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Charge Transfer Processes and Environmental Degrees of Freedom: Cooperativity and Non-Linearity

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Summary: To investigate supramolecular effects in samples with high concentration of push-pull chromophores, we propose a model for interacting polar and polarizable molecules. Each molecule is described in terms of the same two-state picture successfully adopted to model solvated chromophores and electrostatic interactions among different chromophores are introduced. Important supramolecular effects are observed even at the lowest mean-field level, showing up the possibility of tuning molecular polarity from the neutral to the zwitterionic regime or vice versa. Supramolecular effects in excitation spectra are more complex. Here we demonstrate large supramolecular effects beyond mean-field in static optical responses.

Keywords: charge transfer; cooperative effects; dyes; modeling; NLO

Introduction

π-Conjugated chromophores and, specifically, molecules where an electron-rich (donor, D) group is linked by a π-conjugated bridge to an electron-poor (acceptor, A) group attract a lot of interest both in view of their practical applications[1,2] and due to the possibility they offer in investigation of fundamental physical phenomena in terms of basic models.[3] DA-conjugated chromophores are used as laser dyes as well as active luminescent materials in organic light-emitting diodes, are common solvation probes, show large non-linear optical (NLO) responses and are good two-photon absorbers. One of these molecules is the first molecular rectifier.[2] All these properties are related to the presence of a low-lying excited state with a different electronic distribution with respect to the ground state (GS). The low-energy physics of these molecules is governed by this state and by its interplay with slow (vibrational and environmental) degrees of freedom.

Following the original suggestion of Oudar and Chemla,[4] we adopted a two-state electronic model for these molecules and extended it to account for molecular vibrations. The resulting model, the Mulliken DA-dimer with Holstein coupling,[5] can also account for solvation, provided

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one of the Holstein coordinates represents an effective solvation coordinate.[6] The model is simple enough to allow for exact non-adiabatic solution[7] or for the construction of exact adiabatic potential energy surfaces (PES) for the ground and excited states.[7,8] The non-adiabatic solution proved useful to understand the physics of vibrational amplification of static NLO responses,[7] whereas the adiabatic PES opened the way to detailed spectroscopic analysis. Specifically, steady-state absorption and fluorescence spectra and their evolution with the solvent polarity are well reproduced based on few microscopic parameters.[8] Time-resolved fluorescence, pump-probe and, more generally, time–resolved experiments involving the evolution of the system in either the ground- or excited-state PES can also be interpreted based on the same model, describing the relaxation of the system in the relevant PES within the Fokker-Planck approach.[9] Vibrational spectra can also be modeled, with vibrational solvatochromism and inhomogeneous broadening in polar solvents concurring, to originate impressive effects in resonance Raman spectra.[10,11]

The detailed analysis of spectral properties of solvated DA chromophores allowed us to show the non-linearity of the electronic system as the most characteristic feature of these molecules.[12] The simple two-state model we adopt for the electronic system in fact accounts for the molecular polarity and polarizability at all orders. Several anomalous spectroscopic features of DA chromophores that were not understood within standard (perturbative) approaches are a natural consequence of the large molecular (hyper)polarizability. Of particular relevance in this respect is the evolution with the solvent polarity of steady-state absorption and fluorescence band shapes as well as their non-specularity,[8,13] the temporal evolution of time-resolved fluorescence bands, and the appearance of temporary isosbestic points in pump-probe and femtosecond hole-burning spectra.[9] The vibrational solvatochromism itself and the related inhomogeneous broadening induced by the solvent polarity[10,11] are a signature of the large non-linearity that characterizes the electronic responses to vibrational and solvation perturbations. Large non-Condon effects in resonant and non-resonant non-linear responses are an additional consequence of the non-linearity, with effects that show up most clearly in two-photon absorption spectra,[14] in the frequency-dependence of the second-harmonic generation signal[15] and, more generally, in the large vibrational amplification of static NLO responses.[5,7]

This same non-linearity is expected to show up in samples with large concentrations of chromophores, including crystalline samples, aggregates, Langmuir-Blodgett films, and polymers doped and/or functionalized with DA chromophores. Electrostatic interactions, which for sure are important in a system of interacting polar chromophores, can lead to really impressive effects if the molecular (hyper)polarizability is accounted for, leading to amplification of the non-linearity that shows up by spectroscopic anomalies as well as by impressive collective effects in the GS like, e.g., phase transitions. In the following we will introduce a simple model for interacting polar and (hyper)polarizable chromophores and investigate supramolecular effects in the corresponding GS properties.

A model for interacting polar-polarizable chromophores

An array of N chromophores can be described by the following general Hamiltonian:

$$\hat{H}=\sum_i\left(2z_0\hat{\rho}_i-\hat{\sigma}_{xi}\right)+\frac{1}{2}\sum_{i,j\neq i}V_{ij}\hat{\rho}_i\hat{\rho}_j \qquad (1)$$

where the first term describes each chromophore in terms of the same two-state model used for the isolated chromophore.[5] Specifically, the two basis states, |DA> and |D$^+$A$^-$>, are separated by an energy gap $2z_0$ and are mixed by a matrix element that, without loss of generality, we set to 1. The ionicity operator $\hat{\rho}_i=\left(1-\hat{\sigma}_{zi}\right)/2$ measures the polarity of the chromophore on site i, where $\hat{\sigma}_{xi}$, $\hat{\sigma}_{zi}$ represent the Pauli spin matrices. The last term in the above Hamiltonian describes inter-chromophore interactions, with V_{ij} measuring the electrostatic interaction between fully ionized chromophores on sites i and j. The Hamiltonian in Eq. (1) applies to molecular clusters of any size and dimension; here, however, we only discuss linear arrays of chromophores with the three different molecular arrangements shown in Fig. 1.

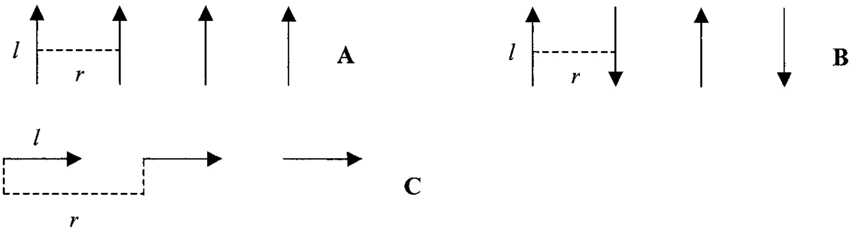

Fig 1. The three different geometrical arrangements discussed in the text. The arrow schematically represents a polar molecule.

As far as electrostatic interactions are concerned, we assign to each chromophore a fixed dipole length, l, so that:

$$V_{ij} = (\pm 1)^{|i-j|} 2vw \left[\frac{1}{d_{ij}} - \frac{1}{\sqrt{d_{ij}^2 + w^2}} \right] \tag{2}$$

where + and – sign refer to A and B clusters, respectively, and

$$V_{ij} = 2vw \left[\frac{1}{d_{ij}} - \frac{d_{ij}}{d_{ij}^2 - w^2} \right] \tag{3}$$

for C cluster. In all cases, d_{ij} is the distance between sites i and j in units of r, the distance between adjacent sites, and v measures the magnitude of the intrachromophore electrostatic interactions as relevant to a fully ionized chromophore ($v = e^2/l$). Finally, $w = l/r$ so that $w = 0$ describes non-interacting chromophores, and $w < 1$ C clusters. Interchromophore electron hopping is forbidden in the proposed Hamiltonian, and the direct product of the two basis functions centered on each site forms a complete basis set. The resulting $2^N \times 2^N$ Hamiltonian matrix is diagonalized exactly for clusters with up to 8 chromophores with periodic boundary conditions (PBC).

Results

Figure 2 reports the evolution of the GS chromophore polarity, $\rho = \langle \hat{\rho}_i \rangle$, independent of i for PBC, with w. The three columns refer to molecular arrangements A, B, C in Fig. 1; the top row shows results for $z_0 = 1$, corresponding to an isolated chromophore with a neutral (N) GS ($\rho = 0.15$ at $w = 0$), the bottom row shows results for $z_0 = -1$, corresponding to a zwitterionic (I) chromophore ($\rho = 0.85$ at $w = 0$). Interchromophore interactions disfavor charge separation for the A geometry, and ρ decreases with w in the leftmost panels in Fig. 2, whereas just the opposite occurs for geometry B and C (Fig. 2, middle and left panels). The behavior of an A cluster of I chromophores (Fig. 2b) and of B and C clusters of N molecules (Fig. 2c and e, respectively) are then particularly interesting. In the first case the isolated chromophore is zwitterionic, but, with increasing w (i.e. by decreasing the interchromophore distance), the molecular polarity decreases to the cyanine limit ($\rho = 0.5$) reaching the N regime for $r <\sim 0.7\, l$. Similarly, a N isolated chromophore can be driven to the I regime for large enough interactions in either B and C geometries at $r < 0.5\ l$ and $r < 1.4\ l$, respectively. The corresponding I to N and N to I crossovers are different in shape, as can be understood in a mean-field (mf) picture.

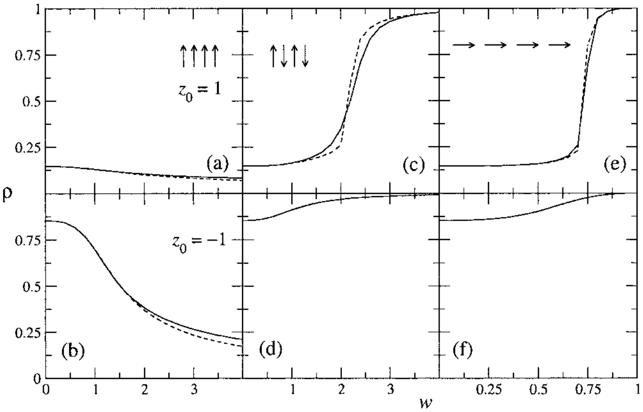

Fig 2. Molecular GS polarity, ρ, as a function of the strength of the interchromophore interaction, w, calculated for clusters of 8 molecules, with $\nu = 1$. Left, middle and right columns refer to geometries A, B and C, respectively; top and bottom rows correspond to $z_0 = 1$ and -1, respectively. Continuous and dashed lines refer to exact and mean-field results, respectively.

The mf treatment of the Hamiltonian has been described many years ago for C geometry[16] and the same treatment applies to other geometries as well. The mf Hamiltonian describes a collection of non-interacting chromophores, i.e., it only retains the first term in Eq. (1), but each chromophore feels the electric field generated by the surrounding chromophores in their GS configuration. The mf problem then reduces to a self-consistent two-state problem with the bare z_0 parameter in Eq. (1) substituted by $z = z_0 + M\rho$, with $M = 1/2\sum_{j\neq i} V_{ij}$. In this picture ρ only depends on z, and hence an explicit expression $z_0(M,z)$ is easily written. Specifically

$$\frac{\partial\rho}{\partial z_0} = \frac{\mathrm{d}\rho}{\mathrm{d}z}\left(1 - M\frac{\mathrm{d}\rho}{\mathrm{d}z}\right)^{-1} \qquad (4)$$

so that for positive M (repulsive interchromophore interaction, A geometry), the slope of ρ vs z_0 decreases with M, justifying the smooth evolution of $\rho(w)$ in Fig. 2b. The opposite occurs for negative M (attractive interaction, B and C geometries). As a matter of fact, for large negative M a divergent $\partial\rho/\partial z_0$ is obtained, marking the occurrence of a discontinuous phase transition from the

N to the I regime.[16] Correspondingly, S-shaped mf $\rho(w)$ curves are calculated for $z_0 > 1$.

The large variation of ρ with w, and particularly the possibility of tuning the molecular polarity across the N-I boundary by simply modifying the relative orientation and/or the separation of the chromophores, demonstrate the importance of supramolecular interactions in clusters of polar-polarizable chromophores. Each polar molecule in fact originates a local electric field, which affects the GS polarity of surrounding molecules in a self-consistent loop that easily creates cooperativity as demonstrated most impressively by the possible occurrence of discontinuous N-I transitions. It is well known that molecular properties of DA chromophores strongly vary with molecular polarity and many efforts have been made to tune the molecular polarity to improve specific properties, including, e.g., static NLO responses.[1] Our results demonstrate large environmental effects in clusters, suggesting, on one hand, a large amount of tunability of molecular properties via supramolecular interactions and, on the other, the need for a careful modeling of the interactions themselves.

The problem of supramolecular interactions in clusters of polar-polarizable chromophores is more complex than recognized within a mf treatment. In fact the mf picture describes reasonably well GS properties like, e.g., the molecular polarity (cf. Fig. 2). However, mf approaches are inadequate for describing excited states and, more generally, molecular properties, including static NLO responses, which strongly depend on the excitation spectrum. The Hamiltonian in Eq. (1) actually describes the excitonic coupling and, indeed, it can be exactly mapped into an Hamiltonian where standard excitonic coupling terms can be explicitly observed. Excitonic (and ultra-excitonic) effects on the excited states of clusters of DA chromophores are particularly large and impressive and their analysis will be the subject of a separate publication.[17] Here we limit ourselves to investigation of (ultra)excitonic effects on static NLO responses of clusters of polar-polarizable chromophores. Figure 3 reports the static linear polarizability, α, and the first and second hyperpolarizabilities, β and γ, calculated, respectively, for geometry A and $z_0 = -1$ (cf. Fig. 2b), and geometry B and C for $z_0 = 1$ (cf. Fig. 2c and e, respectively), with $v = 1$ in all cases. Exact results (continuous lines) are compared with mf data (dashed lines), calculated by modeling the cluster as an oriented gas of mf chromophores. Whereas the mf estimate of the molecular polarity is a reasonable approximation to the exact results, the mf approach badly fails in the calculation of static (hyper)polarizabilities. Specifically, data in the first column of Fig. 3, relevant to an A cluster of I chromophores, demonstrate a large depression of static (hyper)polarizabilities, with effects that become appreciable when the interchromophore distance is about three times larger than the dipole length, i.e., well before the I-N crossover is reached (cf. Fig. 2b). A similar depression of static responses is observed in the case of a B cluster of N chromophores even if, due to the opposite sign of M, a qualitatively different behavior is observed for $\rho(w)$ with respect to the previous case (cf. Figs. 2c and 2b). Again sizeable deviations from the mf results are already observed at $r \sim 3\ l$, with effects that become prominent at the N-I crossover. The C cluster of N molecules shows a similar $\rho(w)$ evolution as the B cluster of N molecules (cf. Figs. 2c and 2e), but, as follows from the rightmost panels in Fig. 3, a *qualitatively different* behavior of optical susceptibilities. In this case, in fact, an amplification of static NLO responses is calculated with respect to the mf result, with the effects that are really huge at the N-I transition and increase fast with the order of the response.

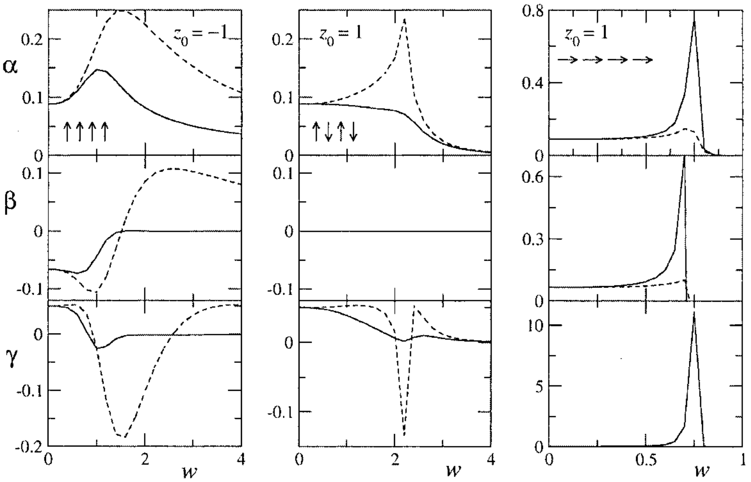

Fig 3. Static susceptibilities (α, β, γ) calculated as a function of the strength of the interchromophore interaction, w, for clusters of 8 molecules, with $v = 1$. Left panels: geometry A, $z_0 = -1$; middle panels: geometry B, $z_0 = 1$; right panels: geometry C, $z_0 = 1$. Continuous and dashed lines refer to exact and mean-field results, respectively. The β response vanishes exactly for the centrosymmetric B-type cluster.

Conclusions

We have demonstrated large supramolecular effects on ground-state properties, including static optical susceptibilities, in clusters of polar-polarizable molecules. The adopted model is relevant to samples of interacting DA chromophores, systems that are currently under active investigation, particularly for their possible use in advanced applications.[1,18] We underline the similarity between the N-I transition observed in C clusters of N molecules with the N-I transition observed in mixed-stack charge transfer (CT) crystals.[16,19] The amplification of α observed in C clusters (Fig. 3, upper-right panel) implies amplification of the static dielectric response, which is reminiscent of recent experimental[20] and theoretical[21] results on CT crystals. The model describes rigid clusters of rigid chromophores, but, similarly to what happens for isolated chromophores[5,7] and for CT crystals as well,[21] we believe that molecular vibrations will lead to a further amplification of non-linearity. Orientational disorder is not accounted for. Disorder is for sure present in aggregates as well as in samples where DA chromophores are dispersed in (or attached to) a polymeric matrix, and possibly has important effects there.[18] However, no reliable modeling of the properties of these intriguing materials can be achieved without fully accounting for the molecular (hyper)polarizability.

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