Conjugated donor-acceptor chromophores in solution: non-linearity at work

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I. INTRODUCTION

Conjugated donor-acceptor (DA) chromophores, also called push-pull chromophores, are molecules constituted by an electron-donor (D) and an electron-acceptor (A) group connected by a π-conjugated backbone. These molecules are widely investigated in several, apparently unrelated fields: they are common solvation probes and are molecules of choice for second order non-linear optics (NLO) applications, and are useful model systems for electron transfer. All these applications exploit the presence of a low-lying excited state, characterized by a different electronic distribution from the ground state. Reactions involving charge migrations are ubiquitous in all fields of chemistry and biochemistry, so that understanding their mechanism is of special interest. These reactions often occur in solution, and are strongly influenced by the medium itself, suggesting a strong coupling between solvent and solute. Nowadays, advances in laser technology allow to study the coupled reactant and solvent dynamics. In the typical experiment, a (series of) short pulse(s) of light is used to perturb the electronic charge distribution of the solute; the system is then interrogated by a retarded probe pulse. Polar conjugated chromophores, due to their strongly solvent-dependent properties, are molecules of choice for this kind of experiments, offering as an additional bonus also the opportunity to investigate the kinetics of electron transfer in the absence of reactant diffusion. A proper interpretation of both steady-state and time-resolved experiments is the key to gain important physical information. However, standard interpretative schemes are based on linear perturbative treatments of the solute-solvent interaction, so that they disregard one of the most characteristic features of push-pull chromophores, i.e. their large non-linearity. We have already proposed a model that, accounting for the intrinsic non-linearity of the electronic system, is able to rationalize steady-state electronic and vibrational spectra of polar chromophores in solution. In this paper the same model is extended to discuss time-resolved experiments.

II. A MODEL FOR NON-LINEAR INTERACTIONS

Since the properties of push-pull chromophores are dominated by the lowest excited state, a two-state model describes the essential physics governing the low-energy behavior of these molecules. The electronic structure of push-pull chromophores can be described as resonating between the fully neutral, $|DA\rangle$, and the zwitterionic, $|D^+A^-\rangle$, states, separated by an energy $2z_0$ and mixed up by the hopping integral, $−√2|\epsilon|$. The ionicity operator, $\rho$, measures the weight of $|D^+A^-\rangle$ in the ground- or excited-state. The expectation value of this operator, $\rho = \langle \rho \rangle$, corresponding to the polarity of the molecule in the relevant state, only depends on the ratio $z_0/t$, so that the electronic problem is fully described by a single parameter. We allow for the coupling of the electronic system with a molecular vibration, $Q$, and a solvation coordinate, $q$, by assigning the two basis states two harmonic potential energy surfaces (PES), with equal curvature but displaced minima along the two coordinates. The resulting Hamiltonian, describing these slow degrees of freedom and their coupling to electrons is:

$$\mathcal{H}' = \frac{1}{2} \Omega^2 Q^2 - \sqrt{2|\epsilon_\text{sp}|} \Omega Q \rho + \frac{1}{2} \omega^2 q^2 - \sqrt{2|\epsilon_\text{or}} \omega q \rho \tag{1}$$

where the first two terms account for the internal vibration, and the last two for the solvation coordinate. $\Omega$ and $\omega$ are the frequencies corresponding to $Q$ and $q$, respectively; $\epsilon_\text{sp}$ and $\epsilon_\text{or}$ are the energies gained by $|D^+A^-\rangle$ due to the relaxation of $Q$ and $q$, respectively, i.e. the small-polaron binding energy and the solvent reorganization energy.

The linear dependence of the energy separation between the two basis states on $Q$ and $q$ coordinates originates a non-linear dependence of $\rho$ on the two coordinates, making the exact potential energy, $V(Q,q)$, anharmonic. This anharmonicity, originating from the coupling of electrons to slow degrees of freedom, has many important consequences: in particular it is responsible for a large amplification of static hyperpolarizabilities.

III. SPECTROSCOPIC PROPERTIES

Absorption and fluorescence spectra are vertical processes, occurring at different $(Q,q)$. The dependence of $\rho$ on slow coordinates (both $Q$ and $q$) then leads to non-trivial effects on absorption and fluorescence frequencies and band-shapes. The vertical excited state reached...
upon photon absorption has a different polarity with respect to the ground state. Immediately after absorption, the slow degrees of freedom readjust in response to the new charge distribution of the solute. But, as long as slow degrees of freedom relax, the solute molecule itself feels a new surrounding and in turn readjusts its polarity. The non-linear, self-consistent relaxation problem can be solved exactly in our simple picture, to calculate the equilibrium polarity of the fully relaxed excited state. Fluorescence is once more a vertical process that, starting from the relaxed excited state, leads to the orthogonal ground state. Our model then predicts different Huang-Rhys factors for absorption and fluorescence, and explains the observation of narrower fluorescence than absorption bands for push-pull chromophores.

The solvent orientational coordinate describes a very slow (actually overdamped) motion and is responsible for inhomogeneous broadening effects in optical spectra. This broadening can be modeled in terms of a statistical distribution of $q$ conformations, $w(q)$. Since the chromophore readjusts its polarity in response to the solvent configuration, one ends up with a distribution of chromophore polarities, $w(p)$. Broadened spectra are then calculated as a sum of spectra corresponding to different molecular polarities.

The self-consistent nature of the interactions implies that slow degrees of freedom are in turn affected by the coupling to electrons. The most apparent effects can be found in the dependence of vibrational properties on the chromophore charge distribution and hence on the solvent polarity. In agreement with experimental data, we predict solvent-dependent vibrational frequencies and inhomogeneous broadening of infrared and Raman bands in polar solvents. Inhomogeneous broadening, affecting both electronic and vibrational states in polar solvents, rationalizes an unusual phenomenon of dispersion of resonant Raman bands with the excitation line observed for the dye phenol blue dissolved in polar solvents.

The dependence of molecular properties and hence of absorption and emission band-shapes on the configuration of slow coordinates (in particular the solvation coordinate) is the key to understand some interesting phenomena observed in time-resolved spectra. Recent pump-probe and femtosecond hole-burning measurements on push-pull chromophores dissolved in polar solvents have in fact revealed the appearance of so-called temporary isosbestic points (TIPs) in transient gain and differential absorption spectra, respectively. This means that spectra collected at different time delays seem to cross in an isosbestic point, whose position actually depends on the chosen time window. The physical origin of TIPs has not been understood so far. The only tentative explanation invokes the active role of two (or more) excited states. This explanation is not adequate, as proved by the fact that TIPs do appear in transient spectra collected for molecules dissolved in polar solvents only, while this feature is not observed in non-dipolar solvents. The appearance of TIPs in transient spectra is then related to solvation dynamics.

In typical time-resolved experiments, the relaxation of internal molecular vibrations is in general completed after the first few hundreds of femtoseconds following the excitation, so that subsequent dynamics can be ascribed to the relaxation of the solvation coordinate toward the new equilibrium configuration. Then, in the framework of our model, we can calculate the time evolution of transient spectra based on the temporal evolution of the probability distribution $w(p)$, which, in turn, can be obtained from the evolution of $w(q)$ on the relevant PES. In the phase space of coordinate and momentum $(q,p)$ the evolution of $w(q,p)$ can be described by the Fokker-Planck equation. In the overdamped regime (friction coefficient, $\gamma$, greater than $\omega$), relevant to the solvation coordinate, the Fokker-Planck equation reduces to the simpler Smoluchowski equation, in the $q$-space only:

$$\frac{\partial w(q)}{\partial t} = \frac{1}{\gamma} \left[ w(q) \frac{\partial^2 V}{\partial q^2} + \frac{\partial V}{\partial q} \frac{\partial w(q)}{\partial q} + kT \frac{\partial^2 w(q)}{\partial q^2} \right]$$

where $V$ is the anharmonic potential energy for the relevant state, $k$ the Boltzmann constant, $T$ the temperature. An example of the temporal evolution of $w(q)$ on one of the PES is given in Fig. 1(a) from $t = 0$, when an out-of-equilibrium population is created, to $t \rightarrow \infty$, when equilibrium is reached. In Fig. 1(b) the corresponding evolution of $w(p)$ is reported: due to anharmonicity and to the non-linear relation between $p$ and $q$, the distribution is asymmetric and evolves in width and shape.

Transient properties only depend on $\gamma$ and $\omega$ via the ratio $\tau = \gamma/\omega^2$. In order not to add any adjustable parameter to the original model, we fix $\tau$ to the longitudinal relaxation time of the pure solvent, as obtained from literature data. In Fig. 2(a), we show transient emission spectra, calculated for the parameters reported in the caption. The evolution of the band-shape, due to the dependence of electronic properties on the configuration of slow variables, together with the red-shift, is responsible for the appearance of a TIP. These data reproduce the gain spectra measured for the polyyene PA2 dissolved in dioxane. The adopted $\tau$ value coincides with the accepted value of the longitudinal relaxation time of dioxane.

Fig. 2(b) refers to a different experiment. In particular, to simulate femtosecond hole-burning spectra of coumarin 102 (C102) dissolved in CH$_3$CN, we have calculated transient differential absorption spectra from an out-of-equilibrium $q$-distribution in the ground state, as obtained by a pump-dump sequence. The spectra, calculated for the model parameters that fit steady-state spectra of C102, and for $\tau = 0.3$ ps (the accepted value for the longitudinal relaxation time of CH$_3$CN), are in good agreement with experimental data. Specifically, the blue-shift of the transient absorption is accompanied by an evolution of the absorption band-shape, so that spectra collected in a narrow temporal window all cross in a unique point. This point is not truly isosbestic and, in agreement with experimental data, we calculate a slow blue-shift of its position at increasing time.
IV. CONCLUSIONS

The proposed model describes the spectral properties of conjugated donor-acceptor chromophores in solution in terms of two electronic states coupled to internal vibrations and to solvent degrees of freedom. The model is simple enough to allow for a full exploitation of the non-linearity of the electronic system, that manifests itself in a self-consistent interplay between electronic, vibrational and solvation degrees of freedom. Signatures of this non-linearity are recognized in several typical spectral features that have not explanation in standard approaches. The model is semiempirical in nature: the few model parameters are fixed against experimental data. Then the applicability of the model itself and the reliability of the model parameters for a specific molecule must be confirmed via the comparison with a large body of experimental data, much wider than the pool of data used to fix the parameters. In this respect we underline that the scope of our model is extremely wide, ranging from steady-state to time-resolved spectra, from electronic to vibrational data. Based on available experimental data, the model has been validated for the phenol blue dye, whose steady-state electronic and vibrational spectra are extensively discussed in Ref. 11. A second interesting case study is offered by C102, whose time-resolved electronic spectra have been discussed in the previous Section. For this molecule, solvation effects have also been observed in steady-state and time-resolved vibrational spectra: also these effects can be rationalized within our model. Linear electron-phonon and solute-solvent interactions originate, in materials with non-linear responses, large and non-trivial effects that cannot be understood based on perturbative treatments.

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FIG. 1. (a) Evolution of the probability distribution $w(q)$ over the represented PES. (b) Corresponding evolution of the probability distribution $w(\rho)$. 
FIG. 2. (a) Transient emission spectra calculated for $z_0 = 0.5$ eV, $\sqrt{2} t = 1$ eV, $\Omega = 0.2$ eV, $\epsilon_{sp} = 0.22$ eV, $\epsilon_{or} = 0.4$ eV, $\tau = 1.7$ ps, $T = 300$ K. Time delays are displayed on the figure, time increasing in the direction of the arrows. (b) Transient differential absorption spectra calculated for $z_0 = 1$ eV, $\sqrt{2} t = 1.2$ eV, $\Omega = 0.2$ eV, $\epsilon_{sp} = 0.3$ eV, $\epsilon_{or} = 0.35$ eV, $\tau = 0.3$ ps, $T = 300$ K. Upper panel and lower panel refer to different time windows, as labeled on the figure. Time increases in the direction of the arrows.