

Dynamical Stokes shift observed by two-dimensional Raman spectroscopy

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Abstract. We analyze the effect of relaxation process of wavepackets created in the electronic excited state on off-resonant two-dimensional Raman spectroscopy, employing the Brownian motion model with a nonequilibrium initial condition described by a displaced Gaussian wavepacket. We calculate three-time correlation functions of the excited state polarizability, which correspond to the fifth-order Raman signal in the excited state by using the Feynman's path integral formalism. It is found that the fifth-order signal is sensitive to the initial position of the Gaussian wavepacket not only for the underdamped case but also for the overdamped case.

I INTRODUCTION

The vibrational mode of molecules in condensed phases has been studied in many experimental and theoretical works. Recently, it was shown that two-dimensional (2D) off-resonant Raman spectroscopy is very sensitive to systems (1). In this paper, we demonstrate that the fifth-order 2D Raman is not only sensitive to the system but also to the initial conditions. The problem in our mind is the relaxation process of wavepackets created in the electronic excited state of a molecule. Suppose the molecular system is described by the displaced harmonic oscillators with the frequency Ω and the displacement Q_0 , and the system is initially in the ground equilibrium state. Then, an impulsive resonant pulse creates the Gaussian wavepacket in the excited state and its center of is displaced by Q_0 from the bottom of the excited potential. Such relaxation process is usually studied by observing the time-dependent emission spectrum. A movement of wavepacket can be seen as the shift of emission peak (the dynamical Stokes shift). In some cases, however, such measurements are very difficult, since the emission peak is often broadened and its movement is very small, if the molecular system is in a solution and is strongly coupled to the solvent molecules. In this paper, we show that

the two-dimensional Raman spectroscopy is useful to analyze the dynamical Stokes shifts even for the overdamped case.

II MODEL SYSTEM

We assume that the vibronic potential on an electronic excited state is a single nuclear mode and is expressed by a harmonic potential. The effects of solvent are taken into account by using the harmonic oscillators bath. The system-bath Hamiltonian is then expressed as

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{M\Omega^2}{2}\hat{Q}^2 + \sum_i \left\{ \frac{\hat{p}_i^2}{2m_i} + \frac{m_i\omega_i^2}{2} \left(\hat{q}_i - \frac{c_i\hat{Q}}{m_i\omega_i^2} \right)^2 \right\}. \quad (1)$$

where \hat{P} and \hat{Q} are the primary nuclear momentum and coordinate, \hat{p}_i and \hat{x}_i are the momenta and coordinates of the bath oscillators with the frequency ω_i and the mass m_i , c_i is the coupling strength between the system and the bath, respectively. The summation over i goes to infinity in order to describe the dissipation on the molecular system. The spectral distribution function is defined by $I(\omega) = \pi \sum_i (c_i^2/2m_i\omega_i)\delta(\omega - \omega_i)$, which describes the character of the heat bath. In the following, we consider the Ohmic dissipation; $I(\omega) = M\gamma\omega$. The constant γ corresponds to the strength of the damping. We assume that the system and the bath are initially decoupled. Since we assume that the initial wavepacket is brought by the impulsive pulse from the ground electronic state at $t = t_I$, then the initial distribution function of the system is given by

$$\rho_I^{(S)}(Q, Q') = \sqrt{\frac{2a}{\pi}} \exp \left(-a(Q - Q_0)^2 - a(Q' - Q_0)^2 \right). \quad (2)$$

The bath system is assumed to be in the equilibrium and its initial state is given by the Boltzman distribution.

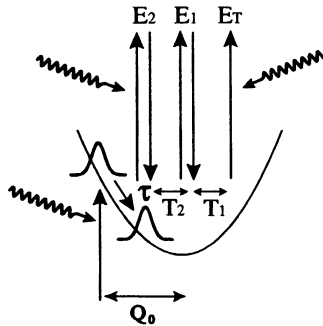
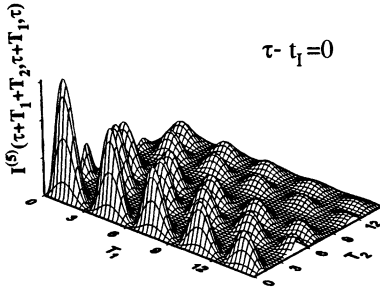


FIGURE 1. The two pairs of pulses interact the system. The last pulse is probe that generates the signal.

(a)

 $\tau - t_I = 0$

(b)

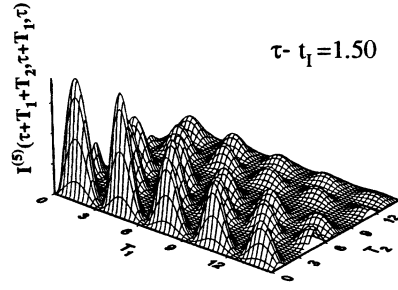
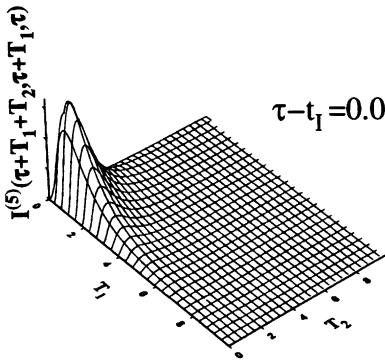
 $\tau - t_I = 1.50$

FIGURE 2. The fifth-order Raman signal for the underdamped case for different time intervals (a) $\tau - t_I = 0$ and (b) $\tau - t_I = 1.5$, where we set $\Omega = 1$.

(a)

 $\tau - t_I = 0.0$

(b)

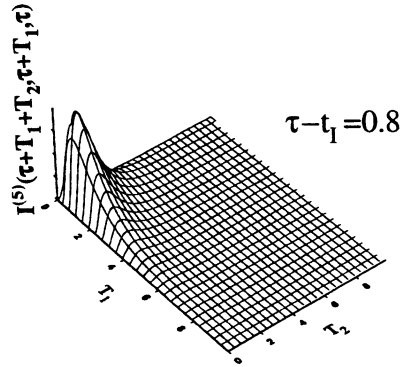
 $\tau - t_I = 0.8$

FIGURE 3. The the fifth-order Raman signal for the overdamped case for different time intervals (a) $\tau - t_I = 0$ and (b) $\tau - t_I = 0.8$, where we set $\Omega = 1$.

III RESULTS

We now apply the off-resonant pulses to probe the dynamics of wavepackets associated through the polarizability. The pulse configuration for the fifth order experiment is depicted in Fig. 1. The system first interacts with two pairs of pulses for the fifth order optical process, and then the last probe pulse generates the signal. The effective Hamiltonian including laser interaction is then given by $H_{\text{eff}} = H - E^2(\mathbf{r}, t)\alpha(Q)$, where $\alpha(Q)$ is the coordinate dependent polarizability denoted by $\alpha(Q) = \sum \alpha_n Q^n/n!$. We set the laser pulses as follows:

$$E_T(t) = \delta(t - \tau - T_1 - T_2), \quad E_1(t) = \delta(t - \tau - T_1), \quad E_2(t) = \delta(t - \tau), \quad (3)$$

where we have assumed the first impulsive pump pulses is applied at time τ . The signals are described in terms of the response functions

$$R^{(5)}(\tau_2, \tau_1, \tau) = \theta(\tau - \tau_1)\theta(\tau_1 - \tau_2)\langle[[\hat{\alpha}(\tau), \hat{\alpha}(\tau_1)], \hat{\alpha}(\tau_2)]\rangle \quad (4)$$

as $I^{(5)}(\tau_2, \tau_1, \tau) = |R^{(5)}(\tau_2, \tau_1, \tau)|^2$. The response functions for displaced-Gaussian initial distribution can be calculated through the Feynman's path integral method (2). We calculate the third-order correlation functions that correspond to fifth-order off-resonant Raman signals. The leading order contribution of $R^{(5)}$ are proportional to $\alpha_1^2\alpha_2$ and $\alpha_1\alpha_2^2$. Fig. 2 and 3 present the fifth-order signal for underdamped case, $\gamma = 0.1$, and overdamped case, $\gamma = 3.0$, for the different time intervals ($\tau - t_I$). Here we have set $\Omega = 1$, $Q_0\alpha_2/\alpha_1 = 0.15$. The position of the wavepacket moves under the Hamiltonian H during the time interval ($\tau - t_I$) until the first Raman pulses irradiate the system and the profile of response function is a function of ($\tau - t_I$). The effect of the wavepacket motion can be seen in the profile of the signal. The main difference between Figs. 2(a) and 2(b) is the peak height at $(T_1, T_2) \simeq (4.0, 0.5)$. For underdamped case, the wavepacket oscillates on the potential surface during ($\tau - t_I$). This oscillation interferes with the correlation caused by Raman pulses. The interference reflects in the difference between Figs. 2(a) and (b). In Fig. 2(b), the interference is large because the wavepacket moves near the bottom of the potential surface and its velocity is larger than one??(=velocity) in Fig. 2(a). In the overdamped case, Figs. 3(a) and 3(b), however, the difference is very small, since the motions decay quickly because of the strong damping. Detailed analysis for different initial conditions for 5th- and 7th-order spectroscopy will be presented in Ref. (2).

REFERENCES

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