Push−pull chromophores: NLO responses, solvatochromism and vibrational spectra in a simple non−perturbative model

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Push–pull chromophores: NLO responses, solvatochromism and vibrational spectra in a simple non-perturbative model

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Abstract

The diverse and fascinating properties of push–pull chromophores demonstrate their intrinsic non-linearity, and suggest that standard perturbative approaches are inadequate to describe their behavior. NLO responses of push–pull chromophores are strongly affected by the surrounding and large environmental effects are observed in absorption and emission spectra. Vibrational spectra show impressive dependence on the embedding medium, with unusual inhomogeneous broadening effects appearing in polar solvents. All these seemingly unrelated phenomena are naturally understood based on a simple two-state model self-consistently accounting for the coupling of electrons to molecular vibrations and to the surrounding medium. The few model parameters are extracted from experiment, leading to a simple yet accurate description of the exotic properties of push–pull chromophores. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Smart materials typically show non-linear responses to the relevant inputs. Non-linear responses imply large susceptibilities and are often related to the presence of low-lying excitations. And in fact π-conjugated systems are among the most promising materials for advanced applications. Push–pull chromophores, π-conjugated molecules with electron-donor (D) and acceptor (A) end groups, are very interesting in many respects [1]. Among them one finds good laser-dyes, common solvation probes, the first molecular rectifier, and materials with large NLO responses. Most of these properties are due to the presence of an excited state with a charge distribution distinctively different from the ground state. The study of spectral properties of push–pull chromophores in solution constitutes an invaluable tool to understand the subtle effects of the environment and of internal vibrations on the properties of non-linear materials.

2. The model

Push–pull chromophores often present a strong absorption band in the visible region, well separated from higher energy absorptions. To first approximation, their electronic structure can be described by a two-state model. The two basis states, $|DA\rangle$ and $|D^+A^-\rangle$, correspond to the neutral and the zwitterionic resonant structures. They are separated by an energy $2z_0$ and mixed by a matrix element $\sqrt{2}t$ that we fix as the energy unit. A different geometry describes the two basis states, we assign them two equal harmonic potential energy surfaces with displaced minima. The resulting Holstein-like Hamiltonian for molecular vibrations and electron-vibration (e-ph) coupling is [2]:

$$H_v = \sum_{i=1}^{N} \frac{1}{2}\omega_i^2 Q_i^2 - \sqrt{2\varepsilon_i}\,\omega_i Q_i \hat{\rho} \tag{1}$$

where Q_i are the N coupled vibrational coordinates of frequency ω_i, and ε_i is the energy gained by the system due to the relaxation of Q_i following the charge separation. The small polaron binding energy is defined as $\varepsilon_{sp} = \sum_i \varepsilon_i$. In the Mulliken approximation $\hat{\rho}$, the charge operator measuring the weight of $|D^+A^-\rangle$, is proportional to the dipole moment operator [2].

Polar molecules in solution also experiment a field due to the polarization of the solvent. In the simplest model, this reaction field (F_R) is proportional to the solute dipole moment. A component of F_R arises from the polarization of the electronic clouds of solvent molecules. This fast polarization component, with typical frequencies in the ultraviolet region, instantaneously follows the slower electronic degrees of freedom of the chromophore with typical

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frequencies in the visible region. In the antiadiabatic approximation, the fast degrees of freedom can be factorized out, simply renormalizing the effective parameters of the two-state model [3]. In polar solvents, a second component of F_R appears, related to the orientation of the solvent molecules around the solute. If the solvent is modeled as an elastic medium, the interaction of the solute with the solvent orientational degrees of freedom can be described by introducing an additional Holstein vibration (Q_0) in the above Hamiltonian. Q_0 describes a very slow motion, yet its frequency is irrelevant to our model. The corresponding reorganization energy (ε_{or}) can be related to the solvent macroscopic properties [3].

Both molecular vibrations and the orientational degrees of freedom of polar solvents are much slower than the relevant electronic degrees of freedom of the chromophore. In the adiabatic approximation, an effective electronic Hamiltonian is obtained by substituting slow coordinates with their expectation values. The resulting adiabatic Hamiltonian once more describes a two-state model, but with z_0 replaced by an effective parameter z, self-consistently depending on the solution of the Hamiltonian itself, $z = z_0 - \varepsilon_T\rho$, where ρ is the expectation value of the charge operator, and $\varepsilon_T = \varepsilon_{sp} + \varepsilon_{or}$ represents the total relaxation energy [2,3]. This simple model allows for exact solutions, offering interesting clues on the role of the interactions in systems characterized by a non-linear behavior. Moreover, its microscopic parameters can be fixed against few experimental data, yielding a full and internally consistent characterization of the chromophores.

3. Electronic and vibrational spectra

In our model, the relevant electronic degrees of freedom are self-consistently related to slow (vibrational and/or solvent orientational) degrees of freedom. This introduces a feedback mechanism that effectively amplifies the intrinsic non-linearity of our system, the most dramatic effects being found in NLO properties. In recent papers [2,3], the exact solution of the self-consistent two-state model allowed us to demonstrate a large amplification of static NLO responses as due to e-ph coupling and/or to the interaction with polar solvents. Our exact results prove the failure of standard sum-over-state approaches, which linearizes the interaction between electrons and slow degrees of freedom, cannot catch the intrinsic non-linearity introduced by these self-consistent interactions.

The non-linear nature of push–pull chromophores also shows up in linear spectroscopic processes. Electronic transitions are 'vertical' processes during the transition slow variables stay frozen in their initial positions. Therefore, the corresponding transition energies are defined by a single parameter that we choose as the polarity ρ, of the relevant state. Since ρ is related to ε_{or} (through ε_T) we can calculate the exact dependence of the absorption frequency (ω_{CT}) on
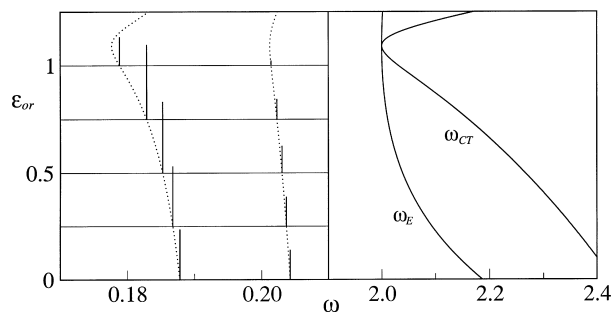

Fig. 1. The dependence of electronic (right panel) and vibrational (left panel, dotted lines) frequencies on the solvent polarity (ε_{or}) for a chromophore with $z_0 = 0.8$, $\omega_1 = 0.19$, $\varepsilon_1 = 0.12$, $\omega_2 = 0.21$, $\varepsilon_2 = 0.39$. In the left panel, for a few ε_{or} selected values, the non-resonant Raman intensities are also reported. Frequencies are reported in $\sqrt{2}t$ units.

the solvent polarity [3], as shown in Fig. 1, right panel. Standard approaches to solvatochromism are based on a linearization of the solute–solvent interaction [4]. In this approximation, electronic transition energies linearly depend on ε_{or}, in contrast with the exact results in Fig. 1. In fact, a push–pull chromophore is a highly polarizable solute, so that it non-linearly responds to the interaction with the solvent. This of course implies a dependence of the electronic wave functions, and then of the chromophore properties, on the solvent polarity. In particular, as detailed in [5], the exact model easily accounts for the dependence of absorption band-shapes on the solvent polarity.

After absorption, the slow degrees of freedom readjust in response to the excited state charge distribution. Standard approaches to solvatochromism assume that this relaxation only affects the chromophore energies, suggesting a linear dependence of the Stokes-shift ($\omega_{CT} - \omega_E$) on ε_{or} and nearly specular absorption and emission band-shapes. On the contrary, the highly polarizable solute readjusts its polarity following the relaxation of slow variables. Steady state emission takes place from a relaxed 'solute–solvent' system, different from the system relevant to absorption. As a consequence, the exact dependence of the emission frequency (ω_E) on the solvent polarity, as reported in Fig. 1, right panel, is far from linear, and the standard procedure of extracting mesomeric dipole moments of the solute from the slope of the Stokes-shift versus ε_{or} is inadequate [5]. Moreover, we can prove that the emission process involves chromophore states with a more homogeneous charge distribution than those relevant to absorption. As a consequence, the Franck–Condon structure underlying emission bands is narrower than for absorption [5], in very good agreement with experimental observation. The same mechanism naturally rationalizes the observed narrowing of emission bands in time-resolved measurements. Moreover, the observation for a few chromophores (coumarin 102 and DCM) of temporary isosbestic points in time-resolved transient absorption spectra measured in pump-dump-probe experiments [6,7] is easily reproduced in our model during the relaxation of slow variables the polarity of the chromo-

phore evolves towards the equilibrium value, so that the absorption band not only shifts in energy, but also modifies in shape, allowing for the presence of quasi-isosbestic points.

Up to now, we have discussed how the coupling with slow coordinates affects the electronic spectra of the chromophore. The self-consistent nature of the interaction, however, implies that slow degrees of freedom are in turn affected by the coupling to electrons. The most apparent effects are found in the dependence of vibrational properties on the chromophore charge distribution and then on the solvent polarity. The harmonic potential energy surfaces describing the two basis states in the Holstein model are distorted when the two states are mixed to give the ground and the excited state. The corresponding harmonic vibrational frequencies are obtained by diagonalizing the relevant force constant matrix, that for the ground state, reads [3]

$$F_{ij} = \omega_i \omega_j (\delta_{ij} - 2\sqrt{\varepsilon_i \varepsilon_j} \alpha_0) \qquad (2)$$

where δ_{ij} is the Kronecker-δ and $\alpha_0 = 2[\rho(1-\rho)]^{3/2}$ is the dimensionless electronic polarizability. For the excited state, the same equation applies, but with a plus sign. Vibrational frequencies are softened (hardened) in the ground (excited) state. Since the chromophore charge distribution, ρ, depends on the solvent polarity, our model accounts for the solvatochromism of vibrational frequencies without introducing any direct coupling between vibrations and solvent. Infrared and non-resonant Raman intensities of coupled vibrations can be related, in the harmonic approximation, to the polarizability and first hyperpolarizability of the chromophore, respectively [3]. In Fig. 1, left panel, we show the dependence on the solvent polarity of the vibrational frequencies of a chromophore with two Holstein vibrations having $\omega_1 = 0.19$, $\varepsilon_1 = 0.12$ and $\omega_2 = 0.21$, $\varepsilon_2 = 0.39$. Although the lowest frequency mode has the smallest relaxation energy, it suffers a much larger softening than the highest mode. This phenomenon is commonly observed in systems with large e-ph coupling involving several modes, like polyacetylene. In the same figure for selected ε_{or} values, we also report the non-resonant Raman intensities, the lowest frequency mode borrows intensity from the highest mode.

4. Inhomogeneous broadening

At room temperature, the solvent orientational degrees of freedom are affected by thermal disorder. In polar solvents, the reaction field then slowly oscillates around its equilibrium value and the solution can be described as a collection of solute molecules in equilibrium with the local reaction field. The probability distribution is of course determined by the solute + solvent energy. In the standard rigid solute approach to solvation, the linear dependence of electronic energies on the reaction field provides a mechanism for inhomogeneous broadening of absorption and/or emission
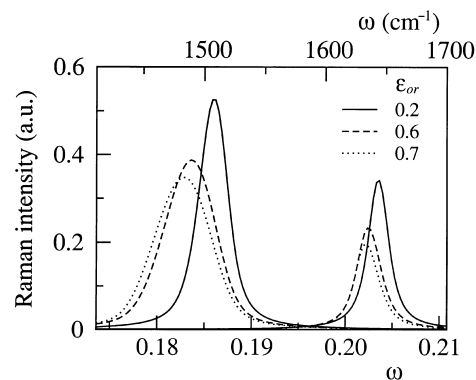

Fig. 2. Non-resonant Raman spectra calculated for the same parameters as in Fig. 1 and three different ε_{or} values. $\sqrt{2}t = 1$ eV fixes the frequency scale on the topmost *x*-axis.

bands in polar solvents. On the other hand, in this perturbative approach, the solute properties are not affected by the local field, so that no broadening of vibrational lines is predicted. In our non-perturbative approach, instead, the self-consistent interaction between electronic and slow degrees of freedom implies a dependence of vibrational frequencies (and intensities) on the solute polarity and then on the local reaction field, resulting in inhomogeneously broadened vibrational bands. Fig. 2 shows the non-resonant Raman spectra calculated for a chromophore with the same parameters as in Fig. 1, for three different ε_{or} values. The bands relevant to the two coupled modes soften and broaden with increasing solvent polarity and, as discussed above, all effects are much larger for the lowest mode. The adopted parameters have been chosen to reproduce the spectral behavior of an interesting dye, phenol blue (PB, also known as dimethylindoaniline). This molecule shows an impressive solvatochromism and a very large first hyperpolarizability [8]. Its large non-linearity makes it a good candidate for observing an anomalous spectral behavior. The spectra in Fig. 2, for increasing ε_{or}, well reproduce the experimental non-resonant Raman spectra measured in CCl_4, $CHCl_3$ and DMSO [9]. Actually, with the same parameters, we are also able to accurately reproduce electronic absorption spectra, in terms of frequencies, intensities and band-widths.

The curve in Fig. 1 clearly demonstrate the correlation between electronic transition energies and vibrational frequencies. In polar solvents, inhomogeneous broadening affects both electronic and vibrational energies. In a resonant Raman experiment, the resonance condition selectively enhances the response of the molecules absorbing at the laser frequency. As a consequence, by varying the excitation line, molecules with different absorption frequencies are sampled, and then according to Fig. 1, different vibrational frequencies are observed. Resonant Raman spectra of PB in solution have been reported in [10]. In apolar solvents, the frequencies do not depend on the excitation line whereas a large dispersion is observed in polar solvents. In Fig. 3 we show that the same parameters that fit absorption and non-
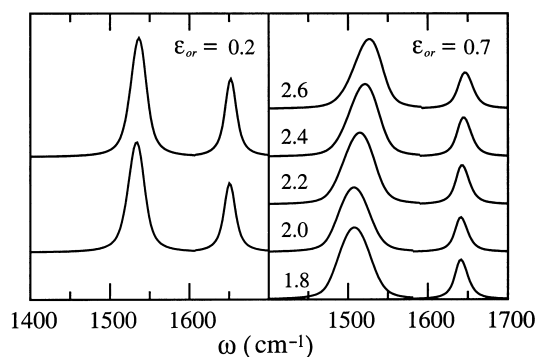
Fig. 3. Resonant Raman spectra calculated for the same parameters as in Fig. 2 for two solvent polarities (ε_{or}). The spectra are labeled by the frequency of the excitation photon (eV).

resonant Raman spectra also reproduce resonant Raman spectra. Specifically, coupled modes soften and broaden with increasing solvent polarity, and in polar solvents, frequencies vary with the excitation line. Our model does not introduce any direct interaction between internal vibrations of the chromophore and the solvent degrees of freedom. Yet the two motions are correlated by their common interaction with the electronic degrees of freedom, leading to characteristic solvation effects in vibrational spectra.

5. Conclusion

We have extended the two-state model for push–pull chromophores to account for e-ph coupling and for the interaction with the solvent. The complex spectral behavior of push–pull molecules is well understood within this simple model, provided its intrinsic non-linearity is fully exploited. The few model parameters can be extracted through an accurate analysis of experimental data. PB has been widely investigated electronic, infrared and Raman spectra are

available in a few solvents, and EFISH data have been collected. All the experimental data are reproduced in terms of a few microscopic parameters, demonstrating the validity of the proposed model. The analysis of a more extensive set of experimental data and/or of data collected on different chromophores is certainly worthwhile. However, irrespective of its applicability to specific push–pull chromophores, the proposed model, with its exact solutions, teaches us an important lesson standard approximation schemes, that are widely applied to understand the properties of linear systems need to be carefully reconsidered if applied to non-linear materials.

Acknowledgements

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