Two-dimensional femtosecond optical spectroscopy of trapping dynamics in a charge-transfer process

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ABSTRACT

We study charge-transfer dynamics monitored by two-dimensional (2D) optical spectroscopy. The often used model consisting of two coupled diabatic electronic states in a single reaction coordinate is used to demonstrate the relation between the vibronic dynamics and the 2D-spectra. Within the employed wave-function approach, dissipation is included via a quantum-jump algorithm with explicit treatment of dephasing. States with long lifetimes which decay slowly due to the interaction with the environment are identified. Using filtered Fourier transforms, energy and time resolved information about the dissipative system dynamics can be obtained.

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1. Introduction

Two-dimensional (2D) optical spectroscopy has evolved into a main experimental tool to investigate the quantum dynamics in molecules and molecular aggregates. After the basic technologies were developed [1–5], recent years have seen many applications [6–15]. The theory of multidimensional coherent spectroscopy was put forward by Mukamel and others [16–18] employing density-matrix theory to calculate non-linear response functions which, for simple models, can be calculated analytically [16]. Within this approach, it is possible to illustrate different pathways contributing to the signals using double-sided Feynman diagrams [16,19]. The latter derive from time-dependent perturbation theory which can be implemented numerically to calculate 2D-spectra. An alternative method to determine time-dependent polarizations which does not rely on perturbation theory was devised by Seidner et al. [20] for pump–probe spectroscopy. The idea is to tack particular phases to the different pulses which then allows for the extraction of the direction-dependent polarization. This approach can also be applied to four-wave-mixing spectroscopy [21,22]. More recently, the Domcke group developed another efficient method for the calculation of four-wave-mixing signals, first for density matrices [23] and then also for wave-functions [24].

If no line-broadening mechanism is present as is realized in a a sample of non-interacting molecules in the gas phase, high-resolution 2D-spectra exhibit peaks at energies corresponding to differences between the eigenenergies of the interrogated system [17,25,26]. For a molecule possessing vibrational degrees of freedom, the participating eigenstates are, within the Born–Oppenheimer approximation [27], vibrational states belonging to different electronic states. For a larger density of vibronic states and an effective coupling to a surrounding, single peaks can no longer be resolved in the spectra. It is then not possible to adopt a direct wave function approach and traditionally a description in terms of reduced density-matrices is applied. However, stochastic Schrödinger equations can be set up which are, within certain approximations, equivalent to the density-matrix description. One such method employs quantum-diffusion theory [28] which has recently been applied to the ultrashort spectroscopy of molecules [29–33]. Another stochastic wave function scheme is the quantum-jump method [34], for molecular applications of this scheme see, e.g., Refs. [35,36]. This methodology, within the extension suggested by Makarov and Metiu [37], has been applied to 2D-spectroscopy recently [38]. The latter work treated a model of two shifted and only field-coupled harmonic oscillators. In the present work we use this approach to apply it to a more complex situation, i.e. a generic charge-transfer (CT) process involving non-adiabatic transitions. As has been discussed by Saalfrank [36], there are situations where the stochastic approach is computationally more effective than a reduced density-matrix calculation.

To describe charge transfer one often regards two diabatic states which are coupled by a constant potential matrix element [39,40]. In fact, this is the basis idea of Marcus-theory [41]. Depending on the coupling strength, situations arise which are described by the motion on diabatic (weak diabatic coupling) or adiabatic (strong diabatic coupling) potentials. Here we treat the case where the

coupling constant is rather large. It is shown that this gives rise to particular interesting states of the isolated system which, if coupled to the bath, have very long lifetimes. The signatures of these states in the 2D-spectra is explored and, in particular, we focus on the decay behavior as extracted from the spectra. In Section 2 we introduce the model and give a brief outline of how the stochastic propagation scheme is used to calculate the 2D-spectra. The numerical results are presented in Section 3, and the article is finished with a summary (Section 4).

2. Theory and model

The most simple model for a charge-transfer process is that of two coupled diabatic electronic states $|1\rangle$ and $|2\rangle$, with harmonic oscillator potentials depending on a dimensionless reaction coordinate q with the Hamiltonian:

$$\hat{H}^d = \sum_{n=1}^{2} (|n\rangle H_n(q)\langle n|) + |1\rangle J\langle 2| + |2\rangle J\langle 1|, \tag{1}$$

with

$$H_n = -\frac{1}{2m^*}\frac{d^2}{dq^2} + V_n^d(q) = -\frac{1}{2m^*}\frac{d^2}{dq^2} + \lambda(q - q_n)^2. \tag{2}$$

In our calculation we use a coupling of $J = 0.237$ eV and the effective mass $m^* = 1005$ eV^{-1} which is motivated by former studies on mixed valence compounds [42,43]. The equilibrium distances are fixed to values of $q_1 = -0.5$ and $q_2 = 0.5$, and the reorganization energy is $\lambda = 0.917$ eV. This gives rise to the diabatic potentials $V_n^d(q)$ shown in Figure 2 (left hand panels). The figure also contains the 'adiabatic' potential curves (right hand panels) obtained by diagonalization of the potential matrix. To obtain the two-component eigenstates (with eigenstates E_α) $|\psi_\alpha\rangle = \psi_{1,\alpha}(q)|1\rangle + \psi_{2,\alpha}(q)|2\rangle$, we employ basis sets consisting of (harmonic) eigenfunctions $\varphi_{n,m}(q)$ of the Hamiltonians $H_n(q)$:

$$\psi_{n,\alpha}(q) = \sum_m c_{n,m,\alpha}\ \varphi_{n,m}(q), \tag{3}$$

where, due to symmetry, $c_{1,m,\alpha} = \pm c_{2,m,\alpha}$. The coefficients are obtained by diagonalization of the Hamiltonian represented in the harmonic set of basis functions. For the purpose of illustration, we also calculate the components of the 'adiabatic' functions $\psi_{\pm,\alpha}(q)$ with the help of the matrix which diagonalizes the diabatic potential matrix. Note, however, that the single components do not diagonalize the Hamiltonian (as is the case for a two-level system [40]) because the coordinate-dependence of the transformation matrix results in kinetic coupling elements.

For the time-propagation of a system with Hamiltonian H which is coupled to a bath [37] the state vector $|\psi(t)\rangle$ at time t is expanded in the set of eigenstates $|\psi_\alpha\rangle$ of H:

$$|\psi(t)\rangle = \sum_\alpha c_\alpha(t)|\psi_\alpha\rangle. \tag{4}$$

The propagation for a small time-step dt involves one of the following three possibilities: For a dephasing-process one has

$$|\psi_n(t + dt)\rangle = \sum_\alpha c_\alpha(t)e^{-i\delta_\alpha(t)}\ |\psi_\alpha\rangle. \tag{5}$$

Here, the coefficients are multiplied by phase factors with randomly chosen phases $\delta_\alpha(t)$ sampled from the interval $[0, 2\pi]$. The next possibility is that a quantum jump $|\psi_\alpha\rangle \rightarrow |\psi_{\alpha'}\rangle$ takes place leading to:

$$|\psi(t + dt)\rangle = \frac{c_\alpha(t)}{|c_\alpha(t)|}\ |\psi_{\alpha'}\rangle. \tag{6}$$

Finally, for a coherent propagation one has:

$$|\psi(t + dt)\rangle = \frac{1}{\sqrt{C}}\sum_\alpha c_\alpha(t)e^{-iE_\alpha dt}e^{-(\Gamma_\alpha + \gamma)dt/2}|\psi_\alpha\rangle, \tag{7}$$

where the normalization constant C is determined numerically such that the state vector is normalized to one, and the rates Γ_α and γ are defined below.

Which of the different propagation steps is taken is determined by the associated probabilities. For the dephasing probability we use:

$$p_d = \gamma\, dt, \tag{8}$$

where the dephasing rate γ is taken as an adjustable parameter. The jump probability is

$$p_{\alpha\alpha'}(t) = k_{\alpha\alpha'}\, |c_\alpha(t)|^2\ \, dt, \tag{9}$$

with the rate $k_{\alpha\alpha'}$ defined as [44,45]:

$$k_{\alpha\alpha'} = 2|\langle\psi_\alpha|q|\psi_{\alpha'}\rangle|^2\ \, J(\omega_{\alpha\alpha'}), \tag{10}$$

where we restrict the calculations to the case of zero temperature so that only down-jumps are allowed. The spectral densities $J(\omega_{\alpha\alpha'})$ which depend on the energy differences $\omega_{\alpha,\alpha'} = (E_\alpha - E'_\alpha)$ are of Ohmic form with an exponential cutoff:

$$J(\omega_{\alpha\alpha'}) = \eta\, \omega_{\alpha\alpha'}\, e^{-\omega_{\alpha\alpha'}/\omega_c}, \tag{11}$$

where the cutoff frequency is set to $\omega_c = 1.0$ eV. The parameter η determines the strength of the system/bath coupling. Calculating the jump probability

$$p_j(t) = \sum_\alpha \sum_{\alpha' \neq \alpha} p_{\alpha\alpha'}(t), \tag{12}$$

leads to the probability for a coherent propagation as $p_c(t) = 1 - p_d - p_j(t)$. Finally, the coherent propagation (Eq. (7)) contains the 'escape rates':

$$\Gamma_\alpha = \sum_{\alpha \neq \alpha'} k_{\alpha\alpha'}. \tag{13}$$

For the numerical propagation, the possible events are arranged on the unit interval $[0, 1]$, which is then partitioned into the intervals $p_d, \{p_{\alpha,\alpha'}(t)\}, p_c(t)$. At each time step a uniformly distributed random number on the unit interval is chosen and, falling into one of the segments, the corresponding event is carried out. Note, that the time step dt has to be sufficiently small in order to obtain reasonable (i.e. small) probabilities. The procedure leads to the states $|\psi_l(t_i)\rangle$, where l denotes the run and t_i the discrete sampling times. Performing N_r independent runs, the expectation value of an observable $\hat{A}$ is:

$$\langle\hat{A}\rangle(t_i) = \frac{1}{N_r}\sum_{l=1}^{N_r}\langle\psi_l(t_i)|\hat{A}|\psi_l(t_i)\rangle. \tag{14}$$

We note that the time-propagation via this algorithm is equal to propagating the reduced density matrix via the Redfield equations within the secular approximation [37,44]. Extensions of the stochastic method which go beyond the secular and Markov approximations are out of the scope of the present work.

To characterize the spectral properties of the investigated system we regard the first order polarization which, within the stochastic approach is calculated as [38]:

$$P^{(1)}(t) = \frac{1}{N_r}\sum_{l=1}^{N_r}\sum_{m=0}^{1}\langle\psi_l^{(m)}(t)|\hat{\mu}|\psi_l^{(1-m)}(t)\rangle. \tag{15}$$

The state $|\psi_l^{(1)}(t)\rangle$ results from an interaction with an external electric field in first-order time-dependent perturbation theory,