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Transient spectroscopy of vibrational coherence induced by relaxation

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Abstract

We propose to use pump–probe spectroscopy for the study of the vibrational coherence related to nonadiabatic dynamics and/or anharmonic interactions. Formally, this coherence is manifested in the off-diagonal elements of the decay matrix. We show that pump–probe spectroscopy enables us to distinguish between situations corresponding to the presence of off-diagonal elements of the decay matrix or their absence. The off-diagonal decay is manifested in a phase of the beat signal that causes a temporal shift of the pattern of quantum beats. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vibrational coherence effects originate from the time evolution of wave packets of nuclear states, which are manifested by oscillatory time evolution, i.e., quantum beats [1–6]. Their characteristic frequencies correspond to the energy differences between coherently excited nuclear (or electronic nuclear) states. A coherent excitation is produced by a perturbation with spectrum that is broader than the energy difference between the excited states. Formally, the vibrational coherence is manifested in off-diagonal elements of the density matrix. Vibrational coherence effects can be produced (a) by broad band fs laser excitation, or (b) via nonadiabatic or anharmonic multiphonon processes, characterized by a broad spectrum. In the last case the vibrational coherence originates from the coupling of different vibrational states with common (intramolecular and/or medium) vibrational (quasi)continuum [7]. Formally, this coupling is manifested in off-diagonal elements of the *decay* matrix; the latter produce nonvanishing off-diagonal elements of the density matrix even in the absence of broadband fs laser excitation. In this context the following question arises: *how can one distinguish between situations corresponding to the presence of off-diagonal elements of the decay matrix or their absence*?

In this work we show that the phase of the quantum beats is sensitive to the decay pattern of the quantum states. We demonstrate how pump–probe spectroscopy can be used to solve the problem under discussion and study vibrational coherence effects in nonadiabatic or anharmonic dynamics.

2. Model of chromophore molecule and calculation of nonlinear polarization

Let us consider a molecule with ground 1 and the excited $e = 2,3$ electronic states. We will describe the molecule by the model system consisting of distinct vibronic manifolds of two (or three) electronic states under consideration: (i) the vibrational states $\{|s\rangle\}$ ($s = 1,2,3,\ldots,n$) of the excited electronic state 2, which carry oscillator strengths from the ground state $|1\rangle$. (ii) The dissipative quasicontinuum states $\{|\alpha\rangle\}$, which do not carry oscillator strength from $|1\rangle$. States $\{|\alpha\rangle\}$ correspond to other vibrational states of the same electronic state 2 or to a lower lying electronic configuration $|3\rangle$. Correspondingly the states $\{|s\rangle\}$ are coupled to the quasicontinuum via the anharmonic couplings in the first

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case or via the interstate nonadiabatic couplings in the second case. Our model system is imbedded in a fast relaxing solvent which strongly changes its configuration upon electronic excitation (solvation effects). The last condition determines a fast dephasing of the optical electronic transition. The molecule is affected by electromagnetic radiation of the pump $\omega, \boldsymbol{k}$ and the probe $\omega', \boldsymbol{k}'$ pulses

$$\boldsymbol{E}(\boldsymbol{r}, t) = \tfrac{1}{2}\{\boldsymbol{E}_{\text{pump}}(t)\exp[\mathrm{i}(\boldsymbol{kr} - \omega t)] + E_{\text{pr}}(t)\exp[\mathrm{i}(\boldsymbol{k}'r - \omega' t)] + \text{c.c.}\}. \qquad (1)$$

Electromagnetic field (1) induces an optical polarization in the medium $\boldsymbol{P}(\boldsymbol{r}, t)$ which can be expanded in powers of $\boldsymbol{E}(\boldsymbol{r}, t)$. For cubic polarization of the system under investigation, we have

$$\boldsymbol{P}^{(3)}(\boldsymbol{r}, t) = \boldsymbol{P}^{(3)+}(\boldsymbol{r}, t) + \boldsymbol{P}^{(3)-}(\boldsymbol{r}, t) = N\mathrm{Tr}_R(\boldsymbol{D}_{12}\rho_{21}^{(3)}(t) + \text{c.c.}), \qquad (2)$$

where N is the density of particles in the system, $\boldsymbol{D}$ is the dipole moment operator of a solute molecule; $\rho_{21}^{(3)}$ is the density matrix of the system calculated in the third approximation with respect to $\boldsymbol{E}(r, t)$, Tr_R denotes the trace over the vibrational substates of a molecule and a solvent.

Off-diagonal with respect to electronic indices element $\rho_{21}^{(3)}$ can be evaluated by applying double-sided Feynman diagrams in the fast electronic dephasing limit [8]. The relevant diagrams for long pump pulses compared with electronic optical dephasing are depicted in Fig. 1. They enable us to calculate the nonlinear polarization $\boldsymbol{P}^{(3)}(\boldsymbol{r}, t)$ that determines a signal in various methods of pump–probe spectroscopy. We will consider here the time-resolved hole-burning spectroscopy and the heterodyne optical Kerr effect (HOKE) spectroscopy [6,9]. The time resolved hole-burning spectroscopy can be realized in the form of the transmission pump–probe experiment at one probe frequency [1] or with the dispersed probe. In the first case a sample is excited with a pump pulse of frequency ω, and a second pulse of frequency ω' probes the sample transmission $\Delta T(\tau)$ at a delay τ. In the time-resolved hole-burning spectroscopy with the dispersed probe, the sample is excited with a ~100 fs pump pulse, and the difference in the absorption spectrum $\Delta\alpha(\omega')$ is measured with a ~10 fs [10] or broadened up to a continuum [11] probe pulse that is delayed in relation to the pump pulse by a variable τ. The resonance HOKE spectroscopy, under certain conditions, provides information similar to that of the transmission pump–probe spectroscopy at one probe frequency.

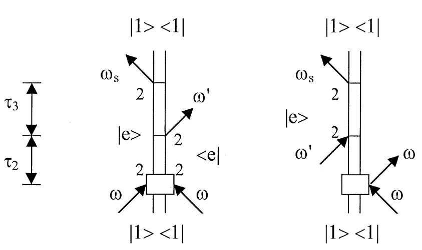

Fig. 1. Double-sided Feynman diagrams for $\rho_{21}^{(3)}$ in the fast electronic dephasing limit [8].

For the model under consideration, a signal in the time-resolved hole-burning spectroscopy can be written in the form

$$\Delta T(\tau), \Delta\alpha(\omega') \sim F_{\alpha,\text{slv}}(\omega' - \omega_{21}^{\text{el}})\rho_{11}^{\text{M}}(\tau) + F_{\phi,\text{slv}}(\omega' - \omega_{21}^{\text{el}})\sum_{\text{ss}'}\rho_{2\text{s},2\text{s}'}^{\text{M}}(\tau), \qquad (3)$$

where $F_{\alpha(\phi),\text{slv}}$ is the "intermolecular" absorption (emission) spectrum that is determined by the solvent reorganization induced by electronic optical transition $1 \leftrightarrow 2$, ω_{21}^{el} is the frequency of a pure electronic transition $1 \to 2$, $\rho_{ij}^{\text{M}}(\tau) = \mathrm{Tr}_{\text{slv}}\,\rho_{ij}(\tau)$ is the coarse-grained density matrix of the solute molecule, Tr_{slv} denotes the trace over the solvent degrees of freedom. The density matrix of the solute molecule in the excited electronic state $|2\rangle$ is determined by the propagator $\exp(-\mathrm{i}L_{\text{e}}^{\text{M}}\tau)$ that describes the propagation along the $|e\rangle\langle e|$ double line (see Fig. 1).

$$\rho_{2\text{s},2\text{s}'}^{\text{M}}(\tau) \equiv \rho_{\text{ss}'}^{\text{M}}(\tau) = \sum_{\text{s}''\text{s}'''}[\exp(-\mathrm{i}L_{\text{e}}^{\text{M}}\tau)]_{\text{ss}'\text{s}''\text{s}'''}\,\rho_{\text{s}''\text{s}'''}^{\text{M}}(0), \qquad (4)$$

where L_{e}^{M} is the Liouville operator for the excited electronic states.

For a transmission pump–probe experiment with the pump pulse short and the probe pulse long compared with electronic dephasing [3] we obtain

$$\Delta T(\tau) \sim F_{\alpha,\text{slv}}(\omega' - \omega_{21}^{\text{el}}) + F_{\phi,\text{slv}}(\omega' - \omega_{21}^{\text{el}})\sum_{\text{ss}'}\rho_{\text{ss}'}^{\text{M}}(\tau). \qquad (5)$$

Comparing Eqs. (3) and (5), one can see that $\Delta T(\tau)$ for very short pump pulses depends only on nuclear dynamics in the excited electronic states. Therefore, the method of choice for the study of vibrational coherence in nonadiabatic dynamics is the transmission pump–probe experiment with the pump pulse short compared with electronic dephasing.

3. Model calculations

To explore the effects of the off-diagonal decay on the signal of pump-probe spectroscopy, we will consider a single ground state $|1\rangle$ and two excited states $s = \text{a}, \text{b}$ with the energies E_{a} and E_{b} ($E_{\text{b}} > E_{\text{a}}$) coupled to a common quasicontinuum [7]. For the sake of simplicity we take into account only the imaginary contribution to the relaxation matrix and set $\Gamma_{\text{aa}}^{\text{M}} = \Gamma_{\text{bb}}^{\text{M}} = \Gamma_{\text{ab}}^{\text{M}} = \Gamma_{\text{ba}}^{\text{M}} = \Gamma^{\text{M}}$.

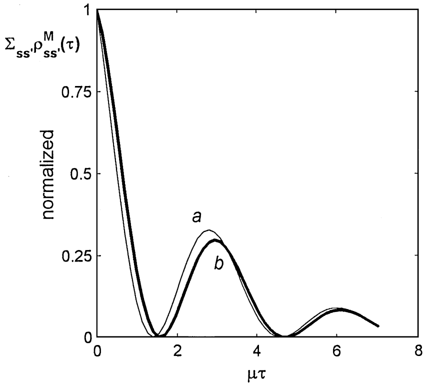

Fig. 2. Beats in pump–probe spectroscopy (Eq. (6)) with the off-diagonal decay present (a) ($\eta = 1$) and in the absence of the off-diagonal decay (b) ($\eta = 0$); $\Gamma^M/\mu = 0.2$.

The elements of the relaxation matrix $\{\Gamma^M_{ss'}\}$ differ by the thermal averaging over the solvent states from those of model [7]. To explore the effects of correlations in nonadiabatic and anharmonic dynamics, we write Γ^M_{ab} and Γ^M_{ba} in the form $\Gamma^M_{ab} = \Gamma^M_{ba} = \eta\Gamma$, where $0 \le \eta \le 1$. Then we obtain

$$\sum_{ss'} \rho^M_{ss'}(\tau) = 4\rho^M_{22}(0)\exp(-2\Gamma^M\tau)(\mu/\kappa^M)^2 \sin^2(\kappa^M\tau + \theta), \quad (6)$$

where $\mu = (E_b - E_a)/(2\hbar)$, $\kappa^M = [\mu^2 - (\eta\Gamma^M)2]^{1/2}$, $\sin\theta = \kappa^M/\mu$, $\cos\theta = -\eta\Gamma^M/\mu$.

Comparing Eqs. (3) and (5) for the model under consideration, one can see that the signal in all the methods of pump–probe spectroscopy under discussion is proportional to the right-hand side of Eq. (5) where the quantity $\Sigma_{ss'}\rho^M_{ss'}(\tau)$ describes the quantum beats (see Eq. (6)). The off-diagonal decay is manifested by a phase of the beat signal that causes a temporal shift of the pattern of quantum beats (see Fig. 2). The minima of pump–probe signals correspond to $\kappa^M\tau + \theta = n\pi$ where n is an integer. As a result we obtain $\tau_2^{\min}/\tau_1^{\min} = (2\pi - \theta)/(\pi - \theta)$, where $\tau_{1,2}^{\min}$ are the delay times which determine the positions of the first and second minima. We have $\theta = \pi/2$ and $\tau_2^{\min}/\tau_1^{\min} = 3$ in the absence of nondiagonal atttenuation ($\eta = 0$, $\kappa^M = \mu$), and $\tau_2^{\min}/\tau_1^{\min} > 3$ with the off-diagonal decay present. For example, if $\eta\Gamma^M/\mu = 0.5$, then $\tau_2^{\min}/\tau_1^{\min} \approx 4$.

Thus, in this work we have shown that the phase of quantum beats is sensitive to the decay pattern of the quantum states involved in beats. The methods of pump–probe spectroscopy enable us to distinguish between situations corresponding to the presence or absence of vibrational coherence in nonadiabatic and/or anharmonic dynamics. The method of choice for the study of vibrational coherence in nonadiabatic dynamics is the pump–probe experiment with very short pump pulses since the corresponding signal depends only on nuclear dynamics in the excited electronic states.

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