Temperature dependence and non-Condon effects in pump-probe spectroscopy in the condensed phase

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We analyze the effects of the coordinate dependence of the transition dipole (non-Condon dipole moment) on impulsive pump-probe spectroscopy at finite temperatures, using expressions for the response functions derived by the path-integral approach. We calculate the difference probe absorption spectrum and show that the non-Condon dipole shifts the absorption to the blue and that the shift increases with temperature.

The multimode Brownian oscillator model provides a convenient means for incorporating nuclear degrees of freedom in optical response functions. We recently used a path-integral approach to develop exact closed expressions for the nuclear wave packets in phase space and for the nonlinear response functions for this model.

In this paper we apply these results to pump-probe spectroscopy. We consider an electronic two-level system, denoted by \( g \) (the ground state) and \( e \) (the excited state), and frequency \( \omega_0 \). The optically active vibration of polyatomic molecules in the condensed phase can often be described with a Brownian oscillator model in which the ground state and the excited state are represented by displaced harmonic oscillators. We denote the nuclear mass, the coordinate, the harmonic frequency, and the dimensionless displacement of the oscillators by \( M \), \( q \), \( \omega_0 \), and \( D \), respectively. We would like to include relaxation of the optically active mode. This is commonly taken into account by using the Langevin equation. However, the quantum coherence between the heat bath and the vibrational system plays an important role at low temperatures. This effect cannot be taken into account with the classical Langevin equation, and therefore we explicitly introduce a model for a heat bath. The heat-bath system may represent optically inactive vibrational modes, phonons, solvent modes, etc. We assume that the optically active vibration is linearly coupled to a heat bath, with the coordinates, the momentum, the mass, and the frequency of the \( n \)th bath oscillator given by \( x_n, p_n, m_n, \) and \( \omega_n \), respectively. The total Hamiltonian is then expressed as

\[
H = |g\rangle H_g(p,q)\langle g| + |e\rangle H_e(p,q)\langle e| + \sum_n \left[ \frac{p_n^2}{2m_n} + \frac{m_n\omega_n^2}{2} \left( x_n - \frac{c_n q}{m_n\omega_n^2} \right)^2 \right],
\]

where

\[
H_g(p,q) = \frac{p^2}{2M} + \frac{1}{2} M \omega_0^2 q^2,
\]

\[
H_e(p,q) = \frac{p^2}{2M} + \frac{1}{2} M \omega_0^2 (q + D)^2 + \hbar \omega_0^2 D.
\]

The two states are connected by the optical–dipole interaction

\[
H_I = E(t)V = E(t)[|g\rangle \mu(q)\langle e| + |e\rangle \mu(q)\langle g|],
\]

where \( E(t) \) is the laser field and \( \mu(q) \) is the dipole matrix element between the two states that depends on the nuclear coordinate. We assume that the transition dipole has the form

\[
\mu(q) = \mu_0 \exp(cq),
\]

where \( c \) is the coupling constant. Typically in molecular systems \( c \) is small \((cq_L \ll 1, \) where \( q_L \) is the size of the nuclear wave packet\), so that \( \mu(q) = \mu_0(1 + cq) \).

The optical polarization for a third-order optical process is obtained by expanding the density matrix elements in \( H_I \) and is expressed as

\[
P^{(3)}(t) = i \int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 E(t - t_3) E(t - t_2 - t_3)
\]

\[
\times E(t - t_1 - t_2 - t_3) \operatorname{tr} \left[ V \exp\left(-\frac{i}{\hbar}t_3 H^X\right)V^X \right]
\]

\[
\times \exp\left(-\frac{i}{\hbar}t_2 H^X\right)V^X \exp\left(-\frac{i}{\hbar}t_1 H^X\right)V^X \rho_g.
\]

Here, \( \rho_g \) is the ground equilibrium state of the total system, and we use the superoperator notation defined by \( A^X B = AB - BA \), \( A^X B^X C = ABC - CB \) - \( (BC - CB)A \), and so forth, where \( A, B, \) and \( C \) are ordinary operators. Since each \( V^X \) can act either from the left or from the right, and since \( P^{(3)}(t) \) contains \( V^X \) factors, Eq. (5) naturally separates into \( 2^3 \) terms denoted by Liouville-space paths. In practice we need to evaluate only half of these terms, since they always come in Hermitian conjugate pairs, and, for the third-order polarization, we need four Liouville-space paths, denoted by \( \alpha = 1 \rightarrow 4 \) (see Fig. 1).
All dynamical characteristics of the system can be expressed in terms of the phase function defined by
\[ g_{\pm}(t) = \xi^2 \int_0^t dt' \int_0^{t'} dt'' \langle q(q(t'')) \rangle, \]
\[ \xi = MD\omega_0^2/\hbar. \]  \hspace{1cm} (6)

To express the results in a compact form, we assign three sign parameters, \( \epsilon_1, \epsilon_2, \) and \( \epsilon_3 \) (see Table 1) to each of the Liouville-space paths. With this notation the optical polarization for a third-order optical process is given by
\[ P^{(3)}(t) = i \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^{t_3} dt_1 E(t - t_3)E(t_3 - t_2 - t_3) \]
\[ \times \sum_{c_1, c_2, c_3} \mu_0^4 R_{c_1 c_2 c_3}^{(3)}(t_3, t_2, t_1; c) \]
\[ + \text{c.c.} \]  \hspace{1cm} (8)

Here the response function is given by
\[ R_{c_1 c_2 c_3}^{(3)}(t_3, t_2, t_1; c) = \exp[Q_{c_1 c_2 c_3}(t_3, t_2, t_1) + X_{c_1 c_2 c_3}(t_3, t_2, t_1; c)], \]  \hspace{1cm} (9)

where
\[ Q_{c_1 c_2 c_3}(t_3, t_2, t_1) = -i\omega_c(\epsilon_1 t_1 + \epsilon_2 t_2) - g_{-c}(t_1) - g_{c_3}(t_3) \]
\[ - \epsilon_1 \epsilon_2 [g_{c_1 c_2}(t_2) - g_{-c_1 c_2}(t_2 + t_3)] \]
\[ - g_{-c}(t_1 + t_2) + g_{-c}(t_1 + t_2 + t_3)], \]  \hspace{1cm} (10)

with
\[ X_{c_1 c_2 c_3}(t_3, t_2, t_1; c) = c_1(\overline{g_1}(t))_{c_1 c_2 c_3} + \langle \overline{g_2}(t) \rangle_{c_1 c_2 c_3} + \langle \overline{g_3}(t) \rangle_{c_1 c_2 c_3} \]
\[ + \langle \overline{g_4}(t) \rangle_{c_1 c_2 c_3} + c_2^* \xi^{\ldots} \overline{g_{-c_1 c_2}}(t_1) + \overline{g_{-c_2}}(t_1 + t_2) \]
\[ + \overline{g_{c_3}}(t_2) + \overline{g_{-c_3}}(t_1 + t_2 + t_3) + \overline{g_{c_1 c_2}}(t_2 + t_3) \]
\[ + \overline{g_{c_1 c_2}}(t_3) + 2\overline{g}(0)], \]  \hspace{1cm} (11)

\[ \omega_c = \omega_{c0} + \lambda, \quad \lambda = MD^2\omega_0^2/(2\hbar), \]  \hspace{1cm} (12)

Equation (10) is identical to the phase of the response function with the Condon approximation, which may be derived by use of the cumulant expansion; however, the present notation is more convenient for numerical studies.

The probe absorption spectrum, obtained by dispersion of the transmitted probe through a monochromator, is given by
\[ S(\omega_2 - \Omega_2) = -2 \text{Im} E_2(\omega_2 - \Omega_2)P^{(3)}(\omega_2 - \Omega_2), \]  \hspace{1cm} (14)

where
\[ E_2(\omega_2 - \Omega_2) = \frac{1}{(2\pi)^{1/2}} \int_0^\infty dt \exp[i(\omega_2 - \Omega_2)t]E_2(t), \]  \hspace{1cm} (15)

\[ P^{(3)}(\omega_2 - \Omega_2) = \frac{1}{(2\pi)^{1/2}} \int_0^\infty dt \exp[i(\omega_2 - \Omega_2)t]P^{(3)}(t), \]  \hspace{1cm} (16)

and \( \Omega_2 \) is the central frequency of the probe. We assume impulsive pump and probe fields, i.e.,
\[ E_1(t) = \theta_1 \delta(t + \tau), \quad E_2(t) = \theta_2 \delta(t), \]  \hspace{1cm} (17)

where \( \theta_1 \) and \( \theta_2 \) are the pump and the probe areas. For the impulsive pump case, we have
\[ S(\omega_2 - \Omega_2; \tau) = S_{\omega_0}(\omega_2 - \Omega_2; \tau) + S_{\omega_2}(\omega_2 - \Omega_2; \tau), \]  \hspace{1cm} (18)

Table 1. Auxiliary Parameters for Eqs. (9)–(13)

<table>
<thead>
<tr>
<th>Liouville Space Path ( \alpha )</th>
<th>( \epsilon_1 )</th>
<th>( \epsilon_2 )</th>
<th>( \epsilon_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>
Here $S_{a\tau}$ represents the contribution from the Liouville paths $a = 1$ and $a = 2$, which pass through the excited state ($\rho_{ee}$) during the $t_2$ time interval, whereas $S_{ee}$ represents the contributions of the other paths $a = 3$ and $a = 4$, which pass through the ground state ($\rho_{gg}$) during that interval:

$$S_{a\tau}(\omega_2 - \Omega_2; \tau) = 2 \text{Re} \int_0^\infty dt_3 \exp[i(\omega_2 - \Omega_2)t_3] \times \left[ R_{++}(t_3, \tau, 0) + R_{0+}(t_3, \tau, 0) \right], \quad (19)$$

$$S_{ee}(\omega_2 - \Omega_2; \tau) = 2 \text{Re} \int_0^\infty dt_3 \exp[i(\omega_2 - \Omega_2)t_3] \times \left[ R_{0+}(t_3, \tau, 0) + R_{++}(t_3, \tau, 0) \right], \quad (20)$$

and we set $\mu_0 \theta_1 = \mu_0 \theta_2 = 1$.

By formulating pump–probe spectroscopy in Liouville space, it becomes possible for us to separate the process into three steps: First the pump beam creates a wave packet during the $t_1$ period (the doorway state). There are actually two wave packets in the excited-state (hereafter denoted the particle) paths 1 and 2, and the other is the ground state (the hole) coming from paths 3 and 4. These two wave packets then propagate during the delay time between the pump and the probe. This evolution is the most significant information obtained from pump and probe spectroscopy. Finally, the system interacts with the probe, and the signal is generated. We denote the wave packet of the particle and the hole by $W_+ \text{ and } W_-$, respectively. These wave packets are given by

$$W_+(p; t) = \int \text{d}p W_+(p, q; t), \quad W_-(q; t) = \int \text{d}p W_-(p, q; t). \quad (26)$$

The calculations performed for the Condon case ($c = 0$) and the non-Condon case ($c = 0.1 \text{EMrad}/\text{s}$) are denoted by (a) and (b), respectively, in Figs. 2–7 below. We assume that the damping induced by the heat bath is frequency independent, and it is denoted by $\gamma$ (Ohmic dissipation).

The phase function is then expressed as

$$\theta(t) = \lambda \left\{ \frac{\lambda_2^2}{2\hbar \omega_0} \left[ \exp(-\lambda_2 t) + \lambda_2 t - 1 \right] \coth \left( \frac{i\hbar \lambda_2}{2} \right) \right. \right. + \left. \left. - \frac{\lambda_1^2}{2\hbar \omega_0} \left[ \exp(-\lambda_1 t) - \lambda_1 t - 1 \right] \coth \left( \frac{i\hbar \lambda_1}{2} \right) \right\}$$

$$- \frac{4\gamma \omega_0}{\beta \hbar} \sum_{n=1}^{\infty} \left[ \exp(-\nu_n t) + \nu_n t - 1 \right]^\nu_n \sin(\Omega t) + \frac{\gamma}{\omega_0^2} \cos(\Omega t)$$

$$+ t - \frac{\gamma}{\omega_0}, \quad \gamma = 2\pi n/\beta \hbar$$

and

$$\lambda_1 = \frac{\gamma}{2} - i\zeta, \quad \lambda_2 = \frac{\gamma}{2} + i\zeta, \quad \zeta = (\omega_0^2 - \gamma^2/4)^{1/2}.$$  

This expression interpolates between several important limits:

Coherent motion limit ($\gamma \to 0$),

$$g_\varepsilon(t) = \frac{\lambda}{\omega_0} \left[ 1 - \cos(\omega_0 t) \cosh \left( \frac{\beta \hbar \omega_0}{2} \right) - \frac{i\lambda}{\omega_0} [\omega_0 t - \sin(\omega_0 t)] \right]. \quad (29)$$
Strongly damped limit ($\gamma \gg \omega_0$ and $\Lambda = \omega_0^2/\gamma$),

\[ g_z(t) = \frac{\Lambda}{\beta \Lambda^2} \left[ (e^{-\Lambda t} + \Lambda t - 1) \cot(h\beta\Lambda/2) + \frac{4\Lambda^2}{\beta h} \sum_{n=1}^{\infty} e^{-\gamma t} \right] \pm i \frac{\Lambda}{\beta \Lambda} (e^{-\Lambda t} + \Lambda t - 1) ; \]

\[ g_z(t) = \frac{2\lambda}{\beta \Lambda^2} [\exp(-\Lambda t) + \Lambda t - 1] \pm i \frac{\Lambda}{\beta \Lambda} [\exp(-\Lambda t) + \Lambda t - 1]. \]  

We first show the time evolution of the wave packets of the particle (Fig. 2) and the hole (Fig. 3) for an underdamped mode, $\gamma = 40 \text{ cm}^{-1}$ at $T = 100 \text{ K}$ and $T = 300 \text{ K}$. The frequency and the dimensionless displacement are given by $\omega_0 = 600 \text{ cm}^{-1}$ and $\beta = 2\sqrt{\omega_0/\hbar} = 1.0$. As is seen from Fig. 2, the particle moves from the initial posi-

![Fig. 2. Time evolution of the wave packet of the particle for the underdamped mode at $T = 100 \text{ K}$ and $T = 300 \text{ K}$ for (a) the Condon approximation, (b) the non-Condon interaction, and (c) their difference.](image)

![Fig. 3. Time evolution of the wave packet of the hole for the underdamped mode at $T = 100 \text{ K}$ and $T = 300 \text{ K}$ for (a) the Condon approximation, (b) the non-Condon interaction, and (c) their difference.](image)
Figures 4 and 5 show the time evolution of the wave packets of the particle (Fig. 4) and the hole (Fig. 5) for an overdamped mode $\gamma = 2000 \text{ cm}^{-1}$, $\omega_0 = 600 \text{ cm}^{-1}$, and $d = 1$ at $T = 100 \text{ K}$ and $T = 300 \text{ K}$. As is seen from Fig. 4, the motion of the particle is critically damped in both the Condon and the non-Condon cases [see Eqs. (30) and (31)]. The hole motion is also strongly suppressed by the heat bath and, even with non-Condon interaction, the hole cannot move and shows behavior similar to the Condon case. The peak positions of the particle and the hole, however, shift to the positive side for the non-Condon case, because of the Condon dipole interaction Eq. (4). As is seen from the figures, this shift becomes large at $T =$
Fig. 6. Impulsive pump–probe spectrum for the two-mode case $\gamma = 40 \text{ cm}^{-1}$ and $\gamma = 2000 \text{ cm}^{-1}$ at the low temperature $T = 100 \text{ K}$. Here we define $\Delta \omega = \omega_2 - \Omega_2 - \omega_d$. (a) is for the Condon approximation; (b) is for the non-Condon interaction. In each of these, we display the contributions of the hole, the particle, and their sum separately.

Fig. 7. Impulsive pump–probe spectrum for the two-modes case at the high temperature $T = 300 \text{ K}$. Other parameters are the same as in Fig. 6.

Fig. 8. Time evolution of the total absorption peaks in Figs. 6 ($T = 100$) and 7 ($T = 300$). Solid curves, the non-Condon approximation; dashed curves, the Condon approximation.

300 K. The reason for the large shifts at high temperatures in the case of the non-Condon interaction is as follows: before the pump excitation, the system is in the ground equilibrium state and is localized if the temperature is low; however, it broadens if the temperature is high. As is seen from Eq. (4), the dipole element $\mu(q)$ is a linear function of $q$ for small $c$. Since the population of particles at large $q$ will increase at the higher temperatures, the non-Condon effect becomes larger.

We next calculated the absorption spectrum of a two-mode system that is described by the two nuclear coordinates $q_1$ and $q_2$. For the two modes we took the underdamped mode discussed in Figs. 2 and 3 and the overdamped mode discussed in Figs. 4 and 5. We assume that the dipole moment has the form

$$\mu = \mu_0 \exp(c_1 q_1) \exp(c_2 q_2) = \mu_0 (1 + c_1 q_1 + c_2 q_2), \quad (32)$$

where $c_1$ and $c_2$ are the coupling constants, and we set $c_1 = c_2 = 0.1 \sqrt{M_0 \omega_0 / \hbar}$. The corresponding response functions are given simply by the product of the single-mode response functions discussed above.

Figures 6 and 7 show the difference absorption spectrum for the different delay periods between the pump and the probe $\tau$. Here we set $\Delta \omega = \omega_2 - \Omega_2 - \omega_d$. Figures 6(a) and 7(a) are for the Condon interaction, whereas 6(b) and 7(b) are for the non-Condon interaction. In each case we display the contributions of the hole, the particle, and their sum separately. The motion of the wave packets displayed in Figs. 2–5 is clearly reflected in the spectrum, and we can observe the motion of the hole and a temperature-dependent blue shift, which are both caused by the non-Condon interaction (see also Fig. 8).

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REFERENCES