ELECTRONIC DEPHASING IN FEMTOSECOND CURVE CROSSING SPECTROSCOPY

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Femtosecond nonlinear optical spectroscopies provide a powerful tool for studying electronic and vibrational dynamics, including nonadiabatic curve crossing and electron transfer processes. In this paper we outline a procedure for incorporating microscopically effects of electronic dephasing in coherent spectroscopies involving strong fields. The approach applies to coherent Raman measurements as well as any other four wave mixing including pump-probe spectroscopy. It is based on equations of motion for phase space wavepackets, and provides a simple semiclassical picture for these processes.

We consider a molecular system with electronic states denoted $|j>$. The Hamiltonian of the system is

$$H_S(t)=\frac{P^2}{2M}+\sum_j |j>U_{jj}(R;t)<j|, \tag{1}$$

Here, R is a nuclear coordinate strongly coupled to the electronic state and P is its conjugate momentum. The potential of j'th state is denoted by U_{jj} which may depend on time. The system interacts with optical field and the total Hamiltonian is

$$H_A(t)=H_S(t)+\sum_{jk}\frac{\hbar}{2}\left(E_p(\boldsymbol{r},t)+E_T(\boldsymbol{r},t)\right)\mu_{jk}(R)|j><k| , \tag{2}$$

where $E_P(\boldsymbol{r}, t)$ is a strong field that can represent a sequence of pulses with an arbitrary time profile and $E_T(\boldsymbol{r}, t)$ is a weak field hereby denoted the "probe". In the following calculations the optical signal will be calculated to lowest order in $E_P(\boldsymbol{r}, t)$ but to arbitrary order in $E_T(\boldsymbol{r}, t)$. The transition dipole matrix element between the j and k states which may depend on R (non-Condon effects) is given by $\mu_{jk}(R)$.

Optical measurements can be calculated from the polarization

$$P(\boldsymbol{r},t)\equiv \mathrm{tr}\{\mu(R)\hat{\rho}(\boldsymbol{r},t)\} , \tag{3}$$

where $\mu(R)=\Sigma\mu_{jk}(R)|j><k|$ and $\hat{\rho}(\boldsymbol{r},t)$ is the total density matrix. We next expand the polarization in momentum ($\boldsymbol{k}$) space

$$P(\boldsymbol{r},t)=\sum_{j} \exp[i\boldsymbol{k}_j\boldsymbol{r}-i\Omega_j t]P(\boldsymbol{k}_j,t) . \tag{4}$$

Optical measurements are most commonly carried out using one of the following two detection schemes. First, in *homodyne* detection one simply measure the outgoing field in a specified direction $\boldsymbol{k}_j$;

$$(i) \quad S(\boldsymbol{k}_j, t) = |P(\boldsymbol{k}_j, t)|^2 \ . \tag{5}$$

Second, in the *heterodyne* detection mode, the outgoing field is mixed with a reference field denoted the local oscillator E_{LO}, and the signal is given by

$$(ii) \quad S(\boldsymbol{k}_j, t) = Im[E_{LO}(\boldsymbol{k}_j, t) P(\boldsymbol{k}_j, t)] \ . \tag{6}$$

Example of (*i*) are four wave mixing and coherent Raman which is observed in the $\boldsymbol{k}_j = 2\boldsymbol{k}_1 - \boldsymbol{k}_2$ direction, whereas pump-probe experiment with $\boldsymbol{k}_j = \boldsymbol{k}_1 - \boldsymbol{k}_1 + \boldsymbol{k}_2$ corresponds to heterodyne detection.

Let us recast the Hamiltonian in the form,

$$H_A(t) = \frac{P^2}{2M} + \sum_j \sum_k |j\rangle U_{jk}(R; t) \langle k| \ , \tag{7}$$

where we set $U_{jk}(R, t) \equiv \hbar \mu_{jk}(R)(E_P(\boldsymbol{r}, t) + E_T(\boldsymbol{r}, t))$. The multi-state density matrix in the nuclear phase space (The Wigner representation) is expanded as

$$\hat{\rho}(t) = \sum_{j,k} |j\rangle W_{jk}(P, R; t) \langle k| \ . \tag{8}$$

The Wigner representation has the following advantages; first it allows us to compare the quantum density matrix directly with its classical counterpart. Second, using phase space distribution functions, we can further easily impose the necessary boundary conditions (*e. g.* periodic or open boundary conditions), where particles can move in and out of the system. This is much more difficult in the coordinate representation.

The quantum equation of motion for the density matrix of the system interacting with heat bath is known as the quantum Fokker-Planck equation [1]. We have generalize it to a multi-state system with anharmonic potentials and coordinate-dependent nonadiabatic coupling.

$$\begin{aligned} \frac{\partial}{\partial t} W_{jk}(P, R; t) = &- \frac{P}{M} \frac{\partial}{\partial R} W_{jk}(P, R; t) + \zeta \frac{\partial}{\partial P} \left(P + \frac{M}{\beta} \frac{\partial}{\partial P} \right) W_{jk}(P, R; t) \\ &- \frac{1}{\hbar} \int \frac{dP'}{2\pi\hbar} \sum_m \Big[X_{jm}(P-P', R; t) W_{mk}(P', R; t) \\ &\qquad + X_{mk}^{*}(P-P', R; t) W_{jm}(P', R; t) \Big] \ . \end{aligned} \tag{9}$$

Here, ζ is the friction constant and

$$X_{ij}(P,R;t) = i\int_{-\infty}^{\infty} dr \exp\left(iPr/\hbar\right) U_{ij}\left(R-r/2;t\right) ,$$
$$X_{ij}^{*}(P,R;t) = -i\int_{-\infty}^{\infty} dr \exp\left(iPr/\hbar\right) U_{ij}\left(R+r/2;t\right) . \tag{10}$$

This equation of motion is valid only when the following high temperature condition applies;

$$\beta\hbar\omega_{c} \ll 1, \tag{11}$$

where ω_c is a characteristic frequency of the system and $\beta = 1/k_B T$ is the inverse temperature of the environment (bath). This limitation can be relaxed, if we consider a Gaussian-Markovian bath with a finite correlation time [2, 3].

There are several possible strategies for computing the optical signal. The first is based on a perturbative expansion of the density matrix in the entire electromagnetic field E_P+E_T. In this procedure the signal is expresses in terms of multitime correlation functions of the dipole operator, which constitute the nonlinear response functions [4]. This procedure is particularly useful for weak fields and it has been applied to a wide range of experiments such as the pump-probe or coherent Raman spectroscopy. The second method involves a direct integration of the equations of motion with all fields present. The third approach is intermediate between the two. We assume weak probe and expand the density matrix to linear order in E_P. We then get

$$P(r,t) = -\frac{i}{\hbar}\int_{-\infty}^{t} d\tau \langle[\mu^{0}(t), \mu^{0}(\tau)]\rho_{eq}\rangle E_T(r,\tau) , \tag{12}$$

where,

$$\mu^{0}(t) \equiv \exp\left\{\frac{i}{\hbar}\int_{0}^{t} d\tau H_A^{0}(\tau)\right\}\mu(R)\exp\left\{-\frac{i}{\hbar}\int_{0}^{t} d\tau H_A^{0}(\tau)\right\} , \tag{13}$$

and $H_A^{0}(t)$ is the Hamiltonian without the probe field (Eq.(2) with $E_T(r, t)=0$) and ρ_{eq} is the equilibrium density matrix.

A technical difficulty with this calculation is the necessity to select the polarization with the given wavevector. Formally atoms located in the different positions will see the optical fields with different phases ($\cos(\omega t-kr)$). For non-interacting atoms, the integration over r is equivalent to solving the problem repeatedly for various phases of the fields and then averaging over the phases, thereby selecting the desired wavevector component. This procedure is computationally intensive but in some cases it may be possible to avoid it by a suitable transformation [5].

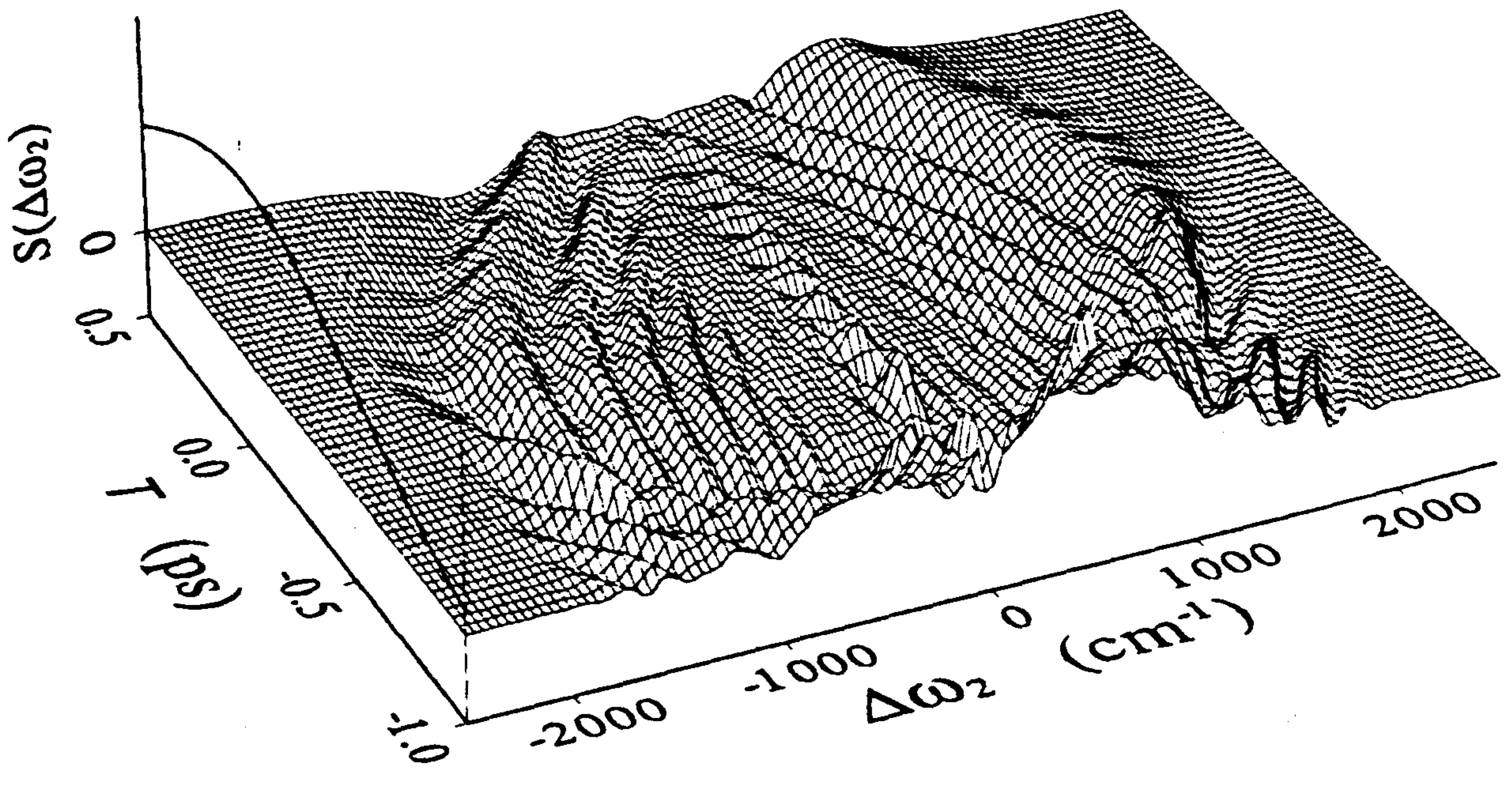

Fig. 1 Pump-probe spectrum of a two-level system subjected to a strong excitation for different pulse delays T[ps] and probe dispersed frequency $\Delta\omega_2$. The nuclear degree of the freedom R is modelled as an underdamped Brownian oscillator with the following parameters: frequency ω_0=500[cm^{-1}] and friction γ=50[cm^{-1}]. Its equilibrium position is linearly displaced between the two-electronic states with the dimensionless displacement D=1, and the temperature T=200[K]. We assumed that both the pump and probe pulses are Gaussian $E_1(t)=E_1\exp[-(t/\tau_1)^2]$ and $E_2(t)=E_2\exp\{-[(t-T)/\tau_2]^2\}$ with resonance central frequencies, *i.e.* $\Omega_1=\Omega_2=\omega_{eg}$, where ω_{eg} is the electronic transition frequency of the two-level system. The pulse durations were taken to be τ_1=700[fs] and τ_2=30[fs] and the time delay was varied between T=-2[ps] to T=0.5[ps]. The trace above the T axis shows the pump envelope. The dynamical Stark effect shows up when the pump and the probe overlap in time [5].

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