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Linear and non-linear optical properties of push–pull chromophores: vibronic and solvation effects beyond perturbation theory

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Abstract

A model for optical properties of push–pull chromophores in solution is summarized and applied to describe femtosecond hole-burning spectra of coumarin 102. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Models for non-linear phenomena; Optical absorption; Emission spectroscopy

1. Introduction

Molecules for NLO are characterized by large non-linear responses to electric fields. Besides externally applied electric fields, internal fields are also expected to play an important and non trivial role. Internal fields are introduced to model the interaction of the relevant molecular system with ‘bath’ coordinates, the reaction field felt by a polar molecule in solution being a typical example. In push–pull chromophores, molecular vibrations drive the electronic charge back and forth among donor (D) and acceptor (A) sites, then playing the same role as an electric field. Internal fields are determined by the properties of the relevant system, that in turn non-linearly depend on electric fields. Accounting for this feedback mechanism is the key to understand the behavior of NLO materials. Push–pull chromophores in solution are an interesting case study: here, we summarize a simple model for their optical properties [1–4] and apply it to understand recent femtosecond hole-burning data [5].

2. A polarizable-solute model for spectral properties

The simplest model for push–pull chromophores considers two basis states, $|DA\rangle$ and $|D^+A^-\rangle$, separated by an energy gap $2z_0$. In the Mulliken approximation, an electric field modulates z_0 [1], and the Hamiltonian for a push–pull chromophore, also accounting for internal fields, reads:

$$H = 2z_0\hat{\rho} - \sqrt{2}\hat{\sigma}_x - \sum_{i=0}^N \frac{1}{2r_i} F_i^2 - \sum_{i=0}^N \mu_0 F_i \hat{\rho} \quad (1)$$

where $\hat{\rho} = (1 - \hat{\sigma}_z)/2$ is the ionicity operator, and $\hat{\sigma}_x, \hat{\sigma}_z$ the Pauli spin operators. The first two terms in Eq. (1) describe the electronic system. The internal fields, F_i , couple directly to the dipole moment operator, $\mu_0\hat{\rho}$, μ_0 measuring the dipole moment of $|D^+A^-\rangle$. F_0 describes the orientational component of the reaction field (the fast electronic component of the reaction field is not explicitly included since it only leads to a renormalization of z_0 [2]). The remaining fields describe molecular vibrations modulating on-site energies (Holstein coupling), with $F_i = \sqrt{r_i}\omega_i Q_i$, where Q_i is the normal coordinate and ω_i the corresponding frequency. The elastic energy associated to each field fixes its equilibrium amplitude to $(F_i)_{eq} = r_i\mu_0\rho$, where ρ is the expectation value of $\hat{\rho}$ [2].

In the absence of coupling to internal fields, the above Hamiltonian has a trivial solution, and ρ is only function of z_0 [1]. Internal fields in Eq. (1) describe slow degrees of freedom, so that, in the adiabatic approximation, we can define an effective electronic Hamiltonian by fixing the F_i 's to their equilibrium values. The resulting Hamiltonian still describes a two-state system, but z_0 is replaced by an effective parameter self-consistently depending on the equilibrium charge distribution: $z = z_0 - \sum_{i=0}^N \mu_0^2 r_i \rho / 2 = z_0 - \varepsilon_T \rho$, where ε_T , the total relaxation energy of slow degrees of freedom, is conveniently partitioned into a contribution from the orientational reaction field, $\varepsilon_{or} = \mu_0^2 r_0 / 2$, plus the small polaron binding energy, measuring the total relaxation energy from internal vibrations, $\varepsilon_{sp} = \sum_{i=1}^N \mu_0^2 r_i / 2$. The self-consistent interaction that involves (slow) internal fields makes the physics of the model very interesting and highly non-trivial: it largely amplifies static NLO responses [1,2], and it is also the key to understand the diverse spectroscopic properties of push–pull chromophores [3,4]. However, the fundamental role of this non-linear interaction can only be

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appreciated in truly non-perturbative approaches. Our model, in spite of its non-linearity, is amenable to exact solutions.

Push–pull chromophores, typical molecules for NLO applications, have large linear and non-linear polarizabilities. Standard approaches to spectroscopic solvent effects indeed neglect even the linear molecular polarizability. In those approaches, molecular energy varies with solvent polarity, whereas all molecular properties are taken as solvent independent. Our model predicts an increase of the molecular dipole moment with the solvent polarity, yielding to a non-linear dependence of the Stokes-shift on the solvent polarity [3]. The standard procedure for extracting mesomeric dipole moments from solvatochromic data is then invalidated. The dependence of molecular properties on the solvent polarity also implies solvent-dependent Huang–Rhys factors, i.e. solvent-dependent absorption and/or emission band-shapes [3]. Vibrational properties are affected too: we easily predict solvent dependent harmonic frequencies, infrared and non-resonant Raman intensities [2,4].

Oriental degrees of freedom of polar solvents are much slower than molecular vibrations. We then account for a static distribution of the orientational reaction field around the equilibrium. Since the molecule readjusts its polarity in response to the local reaction field, the solution can be modeled as a collection of chromophores with different polarity, each one in equilibrium with the local solvent arrangement. The resulting inhomogeneous broadening affects in different ways absorption and emission band-shapes, but also shows-up in vibrational spectra with the broadening of infrared and Raman frequencies and with the observation of anomalous dispersion of resonant Raman frequencies with the excitation line [4].

3. Time-resolved experiments: the case of C102

The molecular charge distribution of largely polarizable molecules, like push–pull chromophores, also readjusts following the relaxation of slow coordinates. This is the basis to rationalize the non-specularity of absorption and

emission spectra, but it is also the key to understand time-resolved experiments. In this respect, recent femtosecond hole-burning spectra collected on coumarin 102 (C102) in CH_3CN constitute an interesting case study [5]. In this experiment, a pump and dump pulse sequence prepares C102 into a ‘particle’ state, i.e. in the ground state electronic configuration, but with slow degrees of freedom out of equilibrium. The time dependence of transient absorption spectra from this particle state then gives information on the relaxation of slow coordinates towards the equilibrium. According to the authors of [5], vibrational coordinates re-equilibrate within the first 40 fs from dumping, so that all the subsequent evolution can be assigned to the evolution of the solvent orientational degrees of freedom. Moreover, the differential optical density signal measured for $\lambda > 460$ nm are largely dominated by stimulated emission and excited state absorption processes. We do not attempt to model this portion of the spectrum (the absorption from the excited state is beyond the scope of a two-state model). Around 400 nm, the spectrum is dominated by the transient absorption from the particle state. The blue-shift of the transient absorption is easily rationalized even in standard treatments of solvation effects. More subtle is the appearance, in the time evolution of transient absorption spectra, of a quasi-isosbestic point that slowly moves higher in energy with time. The physical origin of this isosbestic point has not been understood so far, but it is an obvious consequence of the large solute polarizability. The relaxation of solvent coordinates monitored by the transient absorption spectrum affects the solute energies and justifies the blue-shift of the absorption maximum. But a polarizable solute also readjusts its polarity following slow coordinates, so that the shape of transient absorption evolves with time, rationalizing the observation of a quasi-isosbestic point.

The analysis can be made quantitative; in fact, from a detailed fit of absorption and emission spectra of C102 dissolved in polar and apolar solvents, a reliable set of microscopic parameters has been extracted [6], summarized in the caption of Fig. 1. With these parameters we predict an evolution of the solute polarity from $\rho = 0.25$ in the vertically damped state (vibrational and solvent coordinates fixed

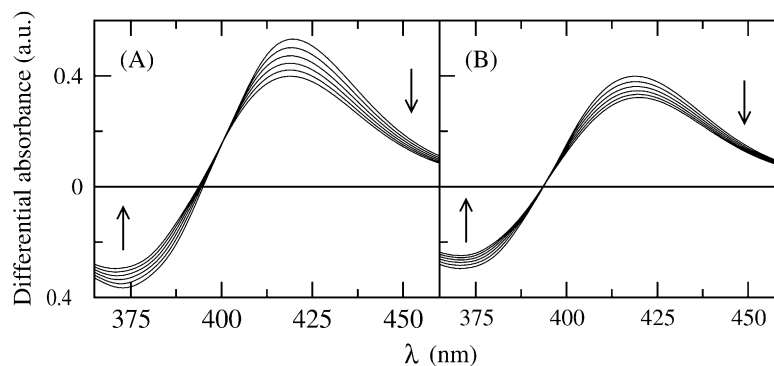


Fig. 1. Differential absorption spectra calculated for ρ evolving from 0.202 to 0.197 (panel A) and from 0.197 to 0.192 (panel B) in the direction of the arrows. The model parameters are fixed to $z_0 = 1.2$ eV, $\sqrt{2}t = 1.2$ eV, $\omega_1 = 0.12$ eV, $\epsilon_1 = 0.27$ eV and $\epsilon_{\text{or}} = 0.47$ eV.

to their equilibrium positions relevant to the excited state) to $\rho = 0.22$ after the relaxation of vibrational coordinates, to finally reach the ground state equilibrium value $\rho = 0.16$ at infinite time. In order to compare directly with raw data in Fig. 5 of [5], in Fig. 1, we report the differential absorption spectra calculated as the difference between the transient absorption spectrum of the particle state of C102, with variable ρ and the static absorption spectrum. In [5], the differential optical absorption spectra are shown in two different time-delay windows (80–240 and 240–600 fs), showing quasi-isosbestic points at 400 and 390 nm, respectively. These data are fairly well reproduced by modeling the temporal evolution from 80 to 240 fs in terms of transient absorption from states with ρ ranging from 0.202 to 0.197 (Fig. 1A) and the subsequent evolution from 240 to 600 fs in terms of states with $\rho = 0.197$ –0.192 (Fig. 1B). The agreement with experimental data is impressive.

Linear and non-linear optical spectra of push–pull chromophores show several unusual features that so far resisted simple interpretation. Specific solute–solvent interactions are indeed often invoked. Many of these features are fairly obvious consequences of the large and non-linear responses

of these molecules to effective electric fields originated by bath degrees of freedom. When modeling NLO materials their intrinsic non-linearity cannot be disregarded.

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