FROM MOLECULES TO DEVICES:
SUPRAMOLECULAR INTERACTIONS IN MATERIALS FOR ADVANCED APPLICATIONS
Anna Painelli\(^1\) and Francesca Terenziani\(^2\).

\(^1\)Dip. Chimica GIAF, Parma University and INST-UdR Parma, Viale delle Scienze, 17/A, 43100 Parma, Italy,
\(^2\)Institut de Chimie, UMR 6510, Université de Rennes 1, Campus de Beaulieu, Bât. 10A, 35042 Rennes Cedex, France.

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 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.

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
cooperaivity. 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
chromophores. The basic Hamiltonian we propose for interacting
chromophores reads as \([4, 5]\):

\[
H = \sum_{i,j} \varepsilon_{i,j} \hat{\rho}_{i,j} - \sqrt{2} \hat{\Sigma}_{i,j} \hat{\sigma}_{i,j} + \sum_{n} V_n \hat{\rho}_{i,j}
\]  

(1)

where the first term describes each chromophore in terms of the two-state
model: \(\varepsilon_{i,j}\) is the energy gap between the two basis state, the neutral \(DA^+\)
and the zwitterionic \(DA^-\), \(\hat{\Sigma}_{i,j}\) is the mixing matrix element, 
\(\hat{\rho}_{i,j}\) measures the polarity of the \(j\)-th chromophore. The second term
accounts for classical electrostatic intermolecular interactions, with \(V_n\)
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.

3. Optical spectra

In order to keep the discussion simple we concentrate on two
one-dimensional clusters where all molecules have parallel orientation as
\(\cdots \pi \pi \pi \cdots\) (case A, the arrow represents the molecular dipole) or as
\(\cdots \cdots \cdots\) (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 \(\nu\), 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 \(w\) is
of the order of 1 eV, i.e. of the same order of magnitude as \(\sqrt{\nu} [3]\). In the
following energies are measured in units with \(\sqrt{\nu} = 1\).

The lowest panels in Fig. 1 show the evolution of the molecular polarity,
\(\rho\), 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. 3 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 \(\nu\)-dependence of the
absorption frequency (\(\omega_0\)) and the squared transition dipole moment (\(\beta^2\)).
In both A and B clusters a large and non-trivial dependence of the optical
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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 models, respectively. 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 models. 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 models, respectively. 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 models.