

FROM MOLECULES TO DEVICES: SUPRAMOLECULAR INTERACTIONS IN MATERIALS FOR ADVANCED APPLICATIONS

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Abstract

To fully exploit the promise of molecular materials for advanced applications a thorough understanding of supramolecular structure-properties relationships is needed, a non-trivial problem because non-additive, collective behavior appears as a result of intermolecular interactions. We present a model for interacting polar and polarizable molecules that applies to clusters (films, crystals, aggregates...) of D- π -A molecules for molecular electronics and/or NLO applications. The model is based on a two-state description of the isolated molecules, validated by an extensive spectroscopic study of solvated molecules. Classical electrostatic interactions in molecular clusters are then accounted for in a bottom-up theoretical approach that parallels the synthetic strategy. We demonstrate that the molecular polarity, and hence all molecular properties are largely affected by supramolecular interactions: the same molecule behaves in qualitatively different ways in different environments. Even more important, brand new phenomena appear in molecular materials with no counterpart at the molecular level. These phenomena largely extend the scope of potential application of molecular materials. In particular, in lattices with attractive interactions, large bistability regions appear where the material can be switched between two different regimes by slight variations of external conditions. In the proximity of the bistable region, important collective effects show up in the excitation spectrum, and the absorption of a single photon directly drives a concerted multielectron transfer occurring on several nearby molecules.

1. Introduction

The properties of molecular materials (mm) are very sensitive to the supramolecular arrangement of the molecular units, and much attention is currently devoted to extend the structure-properties relationships from the molecular to the supramolecular level [1]. Intermolecular interactions are weak if compared with the strong chemical forces that bind atoms together within a molecule, but they are fundamental in the definition of the actual supramolecular arrangement and are quite actively investigated in this perspective. However mm of interest for advanced applications are most often based on largely polarizable molecular units, and intermolecular interactions can play an even more important role. In fact the interaction of each polarizable molecular unit with its polarizable surrounding leads to cooperative phenomena and to the appearance of new physics with no counterpart at the molecular level. Important collective phenomena are also expected due to the delocalization of excited state wavefunctions. The standard excitonic approach to mm [2] disregards the molecular polarizability and cannot account for cooperativity. In this paper we discuss the interplay between cooperative and collective phenomena as driven by classical electrostatic interactions in mm made up of polar and polarizable molecules. The model quite naturally describes aggregates, films or crystals of push-pull (pp) chromophores.

2. Modeling molecular materials

Much information can be obtained on pp chromophores by studying their solution spectra. In recent years we have developed a model to describe optical spectra of pp chromophores in solution [3]. The model is based on a two-state description of the electronic structure of the chromophore, and accounts for Holstein coupling to molecular vibrations and to an effective solvation coordinate. An extensive comparison with experimental data demonstrates it describes the fundamental physics of pp chromophores. It therefore offers a good starting point to describe materials based on pp chromophore. The basic Hamiltonian we propose for interacting chromophores reads as [4, 5]:

$$H = \sum_i \left(2z_0 \hat{\rho}_i - \sqrt{2}t \hat{\sigma}_{x,i} \right) + \sum_{i>j} V_{ij} \hat{\rho}_i \hat{\rho}_j \quad (1)$$

where the first term describes each chromophore in terms of the two-state model: $2z_0$ is the energy gap between the two basis state, the neutral $|DA\rangle$ and the zwitterionic $|D^+A^-\rangle$, $\sqrt{2}t$ is the mixing matrix element, $\hat{\rho}_i$ measures the polarity of the i -th chromophore. The second term accounts for classical electrostatic intermolecular interactions, with V_{ij} measuring the interactions between two zwitterionic chromophores at ij sites. Molecular parameters can be extracted from the analysis of solution spectra, whereas electrostatic interactions are fixed by the cluster geometry [5]: we can then follow the evolution of the material properties from the molecular to the supramolecular level.

The above Hamiltonian can be diagonalized exactly on clusters of finite size but it is interesting to introduce some common approximation scheme. As for ground state (gs) properties are concerned, the mean field

(mf) approximation offers a powerful approach. Within mf the interactions of each molecule with its surrounding is modelled in terms of an effective electric field [5]. The mf gs then describes a collection of chromophores each one in its local gs [5]. The mf approximation fully accounts for the molecular polarizability, and, via the self-consistent interaction of each molecule with its surrounding, it captures the cooperative nature of the problem. However, by construction, it disregards any correlation among different molecules.

The mf gs is a good starting point to build up the excitonic picture: in fact the best excitonic picture is constructed out of mf states [5]. States with one, two, ... n -excitations are obtained from the mf gs by simply switching one, two, ... n molecules from the local gs to the local excited state. States with the same number of excitations have similar energies, and the excitonic approximation only accounts for the mixing of states with the same n [2]. Excitonic states can then be classified according to the total number of excitations, n . The mf gs coincides with the vacuum ($n=0$) state in the exciton picture, and, upon photoexcitations, only states with $n=1$ are accessible. The excitonic approximation introduces some correlation, but, not allowing for the mixing of states with different excitation number, fully neglects the molecular polarizability: indeed the state of the molecules is not allowed to readjust in response to excitation occurring on the same or on neighboring molecular sites.

3. Optical spectra

In order to keep the discussion simple we concentrate on two one-dimensional clusters where all molecules have parallel orientation as $\dots\uparrow\uparrow\uparrow\dots$ (case A, the arrow represents the molecular dipole) or as $\dots\rightarrow\rightarrow\rightarrow\dots$ (case B). Periodic boundary conditions are enforced to ensure the equivalence of all molecular sites. Electrostatic interactions [5] are then fully defined in terms of v , the interaction energy between two unit charges at the two ends of a molecular dipole, and by w , the ratio between the length of the molecular dipole and the intermolecular distance ($w=0$ corresponds to the limit of isolated molecules). For typical pp chromophores molecular lengths are of the order of 0.5-1 nm, so that v is of the order of 1eV, i.e. of the same order of magnitude as $\sqrt{2}t$ [3]. In the following energies are measured in units with $\sqrt{2}t=1$.

The lowest panels in Fig. 1 show the evolution of the molecular polarity, p , with w . In A cluster, or more generally in clusters with dominant repulsive interactions, the polarizable molecular units decrease their polarity with w (i.e. with increasing intersite interactions) as to release repulsive interactions. Just the opposite occurs in B clusters, or more generally in clusters with attractive interactions. The examples shown in Fig. 1 are particularly impressive with very large polarity variations that lead to large variations of the molecular properties. Collective effects add on top of that, leading to a very complex behavior. In Ref. 5 we have discussed these phenomena with reference to NLO responses; here we focus attention on optical spectra.

Middle and upper panels in Fig. 1 show the w -dependence of the absorption frequency (ω) and the squared transition dipole moment (μ_{CT}^2). In both A and B clusters a large and non-trivial dependence of the optical

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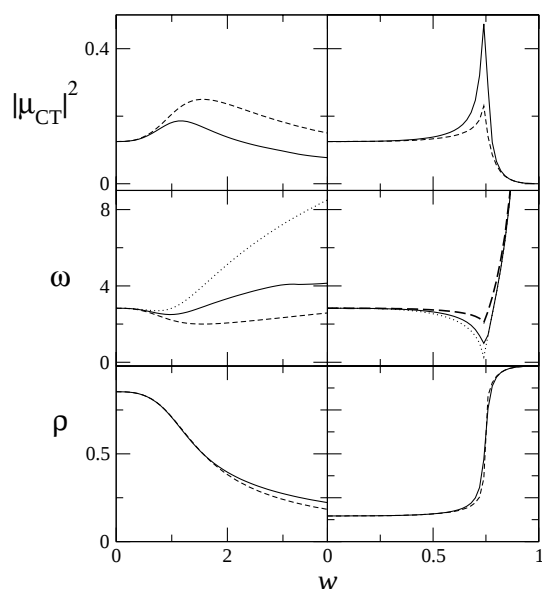


Fig. 1 The gs polarity, the optical frequency and the squared transition dipole moment vs w for 16 sites clusters. Left panels: A-type lattice, $v=1$, and $z_0=-1$; Right panels: B-type lattice, $v=1$, and $z_0=1$. Continuous lines show results from exact diagonalization, dashed and dotted lines correspond to mf and excitonic results, respectively (mf and excitonic results coincide in the top and bottom panels).

frequency with the cluster geometry is observed. Excitonic corrections to the frequency are positive (negative) in repulsive (attractive) clusters, however in the repulsive A cluster the optical frequency is redshifted, at low w , with respect to the isolated molecule. This results from the large red-shift of the mf frequency for molecules that are driven towards intermediate polarity: the observed frequency is due to a combined effect of cooperative and collective effects, as described within the mf and excitonic picture. But the excitonic approximation itself breaks down with increasing interactions and sizeable ultraexcitonic corrections are observed for $w > 1.5$. In the attractive B cluster, most sizeable effects are observed in the region of intermediate polarity: for $w \rightarrow 1$ the mf frequency increases steeply as the molecular polarity goes towards 1.

4. Bistability and multielectron transfer

Attractive lattices are particularly interesting since they support discontinuous polarity crossovers. Fig. 2 shows the w -dependence of the gs polarity of B-type lattices with continuous (left panels) and discontinuous polarity crossover (right panels). Discontinuous crossovers, also observed within mf, represent the extreme manifestation of cooperativity: a discontinuous crossover in fact cannot be supported at the single molecule level, but appears in molecular clusters as a consequence of classical electrostatic intermolecular interactions.

The properties of the material in the proximity of a discontinuous crossover are very interesting as they are governed by a subtle interplay of cooperative and collective phenomena that generate new and interesting physics. In the top panel of Fig. 2 we report Δ , the average number of fully polar sites created upon photoexcitation. Within the excitonic approximation a single exciton is created upon photoexcitation, i.e. a single molecule is switched from the local gs with polarity ρ to the local excited state with polarity $1-\rho$, so that $\Delta=1-2\rho$. Within the excitonic picture then $-1 < \Delta < 1$, and the absorption of a single photon can drive at most a single electron across a molecule from the D to A site ($\Delta=1$) or viceversa ($\Delta=-1$). Results compatible with the excitonic model should therefore stay within the dashed lines in the upper panels of Fig. 2. This condition is satisfied for A-type lattices, but breaks down for attractive (B) lattices near the polarity crossover. Already for the parameters relevant to left panels in Fig. 2, where a smooth crossover is observed, Δ values significantly larger than 1 in absolute value are found, a result that becomes more impressive for discontinuous charge crossovers, as shown in the right panels of Fig. 2 where Δ as large as 7 are found. This result is interesting in several respects: first of all it demonstrates that near a discontinuous charge crossover the excitonic picture is qualitatively inadequate. Moreover, and more importantly, it implies that the absorption of a single photon drives the concerted motion of $|\Delta|$ electrons from the D to A site (or vice versa) in $|\Delta|$ different molecules. Multielectron transfer corresponds to the redmost and most intense

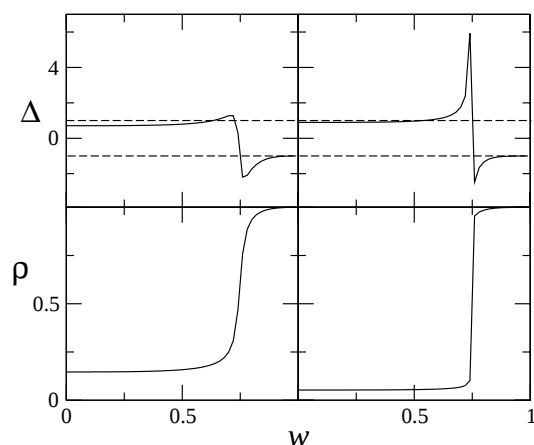


Fig. 2 The w -dependence of the gs polarity and of the number of charge separated species created on photoexcitation. Exact results for 16 sites B-type clusters. Left panels: $v=1$, and $z_0=1$; Right panels: $v=2$, $z_0=2.0$.

transition (at least one order of magnitude more intense than other transitions) and we underline that the relevant frequency and intensity stay finite. The detailed analysis in Refs. 4 and 5 showed that multielectron transfer describes concerted electronic motion occurring on $|\Delta|$ nearby molecules and that it results from the intrinsically correlated nature of the electronic motion in both the excited and the ground state, definitely proving the failure of the mf approximation near the discontinuous charge crossover.

5. Conclusions

We have demonstrated that in a model for non-overlapping polar and polarizable molecules classical electrostatic intermolecular interactions lead to the appearance of new phenomena that extend the scope of applications of mm. The possibility of tuning the polarity of the molecule by tuning the cluster geometry adds new value to the supramolecular engineering of mm. To fully exploit the potential of mm we must however extend our knowledge of structure-properties relationships from the molecular to the supramolecular level, a non trivial task since cooperative and collective phenomena make the materials qualitatively different from a collection of molecules. Here we present a bottom-up approach to the modelling of mm: starting with the analysis of optical spectra of molecules in solution we define a relevant model for materials based on the same molecules. Following the evolution of the molecular properties from solution to the material, and comparing the behavior of different materials made up of the same molecular units opens the way to acquire new fundamental understanding.

The discontinuous charge crossover and the related bistable regime open the possibility of molecular-based switches that can be driven by the applying pressure or stresses to the sample. The observation of multielectron transfer suggests on one side the possibility of photoinduced transformation [4], that were indeed observed in related materials, the charge transfer salts with mixed stack motif. On the other side the possibility to move several electrons upon absorption of a single photon opens new possibilities for improving the efficiency of photoconversion devices.

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