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COMPLETE DETERMINATION OF RELAXATION PARAMETERS FROM TWO-DIMENSIONAL RAMAN SPECTROSCOPY

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Using the model of a weakly-anharmonic, underdamped oscillator coupled to a bath, we demonstrate that the 2D time-resolved Raman signal carries information about the population decay T_1, the homogeneous dephasing T_2, and the inhomogeneous dephasing T_I relaxation timescales. We distinguish between two projections of the 2D signal: first, the echo signal, which is stretched in the diagonal direction decays with T_2, and the second which is stretched along one axis is related to the population relaxation and decays with T_1. The width of both signals reflects T_I. Equations of motion for vibrational coherence and population variables are employed in these calculations.

Keywords: Femtosecond spectroscopy; photon echo; multidimensional Raman spectroscopy; pure dephasing

The advent of femtosecond lasers with pulse durations under 10 fs has opened recently a new field of impulsive Raman vibrational spectroscopy [1, 2]. Such pulses are short compared with vibrational frequencies even for high-frequency $\sim 2000\,\mathrm{cm}^{-1}$ vibrations. This allows to excite vibrational modes impulsively and observe coherent oscillations in real time. Besides oscillations, optical signals are damped due to coupling to lower-frequency bath modes, *e.g.*, intermolecular, solvent, *etc.*, and the signals carry important informa-

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tion on the system-bath coupling. Conventional CARS spectroscopy is based on the third-order optical response which is one-dimensional (1D) and the resulting information is highly averaged. Higher-order techniques *e.g.*, 2D Raman spectroscopy based on the fifth-order optical response provide much more detailed information [3–6]. For underdamped modes whose frequencies are larger than the linewidths Δ, one can clearly distinguish between three line broadening mechanisms contributing to the 1D signal decay rate: homogeneous dephasing, inhomogeneous dephasing and finite lifetime. The inhomogeneous dephasing timescale T_I is induced by static disorder resulting from coupling to low frequency modes. Homogeneous dephasing (T_2) corresponding to fast bath modes consists of pure dephasing (T_2^*) processes which only destroy vibrational coherence and lifetime (T_1) representing vibrational population relaxation $1/T_2 = 1/T_1 + 1/T_2^*$. These three mechanisms result in the T_I, T_2 and T_1 relaxation timescales. CARS spectroscopy provides information on the overall value of $1/T_2 + 1/T_1 + 1/T_2^*$. The capacity of 2D Raman spectroscopy to distinguish between the homogeneous and inhomogeneous dephasing using the photon echo approach has been studied [7]. In this paper we demonstrate that a single 2D measurement can yield all three timescales.

In impulsive Raman spectroscopy the system remains in the ground electronic state at all times and during the time intervals between pulses the evolution is determined by the vibrational Hamiltonian of the ground electronic state. The coupling to the driving field can be described by the electronic polarizability $\alpha(\mathbf{Q})$ which depends parametrically on the set of nuclear coordinates denoted by $\mathbf{Q}$ [8]. The 1D heterodyne detected impulsive signal is given by the two-point Liouville space correlation function

$$S^{(1D)}(t_1) = \langle \alpha_+(t_1)\alpha_-(0)\rangle, \tag{1}$$

where for any operator A in the Hilbert space, $A_\pm$ denote Liouville space superoperators defined by the following action on the density matrix ρ: $A_-\rho = [A, \rho]$, $A_+ = (A\rho + \rho A)/2$ [9]. The 2D signal is expressed in terms of a three point correlation function [9]

$$S^{(2D)}(t_2, t_1) = \langle \alpha_+(t_2 + t_1)\alpha_-(t_1)\alpha_-(0)\rangle. \tag{2}$$

We consider a system with a single primary anharmonic vibration with the Hamiltonian

$$H = H_0 + H_1,$$
$$H_0 = \frac{P^2}{2M} + \frac{M\Omega^2 Q^2}{2}, \qquad H_1 = \sum_{j=3}^{\infty} \frac{Q^j}{j!} V^{(j)}, \tag{3}$$

where H_0 and H_1 represent the harmonic and anharmonic parts respectively. The primary mode is coupled to a bath described by the bath Hamiltonian which depends on a set of bath coordinates $\mathbf{q}$. The coupling is described by the system-bath interaction Hamiltonian H_{int}. We further assume, that the polarization operator α only depends on the primary Raman-active mode coordinate:

$$\alpha(Q) = \alpha^{(1)} Q + \sum_{j=2}^{\infty} \alpha^{(j)} \frac{Q^j}{j!}. \tag{4}$$

In the limit of weak nonlinearity [9] the main contribution to the 2D signal is given by the terms which are first order in $\alpha^{(2)}$ or $V^{(3)}$. This yields three contributions of the form:

$$S_1(t_2, t_1) = \alpha^{(2)}\alpha^{(1)}\alpha^{(1)}\langle Q_+(t_2 + t_1)Q_+(t_1)Q_-(t_1)Q_-(0)\rangle,$$
$$S_2(t_2, t_1) = \alpha^{(2)}\alpha^{(1)}\alpha^{(1)}\langle Q_+(t_2 + t_1)Q_-(t_1 + t_2)Q_-(t_1)Q_-(0)\rangle,$$
$$S_3(t_2, t_1) = \alpha^{(1)}\alpha^{(1)}\alpha^{(1)}\frac{V^3}{3!}\int_0^{t_2} d\tau \langle Q_+(t_2 + t_1)[Q^3(\tau)]_- Q_-(t_1)Q_-(0)\rangle, \tag{5}$$

and the expectation values in Eqs. (5) are taken with respect to H_0. If the bath is harmonic and the system-bath interaction is linear in the primary and bath coordinates, the correlation functions in Eqs. (5) can be evaluated exactly [9, 10]. However this type of system-bath interaction describes lifetime effects only, and cannot represent pure dephasing processes. These can only be described by adding anharmonicities, *e.g.*, $Q^2 q$ terms. In this case the correlation functions in Eqs. (5) may not be computed exactly. They can be, however, calculated by eliminating the bath using projection operator techniques [11] and calculating the necessary kernels to second order in the system-bath coupling. An alternative and more intuitive way is to use

equations of motion for the primary variables, adopting a factorization scheme and eliminating the bath using projection operators. It has been shown [9] that in the case of linearly coupled harmonic bath, the expressions given by Eqs. (5) can be calculated using an equation of motion for the $\langle Q \rangle$ variable only, by factorizing the higher-order products using $\langle Q^j \rangle = \langle Q \rangle^j$. This is a classical approximation [9] and, in the theory of Frenkel exciton systems this is known as the Local Field Approximation (LFA). The LFA fails to describe pure dephasing processes: to this end additional population variables should be included [12, 13].

To derive a closed system of equations for vibrations which is similar to that in Refs. [12, 13] we first express the vibrational coordinate Q and momentum P in terms of the Boson creation (annihilation) operators $\hat{B}^\dagger(\hat{B})$

$$Q = \frac{1}{\sqrt{2M\Omega}}(\hat{B}^\dagger + \hat{B}), \quad P = i\sqrt{\frac{M\Omega}{2}}(\hat{B}^\dagger - \hat{B}). \tag{6}$$

We further retain only the cubic term in the anharmonicity Hamiltonian Eq. (3): $H_1 = \frac{1}{3!}V^{(3)}Q^3$ and add an effective coupling between the primary oscillator and electronically off-resonant radiation field $E(t)$: $H_{\text{eff}} = \alpha(Q)E^2(t)$. After the expansion of the polarization operator $\alpha(Q)$ (Eq. (4)) to second order in Q and substitution of Eq. (6) the Hamiltonian of the system coupled to the driving field becomes:

$$H_T = \Omega\hat{B}^\dagger\hat{B} + \frac{\tilde{V}^{(3)}}{3!}(\hat{B}^\dagger + \hat{B})^3 - \left(\tilde{\alpha}^{(1)}(\hat{B}^\dagger + \hat{B}) + \frac{\tilde{\alpha}^{(2)}}{2!}(\hat{B}^\dagger + \hat{B})^2\right)E^2(t), \tag{7}$$

where we use the notation $\tilde{V}^{(3)} = V^{(3)}/(2M\Omega)^{3/2}$, and $\tilde{\alpha}^{(j)} = \alpha^{(j)}/(2M\Omega)^{j/2}$. The radiation field $E(t)$ is represented by a sequence of two pairs of ultrashort non-overlapping pulses centered at times $\tau_1 > \tau_2$, respectively and followed be the probe pulse $\mathcal{E}_p$:

$$E(t) = \sum_{n=1}^{2} \mathcal{E}_n(t - \tau_n) + \mathcal{E}_p(t). \tag{8}$$

The delay times between pulses $t_1 = \tau_2 - \tau_1$ and $t_2 = t - \tau_2$ were used in Eqs. (5).

Taking into account homogeneous dephasing and population decay requires equations of motion for two observables $B(t) \equiv \langle \hat{B}(t) \rangle$ (and its complex conjugate $B^*(t) \equiv \langle \hat{B}^\dagger \rangle$) and $n(t) \equiv \langle \hat{B}^\dagger \hat{B} \rangle$. Making use of the Heisenberg equation of motion for the operators $\hat{B}$, $\hat{B}^\dagger \hat{B}$ and applying the following factorization procedure: $\langle \hat{B}^\dagger \hat{B}^\dagger \rangle = \langle \hat{B}^\dagger \rangle \langle \hat{B}^\dagger \rangle$, $\langle \hat{B} \hat{B} \rangle = \langle \hat{B} \rangle \langle \hat{B} \rangle$ we obtain:

$$\begin{aligned} \dot{B} &= \left(-i\Omega - \frac{\Gamma}{2} \right) B - i \frac{\tilde{V}^{(3)}}{2} \left(B^{*2} + B^2 + 2N \right) \\ &\quad + i \left(\tilde{\alpha}^{(1)} + \tilde{\alpha}^{(2)} (B^* + B) \right) E^2(t), \\ \dot{N} &= -\gamma N + i \tilde{\alpha}^{(1)} (B^* - B) E^2(t), \end{aligned} \tag{9}$$

where $N = n(t) - n_{\text{eq}}$, n_{eq} is the vibrational population at thermal equilibrium. In the r.h.s. of Eqs. (9) we retain only terms up to Q^2 and take into account the anharmonic renormalization of the vibrational frequency Ω. We also introduce relaxation through the dephasing rate $\Gamma = \gamma + \hat{\Gamma} = 2/T_2$ and population decay $\gamma = 1/T_1$, $\hat{\Gamma}$ being the pure dephasing rate. The induced polarization which determines the optical signal has the following form:

$$P = \left(\tilde{\alpha}^{(1)} (B^* + B) + \frac{\tilde{\alpha}^{(2)}}{2!} \left(B^{*2} + B^2 + 2N \right) \right) E_p \tag{10}$$

By solving Eqs. (9) perturbatively in the driving field and substituting the results into Eq. (10) we obtain the 2D optical signal. The signal can be represented by its coherent and incoherent components. The former can be obtained by factorizing the population variables in the form $N = B^* B$ which is equivalent to the LFA. This implies that the coherent component is given by the expressions derived in [9, 10] provided pure dephasing is added to the decay rate. The incoherent component is conveniently represented in terms of the irreducible part of the population defined by $N^i \equiv N - B^* B$. The first contribution to the signal S_1 in Eqs. (5) contains the coherent component only. The incoherent components corresponding to the terms S_2, S_3 have the form:

$$\begin{aligned} S_2^i(t_1, t_2) &= \tilde{\alpha}^{(2)} N^i(t_1, t_2), \\ S_3^i(t_1, t_2) &= \tilde{\alpha}^{(1)} \tilde{V}^{(3)} \int_0^{t_2} dt' \sin[\Omega(t_2 - t')] e^{-\frac{\Gamma}{2}(t_2 - t)} N^i(t_1, t_2 - t'), \end{aligned} \tag{11}$$

N^i can be evaluated solving Eqs. (9) which yields

$$N^i = 2\tilde{\alpha}^{(1)}\tilde{\alpha}^{(1)}F_1F_2\cos(\Omega t_1)e^{-\frac{\Gamma t_1}{2}}(e^{-\gamma t_2} - e^{-\Gamma t_2}), \tag{12}$$

where $F_j = \int_{-\infty}^{\infty} d\tau|\mathcal{E}_j^2(\tau)|, j = 1, 2$. It should be pointed out that in the absence of pure dephasing ($\hat{\Gamma} = 0$) $\Gamma = \gamma$ and N^i vanishes, and Eqs. (9) and (10) become equivalent to the LFA [14].

We have solved Eqs. (9) and (10) and averaged the signal over an inhomogeneous Gaussian distribution of vibrational frequencies $W(\Omega)$ with central frequency Ω_0 and width Δ. The final expression for the 2D Raman signal is:

$$\begin{aligned} S^{(5)}(t_1, t_2) \propto & \cos[\Omega_0(t_2 - t_1) + \theta]e^{-\frac{\Delta^2(t_1-t_2)^2}{2}}e^{-\frac{\Gamma}{2}(t_1+t_2)} \\ & + A\cos(\Omega_0 t_1)e^{-\frac{\Delta^2 t_1^2}{2}}e^{-\frac{\Gamma}{2}t_1-\gamma t_2} \end{aligned} \tag{13}$$

Equation (13) is the central result of this paper. The signal consists of two components. The first represents an echo which appears at $t_1 = t_2$ and is associated with the excitation of vibrational coherences, and decays on the homogeneous dephasing timescale $T_2 = (\Gamma/2)^{-1}$. The echo signal also shows oscillations with period $T = (\Omega_0/2)^{-1}$. The oscillations phase shift θ reflects the weak anharmonicity and is determined by $\tan\theta = (\tilde{V}^{(3)}\tilde{\alpha}^{(1)})/(\Omega_0\tilde{\alpha}^{(2)})$. The second term in Eq. (13) is stretched along the t_2 direction at $t_1 = 0$ and decays on the population decay timescale $T_1 = \gamma^{-1}$. This signal also shows oscillations along t_1 with the period $T = (\Omega_0/2)^{-1}$. However, in this case the anharmonicity affects the signal intensity (*via* the parameter $A = 1 + \tan\theta$) rather than the oscillations phase. The width of both signals reflects the inhomogeneous dephasing timescale $T_I = \Delta^{-1}$. In Figure 1 we present 2D contour plots of the signal $|S^{(5)}|^2$ computed Eq. (13) using and plotted on the timescale comparable with (T_1, T_2). The echo component in the direction $t_1 = t_2$ and the component associated with the population decay stretched along the t_2-axis at $t_1 = 0$ are clearly seen. Since typically pure dephasing is faster than population relaxation the component stretched along the t_2-axis decays on a longer timescale compared to the echo component. The oscillations of the signal are clearly shown in the insert which displays the same signal but on the timescale comparable with Ω_0^{-1}.

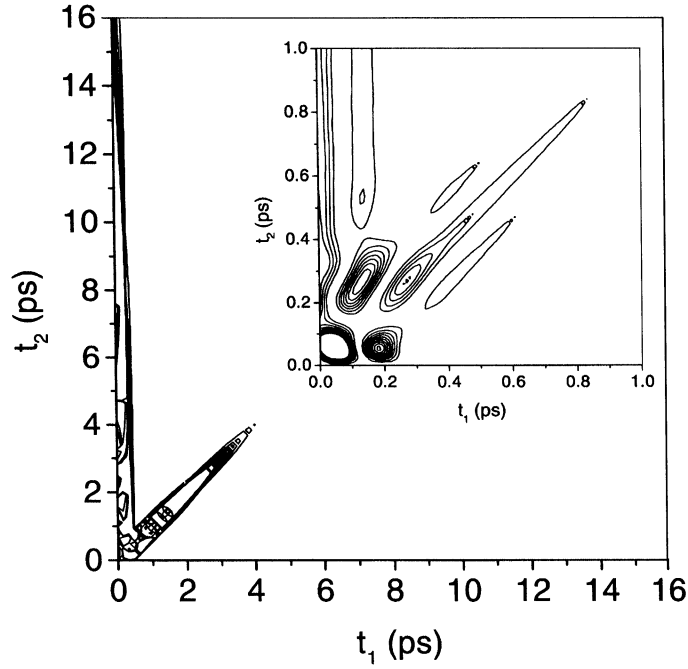

FIGURE 1 Contour plot of the 2D signal $|S(t_2, t_1)|^2$ for a harmonic system ($\tilde{V}^{(3)} = 0$ in Eq. (13)) coupled to a bath with homogeneous dephasing rate $\Gamma = 2.5\,\mathrm{cm}^{-1}$ and population decay rate $\gamma = 1\,\mathrm{cm}^{-1}$ averaged over Gaussian frequency distribution with central frequency $\Omega_0 = 112\,\mathrm{cm}^{-1}$ and inhomogeneous width $\Delta = 30\,\mathrm{cm}^{-1}$. The echo component in the direction $t_2 = t_1$ decays on the $T_2 = (\Gamma/2)^{-1}$ timescale, the component stretched along t_2-axis at $t_1 = 0$ decays on the population decay timescale $T_1 = \gamma^{-1}$. The width of both components reflects inhomogeneous dephasing timescale $T_I = \Delta^{-1}$. The insert shows the signal oscillations with period $T = (\Omega_0/2)^{-1}$.

In summary, usually T_2 is measured by photon echoes, T_1 is obtained by pump probe [15] and the total linewidth depends on T_1, T_2 and T_I. We have demonstrated that a single 2D impulsive Raman echo measurement can provide the complete information about all relaxation parameters T_I, T_1 and T_2 of a weakly anharmonic vibrational system.

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