond to those obtained for chromophore II in ref 25 (again, we neglect electron-vibration coupling and solvation effects, and readjust z to fix ρ). In this case, OPA and TPA bands hardly overlap, and, in the EA spectrum, the $S(\omega)$ and $S'(\omega)$ contributions are well-resolved from the $T(\omega)$ contribution. A fit of the EA spectrum in the region of the one-photon absorption can follow the standard procedure (with the exclusion, based on symmetry considerations, of the $S''(\omega)$ contribution), leading to reliable information on the molecular properties, and, specifically, on the change of the molecular

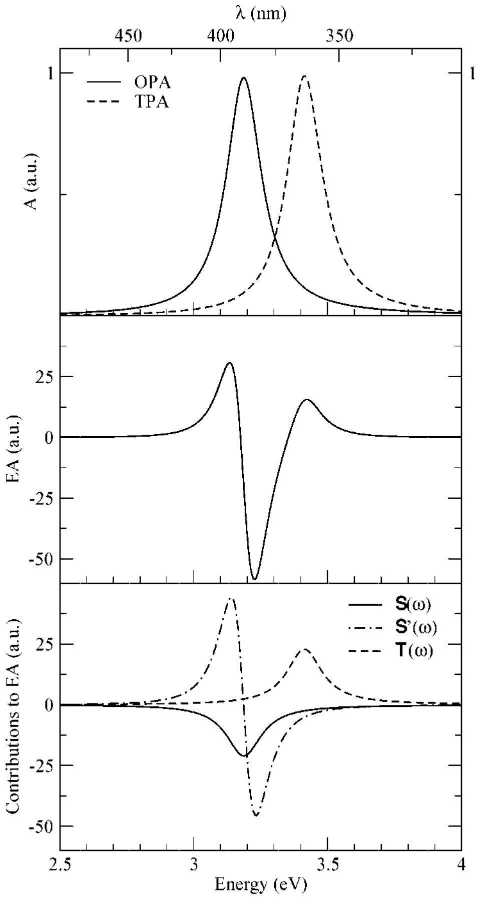

Figure 2. Optical spectra of a largely neutral DAD dye with $\rho \approx 0.07$ ($z = 1.48$ eV, $\sqrt{2}t = 0.6$ eV). Spectra are calculated imposing Lorentzian lineshapes for the absorption processes with $\Gamma = 0.16$ eV (full width at half-maximum). All spectra are in arbitrary units: absolute intensities of linear and third-order (EA and TPA) processes scale with μ_0^2 and μ_0^4, respectively. Top panel: linear absorption spectrum (continuous line) and TPA spectrum (dashed line), reported versus the transition energy (twice the absorbed photon energy for TPA). Middle panel: EA spectrum. Bottom panel: the different contributions to EA: spectrum (full line), first-derivative contribution (dot-dashed line), and $T(\omega)$ (dashed line) (the second-derivative contribution vanishes for quadrupolar dyes).

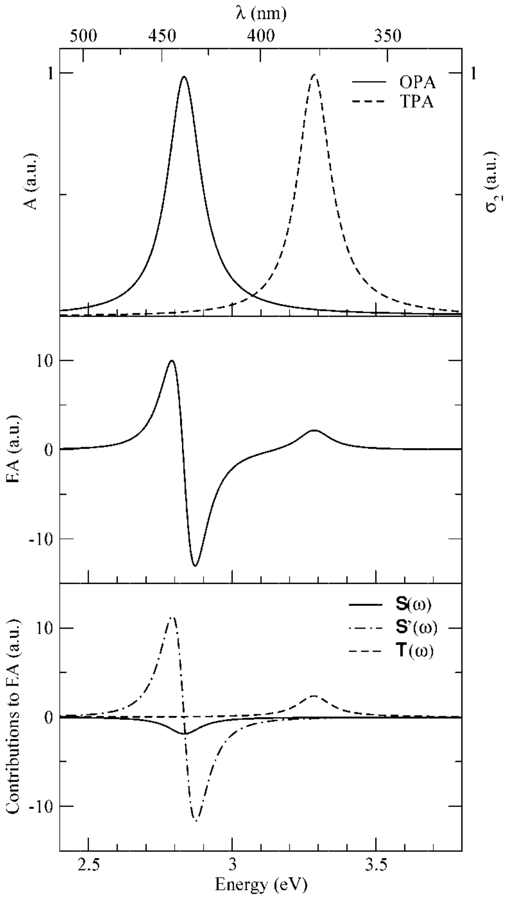

Figure 3. Same as Figure 2, but for a DAD dye with $\rho \approx 0.13$ ($z = 1.24$ eV, $\sqrt{2}t = 0.8$ eV), $\Gamma = 0.14$ eV.

polarizability upon photoexcitation. Moreover, a second, well-resolved peak appears at higher energies, giving information on the location of the dark state.

A further increase of the value of ρ to 0.4 (cf. Figure 4, relevant to the squaraine-dye III in ref 25) moves the energy of the TPA state to almost twice the energy of the OPA state. In these conditions the $T(\omega)$ contribution to the EA signal does not interfere with the $S(\omega)$ and $S'(\omega)$ contributions, and the standard Liptay analysis of the EA spectrum is possible in the OPA frequency region. On the other hand, the intensity of the $T(\omega)$ to EA becomes extremely weak ($D \rightarrow 0$ for $\omega_{gc} \rightarrow \omega_{ce}$, cf Eq. 8), and retrieving information on the position of the dark state from the EA spectrum becomes difficult.

2.3. Octupolar DA$_3$ or AD$_3$ Dyes. Octupolar chromophores are highly symmetric molecules, typically having DA$_3$ (or AD$_3$) motif, where the D and A groups lie on the same plane. The electronic model for this class of dyes, together with EA spectra, have already been addressed in ref 26. Here, we briefly summarize the main results, for the sake of completeness. Octupolar chromophores resonate between a neutral form ($|N\rangle$) and three charge-separated states ($|Z_1\rangle$,$|Z_2\rangle$,$|Z_3\rangle$), corresponding to the three degenerate states $A_2D^+A^+$ (or $D_2A^-D^+$). The essential-state model for octupolar dyes is then defined by four basis states.[26] The three charge-separated states have dipole moments of equal length, μ_0, pointing along the three molecular arms. As previously mentioned, $2z$ is the energy gap between the charge-separated states and the neutral state, whereas $-\sqrt{2}t$ is the matrix element that mixes $|N\rangle$ with each one of the three $|Z_i\rangle$ states. The three arms of the molecule are interchanged by a C$_3$ axis: the three degenerate basis states are conveniently combined into a symmetric wave function: $Z_+ = (Z_1 + Z_2 + Z_3)/\sqrt{3}$ and two E-symmetry functions that may be chosen as $c_1 = (2Z_1 - Z_2 - Z_3)/\sqrt{6}$ and $c_2 = (Z_2 - Z_3)/\sqrt{2}$. The neutral wave function N has the same symmetry as Z_+: the two states are mixed to give a ground state, g, and an excited state, e, that are described by the same expressions, as reported for quadrupolar dyes in eqs 5a and 5b, but with $\rho = 0.5[1 - z/(z^2 + 6t^2)^{1/2}]$ measuring the average charge on the central site, proportional to the octupolar molecular moment.[26] The E-symmetry states stay unmixed and correspond to two degenerate excited states (c_1 and c_2) that are accessible via OPA. At variance with quadrupolar dyes, all excited states can be reached by TPA, even if the transition to the e-state largely dominates the TPA spectrum.[26]

The presence of a dark state immediately suggests that, for octupolar chromophores, a D-like contribution appears in the EA signal. On the other hand, the allowed c-states have permanent dipole moments, even if the ground state is nonpolar by symmetry. Therefore, a second-derivative contribution to the EA signal is also expected. The perturbative treatment of the static electric field leads for octupolar dyes to the same EA expression as reported for DA dyes in eq 3, including contributions from the linear spectrum and its first and second derivative,

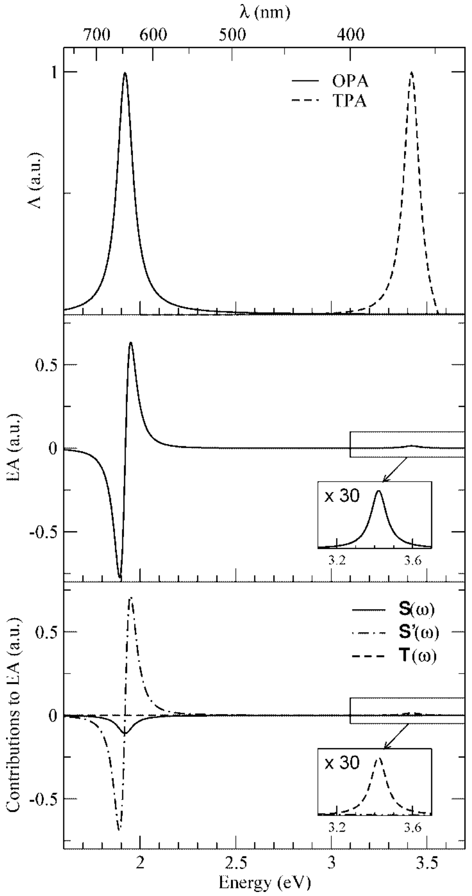

Figure 4. Same as Figure 3 but for a DAD dye with $\rho \approx 0.4$, $z = 0.21$ eV, $\sqrt{2}t = 1.2$ eV, $\Gamma = 0.10$ eV.

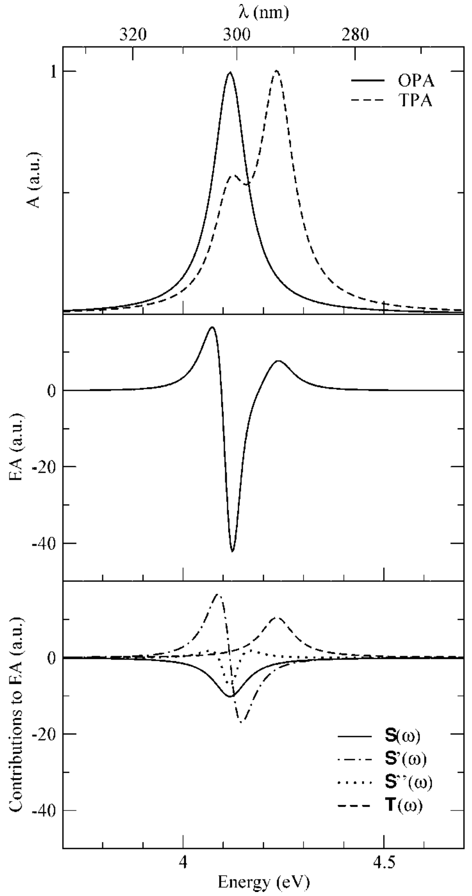

Figure 5. Largely neutral octupolar dye with $\rho \approx 0.03$ ($z = 2.0$ eV, $\sqrt{2}t = 0.4$ eV, $\Gamma = 0.2$ eV). Top panel: linear absorption spectrum (continuous line) and TPA spectrum (dashed line), reported versus the transition energy (twice the absorbed photon energy for TPA). Middle panel: EA spectrum. Bottom panel: the different contributions to EA: spectrum (full line), first-derivative (dot-dashed line), second-derivative (dotted line), and $T(\omega)$ (dashed line).

but with an additional term, equal to the last term in the right-hand side of eq 6.[26] The four *A*-*D* front factors entering the EA expression for octupolar dyes are related to molecular properties via the following expressions that refer to an experiment where the oscillating electric field is polarized parallel to the direction of the static field:

$$A = \frac{4}{5}\left(-4\frac{\mu_{gc_1}^{\;2}}{\omega_{gc_1}^{\;2}} - \frac{\mu_{c_1e}^{\;2}}{\omega_{c_1e}^{\;2}} + 2\frac{\mu_{c_1e}^{\;2}}{\omega_{c_1e}\omega_{gc_1}} + 2\frac{\mu_{c_1e}^{\;2}}{\omega_{ge}\omega_{gc_1}} + 3\frac{\mu_{c_1c_1}^{\;2}}{\omega_{gc_1}^{\;2}}\right) \tag{9}$$

$$B = \frac{4}{5}\left(\frac{\mu_{c_1e}^{\;2}}{\omega_{c_1e}} - 2\frac{\mu_{gc_1}^{\;2}}{\omega_{gc_1}} + 2\frac{\mu_{c_1c_1}^{\;2}}{\omega_{gc_1}}\right) = \frac{4}{5}\left(\frac{1}{2}\Delta\alpha_{c_1,g}^{(xx)} + 2\frac{\mu_{c_1c_1}^{\;2}}{\omega_{gc_1}}\right) \tag{10}$$

$$C = \frac{2}{5}\mu_{c_1c_1}^{\;2} = \frac{2}{5}\mu_{c_1c_2}^{\;2} \tag{11}$$

$$D = \frac{8}{15}K\mu_{c_1e}^{\;2}\mu_{gc_1}^{\;2}\left(\frac{1}{\omega_{gc_1}} - \frac{1}{\omega_{c_1e}}\right)^2 \tag{12}$$

Similar to that observed with dipolar or quadrupolar dyes, *A* turns out to be a fairly complex expression involving permanent and transition dipole moments and energies, so that extracting specific information out of it is very difficult. *C* is directly related to the permanent dipole moment of the degenerate excited state, $|\mu_{c_1c_1}|^2 = |\mu_{c_2c_2}|^2$ (the ground-state dipole moment vanishes by symmetry). This dipole moment also coincides with the transition dipole moment between the two degenerate c_1 and c_2 excited states, $|\mu_{c_1c_1}|^2 = |\mu_{c_1c_2}|^2$.[26] Again, *B* contains the excited-state dipole moment as well as the change in the molecular polarizability upon photoexcitation. Therefore, similar to that observed for dipolar DA dyes, information on the excited-state dipole moment and on the variation of the molecular polarizability upon photoexcitation can be obtained from *C* and *B*. However, as for quadrupolar dyes, the fit of the EA signal in terms of the linear spectrum and of its derivatives may be difficult if the dark state is located near to the allowed state, to originate field-induced absorption features in the EA spectrum that overlap with the EA features.

This situation is exemplified in Figure 5, which shows the EA spectrum calculated for a largely neutral octupolar chromophore ($\rho = 0.03$) for which the one-photon allowed states, c_1 and c_2, are close in energy to the one-photon forbidden state, *e* (see top panel). Despite the second-derivative-like shape of the EA spectrum, only a small contribution from the second derivative of the linear spectrum is found (see bottom panel), whereas major contributions are given by $S(\omega)$ and $S'(\omega)$, and by the $T(\omega)$ feature. In particular, this last feature is responsible for the higher-energy part of the EA signal. A fit of the EA spectrum that does not account for the dark-state contribution, $T(\omega)$, would, for molecules of this type, lead to unreliable information on molecular properties.

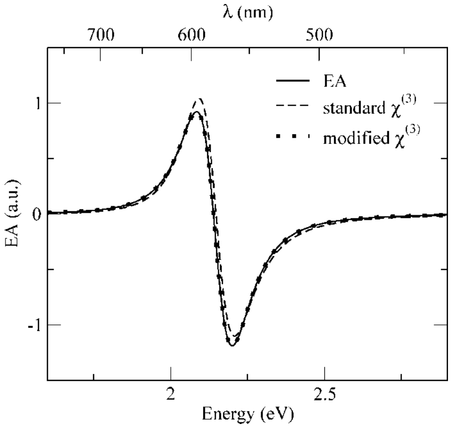

Figure 6. EA spectra for a quadrupolar dye with $\rho = 0.34$ ($z = 0.4$ eV, $\sqrt{2}t = 1.2$ eV, $\Gamma = 0.2$ eV). Full line: the exact EA spectrum obtained from the perturbative expansion or, equivalently, as the difference between linear spectra in the presence and in the absence of an applied field, divided by the squared amplitude of the field. Dashed lines: EA spectrum calculated according to the standard expression for $\gamma(-\omega;\,\omega, 0, 0)$, i.e., incorrectly using complex transition frequencies (finite damping factors) for the $\Omega_{eg} \pm \omega_i$ terms in the denominator with $\omega_i = 0$ (dashed lines); results corresponding to the modified $\gamma(-\omega;\,\omega, 0, 0)$, according to eq 14.

3. EA Spectrum as a Third-Order Nonlinear Response

We explicitly verified that the perturbative results described in previous sections coincide with the EA spectra calculated according to eq 2, at small F. An independent estimate of EA spectra can be obtained from the third-order susceptibility $\chi^{(3)}$:[34]

$$\mathrm{EA}(\omega) = \frac{4\pi\omega}{n(\omega)c}\mathrm{Im}\{\chi^{(3)}_{\mathrm{IJKL}}(-\omega;\omega,0,0)\} = \frac{4\pi\omega N}{n(\omega)c}\mathrm{Im}\{\langle\gamma(-\omega;\omega,0,0)\rangle_{\mathrm{IJKL}}\} \quad (13)$$

where $n(\omega)$ is the refractive index, c the speed of light, N the number density of molecules, and $\langle\gamma(-\omega;\,\omega, 0, 0)\rangle_{\mathrm{IJKL}}$ is the orientational average of the third-order molecular hyperpolarizability tensor measured along the laboratory I-, J-, K-, and L-axes. For linear molecules, γ_{xxxx} is the only nonvanishing component of the polarizability tensor, so that the orientational average simply leads to a proportionality factor (M in eqs 4a–4c, 7, and 8).

Quite surprisingly, EA spectra calculated according to eq 13, using the standard sum-over-state (SOS) expression for γ_{xxxx},[35] do not coincide with spectra calculated either from the perturbative expansion or as the difference of OPA spectra in the presence (and absence) of the static field. The deviations are small, but sizable, as shown in Figure 6. In the SOS expression for $\gamma(-\omega;\,\omega, 0, 0)$, denominators appear that contain sums and/or differences between the transition frequencies Ω_{eg} and the frequency of the applied fields, ω_i. The transition frequencies enter as complex quantities, $\Omega_{eg} = \omega_{eg} - i\Gamma_e$, where ω_{eg} is the real transition frequency and Γ_e is the inverse lifetime of the excited e state. In the EA experiment, one of the applied fields is a static field, with vanishing frequency.[35] To regain the exact EA response, the expression for γ must be modified to enter real transition frequencies (infinite lifetimes, $\Gamma_e \rightarrow 0$) in all the $\Omega_{eg} \pm \omega_i$ terms when $\omega_i = 0$. The expression for the γ_{xxxx} contribution to EA then reads as follows (nonresonant terms are omitted):

$$\begin{aligned}\gamma_{xxxx}(-\omega;\omega,0,0) = {} & \frac{1}{\hbar^3}\sum_{lmn}\langle g|\mu|l\rangle\langle l|\bar{\mu}|m\rangle\langle m|\bar{\mu}|n\rangle\langle n|\mu|g\rangle \times \\ & \Bigg[\frac{1}{(\Omega_{lg}-\omega)(\Omega_{mg}-\omega)(\Omega_{ng}-\omega)} + \frac{1}{\omega_{lg}(\Omega_{mg}-\omega)(\Omega_{ng}-\omega)} + \\ & \frac{1}{(\Omega_{lg}-\omega)(\Omega_{mg}-\omega)\omega_{ng}} + \frac{1}{\omega_{lg}(\Omega_{mg}-\omega)\omega_{ng}} + \\ & \frac{1}{(\Omega_{lg}-\omega)\omega_{mg}\omega_{ng}} + \frac{1}{\omega_{lg}\omega_{mg}(\Omega_{ng}-\omega)}\Bigg] - \\ & \sum_{mn}\langle g|\mu|m\rangle\langle m|\mu|g\rangle\langle g|\mu|n\rangle\langle n|\mu|g\rangle \times \\ & \Bigg[\frac{1}{\omega_{mg}(\Omega_{mg}-\omega)(\Omega_{ng}-\omega)} + \frac{1}{\omega_{mg}\omega_{ng}(\Omega_{ng}-\omega)} + \\ & \frac{1}{(\Omega_{mg}-\omega)^2\omega_{ng}} + \frac{1}{(\Omega_{mg}-\omega)\omega_{ng}^2} + \\ & \frac{1}{(\Omega_{mg}-\omega)\omega_{mg}\omega_{ng}} + \frac{1}{\omega_{mg}\omega_{ng}(\Omega_{ng}-\omega)}\Bigg] \quad (14)\end{aligned}$$

EA spectra calculated with this expression do coincide with spectra obtained via the perturbative expressions discussed in the previous section, or, equivalently, with the spectra calculated according to eq 2 at small F.

4. Interaction with Slow Degrees of Freedom: Exact Electroabsorption Spectra of Multipolar Dyes in Solution

The essential-state electronic models discussed in the previous section for (multi)polar chromophores have the main advantage of leading to analytical expressions for the EA spectra. However, electronic spectra of organic chromophores usually show a vibronic structure that represents a clear signature of the coupling between electronic and vibrational degrees of freedom. Moreover, the interaction between electronic charges and the slow orientational degrees of freedom of polar solvents leads to inhomogeneous broadening effects that are most apparent in absorption spectra of polar dyes,[31,36] while symmetry-breaking phenomena have been recently recognized for excited states of multipolar dyes in polar solvents.[25,26]

As first discussed by Liptay,[4,5] the analytical expression for the EA spectra of polar dyes in eq 3 does not apply in the presence of coupled vibrations, nor does it apply for inhomogeneously broadened bands; therefore, it should be hardly applicable to organic chromophores. However, it is adopted following the assumption that molecular properties (transition and permanent dipole moments) are approximately the same for all transitions that contribute to the observed band.

The essential-state models presented previously for polar and multipolar chromophores can be extended to account for the coupling between electronic and vibrational degrees of freedom and for polar solvation. These models proved fairly successful in the description of linear and nonlinear spectra of several chromophores.[25,26,31,36] Here, we extend the discussion to EA spectra.

The simplest model is set for polar DA dyes, where a single vibrational coordinate (Q) effectively accounts for vibrational coupling. Specifically, the two basis states $|\mathrm{DA}\rangle$ and $|\mathrm{D}^+\mathrm{A}^-\rangle$ are assigned two harmonic potential energy surfaces (PESs) with the same frequency ω, but with displaced minima along Q, to describe the different equilibrium geometry for the two states. The strength of the coupling is conveniently measured by $\varepsilon_{\rm sp}$, which represents the vibrational relaxation energy associated with the $|DA\rangle \rightarrow |D^+A^-\rangle$ process. A direct nonadiabatic diagonalization of the total Hamiltonian that describes both the electronic and nuclear dynamics directly leads to numerically exact nonadiabatic states.[37] Linear and nonlinear spectra are easily calculated from the standard sum over state expressions on the nonadiabatic states.[38]

Polar solvation can be explained by describing the solvent as a continuum dielectric medium.[36] The polar molecules of the solvent reorient around the solute to generate a reaction field $F_{\rm or}$ that is proportional to the solute dipole moment. The reaction field enters the molecular Hamiltonian, adding an interaction term $(-\hat{\mu}F_{\rm or})$ plus an elastic restoring energy $\mu_0^2|F_{\rm or}|^2/4\epsilon_{\rm or}$, where the solvation relaxation energy $\epsilon_{\rm or}$ increases with the solvent polarity. The orientational motion is very slow and can be treated classically.[36] In this approximation, each solute molecule experiences a slightly different local reaction field. The molecular Hamiltonian is then diagonalized for different $F_{\rm or}$, and solution spectra are calculated as sums of contributions from the different molecules, weighted according to the Boltzmann distribution on the energies. This model for polar solvation quite naturally explains the solvatochromic behavior of polar dyes, as well as inhomogeneous broadening effects in polar solvents.[31,32]

The same model of polar solvation also applies to multipolar chromophores, with the only caveat that, for linear (polar and quadrupolar) molecules, only the field component parallel to the molecular axis is relevant, whereas in planar octupolar molecules, two independent components of $F_{\rm or}$ in the molecular plane must be taken into account.[26] Instead, the model for molecular vibrations is more complex for multipolar chromophores, because at least one degree of freedom must be introduced for each molecular arm. In quadrupolar chromophores, two effective vibrational coordinates describe the independent vibrations of the two molecular arms. The two coordinates are conveniently combined into a symmetric vibration and an antisymmetric vibration.[25] Similarly, for octupolar chromophores, three effective molecular coordinates enter the model, which combine to give a symmetric coordinate and two degenerate E-symmetry coordinates.[26] The presence of non-totally symmetric vibrations in quadrupolar and octupolar chromophores leads to interesting spectroscopic effects, such as vibronic activation (through the so-called Herzberg−Teller mechanism) of forbidden transitions,[25] and symmetry-breaking or localization phenomena, whose manifestation has been recently recognized in the largely solvatochromic fluorescence observed for quadrupolar and octupolar dyes.[25,26]

Essential-state models represent minimal models for optical spectra of polar and multipolar dyes in solution, but the inclusion of the coupling to slow degrees of freedom makes the perturbative treatment of a static electric field too complex to obtain a closed expression for the EA spectra. However, the EA spectra can be calculated from F-dependent linear spectra, according to eq 2. Alternatively, EA spectra can be obtained from $\chi^{(3)}$, according to eqs 13 and 14. Specifically, these equations also apply in the presence of vibronic coupling, provided that the sums in eq 14 extend to all vibrational and vibronic states.[38] Extending the same treatment to account for polar solvation is instead more delicate because local-field corrections to the static field must be explicitly taken into account.[39]

The calculation of the EA spectra for dipolar, quadrupolar, and octupolar molecules, accounting for electron−phonon coupling and polar solvation, leads to results that can be directly compared with experimental data. Here, we explicitly discuss two model cases, relevant to a quadrupolar dye and an octupolar dye. Optical spectra in Figure 7 refer to a quadrupolar dye dissolved in a polar solvent. The model parameters refer to one of the chromophores discussed in ref 25 (chromophore 2, $\rho \approx 0.13$) and were obtained via a detailed analysis of solvent-dependent absorption and fluorescence spectra, as well as TPA data.[25] Figure 3 in the previous section shows the spectra calculated for a quadrupolar dye with the same value of ρ, but neglecting the coupling to slow (vibrational and solvation) degrees of freedom. Because of the lack of an underneath vibronic structure, OPA and TPA bands in Figure 3 are narrow and hardly overlap. The coupling to molecular vibrations leads to the wider and partially overlapping bands in Figure 7, whose vibronic structure is smeared as a result of inhomogeneous broadening. Moreover, because of the presence of antisymmetric vibrations, OPA (TPA) states with an odd-occupation number of antisymmetric phonons become TPA (OPA)-allowed via an Herzberg−Teller coupling mechanism, further increasing the spectral overlap between the OPA and TPA features. In the EA experiment, the static electric field breaks the inversion symmetry and allows for the mixing of OPA and TPA states that, in the region of spectral overlap, are almost degenerate. Intense EA signals are then expected, with a complex structure due to the strong mixing of several vibronic states. The EA spectrum

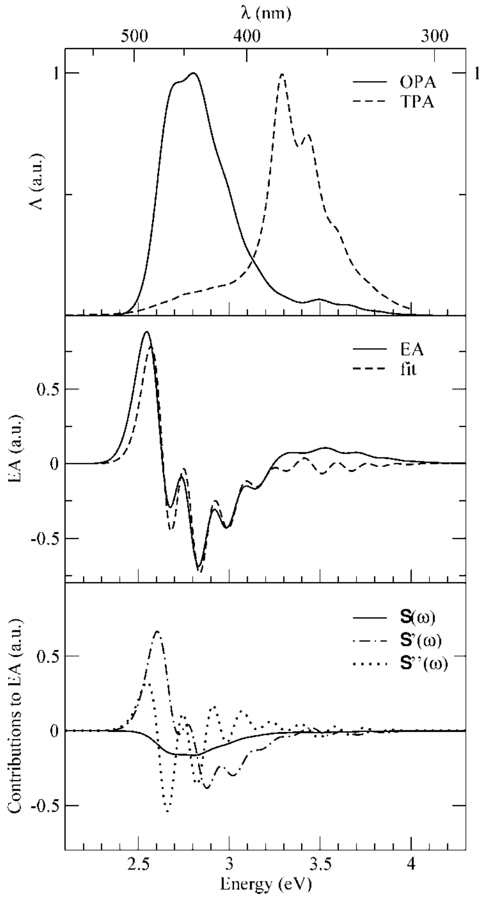

Figure 7. Optical spectra of a quadrupolar dye with $\rho = 0.13$, corresponding to compound 2 in ref 25. Results refer to a polar solvent, acetonitrile, with $\epsilon_{\rm or} = 0.25$ eV. Top panel: linear absorption (full line) and TPA (dashed line). Middle panel: a comparison between the exact EA spectrum (full line) and its best fit (dashed line) obtained in terms of a linear combination of the OPA spectrum and its first and second derivatives. Bottom panel: decomposition of the best fit into its different contributions: linear spectrum ($S(\omega)$, full line), first-derivative ($S'(\omega)$, dot-dashed line) and second-derivative ($S''(\omega)$, dotted line).

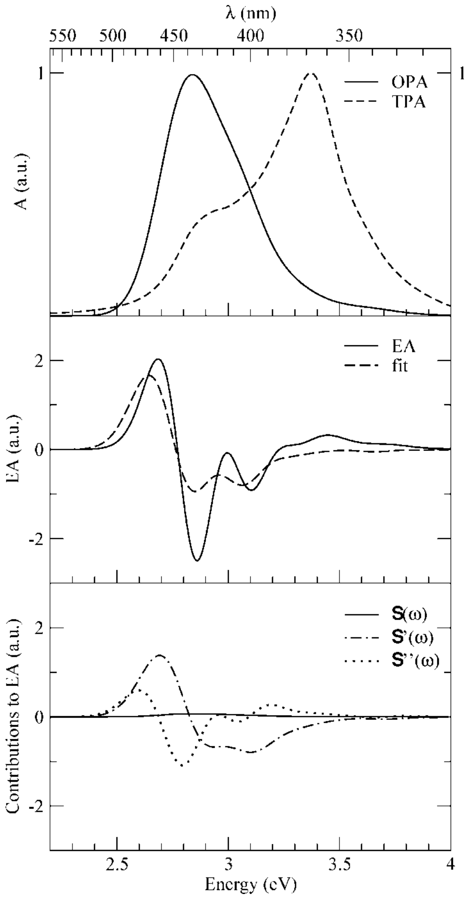

Figure 8. Optical spectra of an octupolar dye with $\rho = 0.11$, corresponding to compound 3b in ref 26. Results refer to toluene as being the solvent, modeled by $\epsilon_{or} = 0.2$ eV. Top panel: linear absorption (full line) and TPA (dashed line). Middle panel: a comparison between the exact EA spectrum (full line) and its best fit (dashed line) obtained, according to the standard Liptay treatment (eq 3), in terms of a linear combination of the OPA spectrum and its first and second derivatives. Bottom panel: decomposition of the best fit into its different contributions: linear spectrum ($S(\omega)$, full line), first-derivative ($S'(\omega)$, dot-dashed line) and second-derivative ($S''(\omega)$, dotted line).

in Figure 7 extends over a large spectral range, including both OPA and TPA regions. The shape is complex, as expected, and difficult to reproduce using the standard Liptay formulation in terms of $S(\omega)$ and its derivatives, as shown in the middle panel of Figure 7. Specifically, the Liptay equation is bound to fail in the high-frequency region where the contribution from the dark state is more important. In any case, as shown in the bottom panel of Figure 7, a fit a la Liptay would suggest a very large contribution from the second-derivative term, which corresponds to a large $\Delta\mu$ value. This is a spurious result, because $\Delta\mu = 0$ for centrosymmetric quadrupolar dyes. As discussed in section 2, the second-derivative-like shape of the EA spectrum results from the electric-field-induced activation of a dark (TPA) state located near to the allowed OPA signal. By the way, for quadrupolar dyes with a larger ρ value, the splitting between OPA and TPA states can be large enough to allow for a separate description of the relevant EA features also in the presence of coupling to vibrations and polar solvation.

In Figure 8, we show results relevant to the largely neutral ($\rho = 0.11$) octupolar dye 3b that is discussed in ref 26. In this case, a fit a la Liptay does not reproduce the exact EA spectrum, not even in the OPA region. Indeed, OPA and TPA bands strongly overlap (cf. Figure 8, top panel), hindering the simple analysis based on the linear spectrum and its derivatives. The large spectral overlap is due, first of all, to the low energy gap between the two degenerate c_1 and c_2 states and the e state, and is further amplified by the fact that both types of excited states are active in TPA processes. The OPA and TPA states are strongly mixed by the electric field, and a reliable analysis of EA spectra cannot neglect the $T(\omega)$ contribution.

5. Conclusions

The electroabsorption (EA) spectra of polar and multipolar dyes in solution offer important information on molecular properties that is well beyond that obtained by linear absorption spectra and complementary to those offered by much more expensive nonlinear spectroscopic techniques (e.g., TPA). The analysis of EA spectra for molecules in solution is commonly based on the Liptay approach. The EA signal is fitted as a linear combination of the linear spectrum and its first and second derivatives and the coefficients of the expansion are related to the variation of the molecular dipole moment and polarizability upon excitation. The Liptay analysis is simple and proved successful. However, as discussed in the original papers, it only applies to EA spectra related to a well-isolated and structureless absorption band, a condition hardly met by most of organic chromophores. In particular, highly symmetric quadrupolar and octupolar chromophores, which are currently investigated for applications in nonlinear optics, show fairly complex excitation spectra, with dark states often lying in close proximity of states reached upon one-photon absorption. Under these conditions, the analysis of optical spectra based on the Liptay approach is hindered by the interference of the signals relevant to the two states. The static electric field applied in EA experiments mixes up dark and allowed states and the analysis of the spectra becomes more and more difficult as the two interfering states come close.

In the first part of this work, we adopted essential-state models for polar and multipolar dyes to obtain closed analytical expressions for the EA spectra. This is only possible if purely electronic models are considered, neglecting the coupling between electrons and slow (vibrational and solvation) degrees of freedom. As expected, the Liptay expression becomes exact for polar dyes whose essential-state model describes just a single electronic transition. For quadrupolar and octupolar dyes, instead, the EA spectrum is described by an expression analogous to that obtained by Liptay, plus an additional term that accounts for the electric-field-induced absorption toward the dark state. This term is not related to any feature appearing in the linear absorption spectrum and cannot be reproduced in terms of $S(\omega)$ and its derivatives. This contribution is due to the perturbative mixing of dark and allowed state and its magnitude increases when a dark state lies in proximity of the allowed state, leading to second-order-derivative-like signals that make the Liptay analysis of EA spectra extremely dangerous. This is particularly apparent for quadrupolar dyes where the second-derivative contribution to the EA spectrum vanishes by symmetry ($\Delta\mu = 0$), but second-derivative-like features appear in the EA spectra (cf. Figure 2). Standard analysis of the EA spectra can yield to reliable results only in cases when the dark state is well-separated from the OPA state (as observed in Class II quadrupolar dyes). More generally, before attacking the analysis of EA spectra for highly symmetric dyes, it is very important to analyze nonlinear spectra and, in particular, TPA spectra, to safely locate possible interfering dark states.

A complete analysis of EA spectra of organic chromophores in solution must account for the important role of molecular vibrations and for the slow dynamics of polar solvation. Essential-state models allow one to set up reasonably simple and tractable models for polar and multipolar dyes that also account for molecular vibrations and polar solvation. However, even with these comparatively simple models, closed expressions for EA cannot be obtained and one must resort to numerical solutions. Here, we have discussed results that have been obtained from exact diagonalization of the nonadiabatic Hamiltonian for coupled electronic and vibrational degrees of freedom, while the slow solvation coordinate is treated classically. Vibrational coupling leads to structured absorption bands and, hence, to EA spectra with fairly complex structures. Moreover, in multipolar dyes, the widening of the absorption bands due to vibronic coupling makes the observation of interference between OPA and TPA states more likely. Even more subtle is the role of non-totally symmetric vibrations that allow for the mixing of states with different symmetry, further amplifying the field-induced mixing of excited states. Under these conditions, the standard analysis of EA spectra is problematic.

In this paper, we have discussed models for perfectly symmetric quadrupolar and octupolar compounds. Structural deviations from linearity for quadrupolar dyes or from planarity for octupolar chromophores can lead to finite permanent dipole moments for these structures. Extending the models to account for structural asymmetry is straightforward, because it only implies a redefinition of the matrix elements of the dipole moment operator. Small deviations from linearity or planarity, however, only have minor spectral effects, as demonstrated by the case of the slightly bent quadrupolar dye 1 discussed in ref 25, whose spectra are well-reproduced by the model for centrosymmetric quadrupoles. More subtle (and interesting) effects are expected for chemical asymmetry, as induced by differences in the D (or A) groups, to give D-A-D′ (or A-D-A′) structures (and analogously for octupolar dyes). The discussion of spectroscopic effects of chemical asymmetry goes beyond the scope of this work and will be the subject of a forthcoming publication.

EA is a nonlinear spectroscopic technique that offers complementary information, with respect to linear absorption spectra. For polar dyes, it may offer valuable information on the excited-state dipole moment and polarizability; however, for more-complex (symmetric) dyes with quadrupolar and octupolar structures, it can also give important information about dark states, i.e., about those states that cannot be reached upon one-photon absorption. Retrieving this information from experimental spectra, however, is more difficult and one must be aware of possible interference effects in the EA spectra of the signals from states with different symmetry. Slow degrees of freedom related to molecular vibrations and polar solvation lead to EA spectra that are even more complex, further hindering the retrieval of reliable information on molecular properties. In this context, essential-state models play an important role: they offer a reliable description of the low-energy physics of polar and multipolar dyes in solution in terms of tractable models, amenable to numerically exact solutions. Linear absorption and fluorescence spectra, as well as nonlinear spectra (including EA, TPA, and others) can be analyzed and quantitatively reproduced based on the same microscopic model. Along these lines, highly reliable molecular models can be defined as required for a thorough understanding of the physics of an important class of molecules.

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References and Notes

(1) Bublitz, G. U.; Boxer, S. G. *Annu. Rev. Phys. Chem.* **1997**, *48*, 213.

(2) Vance, F. W.; Williams, R. D.; Hupp, J. T. *Int. Rev. Phys. Chem.* **1998**, *17*, 307.

(3) Liess, M.; Jeglinski, S.; Vardeny, Z. V.; Ozaki, M.; Yoshino, K.; Ding, Y.; Barton, T. *Phys. Rev. B* **1997**, *56*, 15712.

(4) Liptay, W. *Angew. Chem., Int. Ed.* **1969**, *8*, 177.

(5) Liptay, W. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1974; p 129.

(6) (a) Chowdhury, A.; Locknar, S. A.; Premvardhan, L. L.; Peteanu, L. A. *J. Phys. Chem. A* **1999**, *103*, 9614. (b) Premvardhan, L. L.; Peteanu, L. A. *J. Phys. Chem. A* **1999**, *103*, 7506.

(7) Bublitz, G. U.; Ortiz, R.; Marder, S. R.; Boxer, S. G. *J. Am. Chem. Soc.* **1997**, *119*, 3365.

(8) (a) Karki, L.; Vance, F. W.; Hupp, J. T.; LeCours, S. M.; Therien, M. J. *J. Am. Chem. Soc.* **1998**, *120*, 2606. (b) Stanley, R. J.; Siddiqui, M. S. *J. Phys. Chem. A* **2001**, *105*, 11001. (c) Coe, B. J.; Harris, J. A.; Hall, J. J.; Brunschwig, B. S.; Hung, S.-T.; Libaers, W.; Clays, K.; Coles, S. J.; Horton, P. N.; Light, M. E.; Hursthouse, M. B.; Garín, J.; Orduna, J. *Chem. Mater.* **2006**, *18*, 5907.

(9) Bublitz, G. U.; Laidlaw, W. M.; Denning, R. G.; Boxer, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 6068.

(10) Hush, N. H.; Reimers, J. R. *Chem. Rev.* **2000**, *100*, 775.

(11) Walters, K. A.; Kim, Y.-J.; Hupp, J. T. *Inorg. Chem.* **2002**, *41*, 2909.

(12) Silverman, L. N.; Kanchanawong, P.; Treynor, T. P.; Boxer, S. G. *Philos. Trans. R. Soc. London, A* **2008**, *366*, 33.

(13) Sacra, A.; Norris, D. J.; Murray, C. B.; Bawendi, M. G. J. *Chem. Phys.* **1995**, *103*, 5236.

(14) Brillante, A.; Philpott, M. R. *J. Chem. Phys.* **1980**, *72*, 4019.

(15) Elschner, A.; Weiser, G. *Chem. Phys.* **1985**, *98*, 465.

(16) Sebastian, L.; Weiser, G. *Phys. Rev. Lett.* **1981**, *46*, 1156.

(17) Horvath, A.; Weiser, G.; Baker, G. L.; Etemad, S. *Phys. Rev. B* **1995**, *51*, 2751.

(18) Petelenz, P. *Chem. Phys.* **1993**, *171*, 397.

(19) Slawik, M.; Petelenz, P. *J. Chem. Phys.* **1999**, *111*, 7576.

(20) Kulakov, T. A.; Paraschuk, D. Y. *Chem. Phys. Lett.* **2000**, *325*, 517.

(21) Soos, Z. G.; Mukhopadhyay, D.; Hennessy, M. H. *Chem. Phys.* **1996**, *210*, 249.

(22) Soos, Z.; Mukhopadhyay, D.; Painelli, A.; Girlando, A. In *Handbook of Conducting Polymers*, Second Edition; Skotheim, T., Elsenbaumer, R., Reynolds, J., Eds.; Marcel Dekker: New York, 1998; p 165.

(23) (a) Mongin, O.; Porres, L.; Charlot, M.; Katan, K.; Blanchard-Desce, M. *Chem. Eur.—J.* **2007**, *13*, 1481. (b) Chung, S.-J.; et al. *J. Am. Chem. Soc.* **2006**, *128*, 14444. (c) Marder, S. *Chem. Commun.* **2006**, 131. (d) Rumi, M.; Ehrlich, J. E.; Heikal, A. A.; Perry, J. W.; Barlow, S.; Hu, Z.-Y.; McCord-Maughon, D.; Parker, T. C.; Röckel, H.; Thayumanavan, S.; Marder, S. R.; Beljonne, D.; Brédas, J.-L. *J. Am. Chem. Soc.* **2000**, *122*, 9500. (e) Albota, M.; et al. *Science* **1998**, *281*, 1653.

(24) (a) Rogers, J E.; Slagle, J. E.; McLean, D. G.; Sutherland, R. L.; Brant, M. C.; Heinrichs, J.; Jakubiak, R.; Kannan, R.; Tan, L.-S.; Fleitz, P. A. *J. Phys. Chem. A* **2007**, *111*, 1899. (b) Le Droumaguet, C.; Mongin, O.; Werts, M. H. V.; Blanchard-Desce, M. *Chem. Commun* **2005**, 2802. (c) Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porrés, L; Pons, T.; Mertz, J.; Tretiak, S.; Blanchard-Desce, M. *J. Phys. Chem. A* **2005**, *109*, 3024. (d) Beljonne, D.; Wenseleers, W.; Zojer, E.; Shuai, Z.; Vogel, H.; Pond, S. J. K.; Perry, J. W.; Marder, S. R.; Brédas, J.-L. *Adv. Funct. Mater.* **2002**, *12*, 631. (e) Bhaskar, A.; Ramakrishna, G.; Twieg, R. J.; Goodson, T., III *J. Phys. Chem. C* **2007**, *111*, 14607. (f) Drobizhev, M.; Karotki, A.; Dzenis, Y.; Rebane, A.; Suo, Z.; Spangler, C. W. *J. Phys. Chem. B* **2003**, *107*, 7540.

(25) Terenziani, F.; Painelli, A.; Katan, C.; Charlot, M.; Blanchard-Desce, M. *J. Am. Chem. Soc.* **2006**, *128*, 15742.

(26) Terenziani, F.; Sissa, C.; Painelli, A. *J. Phys. Chem. B* **2008**, *112*, 5079.

(27) Dixit, S. N.; Guo, D.; Mazumdar, S. *Phys. Rev. B* **1991**, *43*, 6781.

(28) Tong, M.; Sheng, C.-X.; Vardeny, Z. V. *Phys. Rev. B* **2007**, *75*, 125207.

(29) Painelli, A. *Chem. Phys. Lett.* **1998**, *285*, 352.

(30) Painelli, A.; Terenziani, F. *Chem. Phys. Lett.* **1999**, *312*, 211.

(31) (a) Painelli, A.; Terenziani, F. *J. Phys. Chem. A* **2000**, *104*, 11041. (b) Terenziani, F.; Painelli, A.; Comoretto, D. *J. Phys. Chem. A* **2000**, *104*, 11049.

(32) Boldrini, B.; Cavalli, E.; Painelli, A.; Terenziani, F. *J. Phys. Chem. A* **2002**, *106*, 6286.

(33) Terenziani, F.; D'Avino, G.; Painelli, A. *ChemPhysChem* **2007**, *8*, 1.

(34) Butcher. P. N.; Cotter, D., *The Elements of Nonlinear Optics*; Cambridge University Press: Cambridge, U.K., 1990.

(35) Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.

(36) Painelli, A. *Chem. Phys.* **1999**, *245*, 185.

(37) Del Freo, L.; Painelli, A. *Chem. Phys. Lett.* **2001**, *346*, 470.

(38) Del Freo, L.; Terenziani, F.; Painelli, A. *J. Chem. Phys.* **2002**, *116*, 755.

(39) Wortmann, R.; Bishop, D. M. *J. Chem. Phys.* **1998**, *108*, 1001.

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