Two-Dimensional Raman-Echo Spectroscopy; Femtosecond View of Vibrational Coherence

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Abstract. Two semiclassical algorithms (high temperature and low temperature, weak nonlinearity) for computing 2D fifth-order Raman spectra are compared. In both cases the response can be described using phase-space wavepackets.

1. Introduction

Time-resolved vibrational spectroscopy is a powerful tool in the studies of intramolecular and intermolecular dynamics of condensed phase systems such as liquids, glasses, polymers, and proteins where nuclear dynamics spans a broad range of timescales [1,2]. The complete control of pulse shapes, durations, and phases allows the development of multidimensional Raman techniques whereby the spectrum is disentangled by spreading it onto several frequency or time axes [3-6]. Their modeling should take into account the quantum character of nuclear motions, the non-linear dependence of electronic polarizability on nuclear coordinates, and anharmonicities. Semiclassical expansions can be used to carry out these simulations.

Two different semiclassical expressions for the necessary nonlinear response functions are developed. The first, high temperature algorithm (HTA), holds when thermal energy is much greater than vibrational frequency ($k_B T >> \hbar\Omega$) [7]. The other, weak nonlinearity algorithm (WNA), applies to systems with weak nonlinearity and anharmonicity [8] and holds better at low temperatures. In both cases the response function is expanded in powers of $\hbar$. In the former this is done for a fixed temperature T whereas in the latter the thermal frequency $\omega_T = k_B T/\hbar$ is fixed.

2. Multiple Echoes

We applied the WNA and HTA to the fifth-order 2D response of a single mode coupled to the off-resonant radiation field via the electronic polarizability $\alpha(Q) = \alpha_0 \exp(Q/Q_0)$, where Q is the oscillator coordinate and Q_0 is characteristic length scale. Since all order terms in the power expansion of $\alpha(Q)$ are finite, the interaction with the radiation field excites coherences between all vibrational states. The fifth-order 2D signal for an underdamped mode is [9]

$$S(t_1,t_2) = \sum_m e^{-im\Omega_0 t_2} \sum_n \exp\left[-\frac{(m\Delta)^2}{2}\left(t_2 - \frac{nt_1}{m}\right)^2\right] e^{in\Omega_0 t_1} F_{nm}\left(e^{-\gamma_2} e^{-\gamma_1}\right) \quad (2.1)$$

Reprinted from *Ultrafast Phenomena XI*, edited by T. Elsaesser, J. G. Fujimoto, D. A. Wiersma, W. Zinth, (Singer-Verlag Berlin Heidelberg) (1998).

where a Gaussian inhmogeneous distribution with central frequency Ω_0 and width Δ is assumed. Equation (2.1) shows multiple echoes at times $t_2 = (n/m)t_1$, m, n = 1,2,3.... The amplitudes of the echo peaks are determined by function F_{nm} which is different for both semiclassical expansions and varies on the homogeneous relaxation timescale.

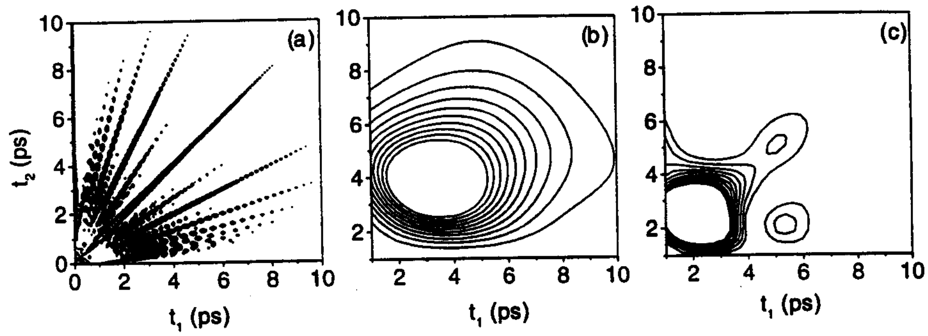

Fig. 1 2D Raman signal: (a) underdamped mode, (b)-(c) low frequency mode.

Figure 1 shows computer simulations of $|S(t_1,t_2)|$. Panel (a) presents an underdamped mode (Eq. (2.1)) with $\Omega_0 = 620\ cm^{-1}$, $\gamma = 0.7\,cm^{-1}$, and $\Delta = 60\,cm^{-1}$. Multiple echoes are clearly seen in the directions t_1 =1, 1/3, 1/2, 2/3, 1/4, 3/2, 2, 3, 4 t_2. The HTA is applied to a low frequency vibration $\Omega_0 = 20\,cm^{-1}$ with strong homogeneous damping. The signal in panel (b) where $\Delta > \Omega_0$ ($\Delta = 10\,cm^{-1}$), shows no echo whereas weak echo is clearly seen in panel (c) where $\Delta < \Omega_0$ ($\Delta = 40\,cm^{-1}$).

3. Phase-Space Wavepackets

The exact fifth-order off-resonance quantum response function is expressed as a sum of four Liouville space pathways each given by a three-point correlation function of polarizability $\alpha(Q)$. Each term is described by a Feynman diagram [10] and is represented by a phase-space wavepacket. For a harmonic system (with $\gamma = 0$) these wavepackets are Gaussian [9]:

$$\rho_\alpha(P,Q) = (-1)^\alpha \frac{\alpha_0^2}{(i\hbar)^2} \exp\left(\frac{\overline{Q}(0)+\overline{Q}_\alpha(t_1)}{Q_0}\right) \times \frac{\Omega}{2\pi\sigma} \exp\left[-\frac{\left(P-\overline{P}_\alpha(t_1+t_2)-\overline{P}_\alpha(t_2)\right)^2}{4M\sigma} - \frac{M\Omega^2\left(Q-\overline{Q}_\alpha(t_1+t_2)-\overline{Q}_\alpha(t_2)\right)^2}{4\sigma}\right] \tag{3.1}$$

where $\alpha = 1,\ldots,4$, $\sigma = (\hbar\Omega/2)\coth(\hbar\Omega/k_BT)$, and center coordinates:

$$\overline{Q}_{\alpha}(t_n) = \overline{Q}(0)\cos(\Omega t_n) + \varepsilon_{\alpha}^{n}\frac{\overline{P}(0)}{M\Omega}\sin(\Omega t_n), \quad n = 1,2 \tag{3.2}$$

$$\overline{Q}_{\alpha}(t_1 + t_2) = \overline{Q}(0)\cos(\Omega(t_1 + t_2)) + \varepsilon_{\alpha}^{1}\frac{\overline{P}(0)}{M\Omega}\sin(\Omega(t_1 + t_2)) \tag{3.3}$$

$$\overline{P}_{\alpha}(t) = M\Omega\dot{\overline{Q}}_{\alpha}(t) \tag{3.4}$$

with initial coordinate $\overline{Q}(0) = \sigma/M\Omega^2 Q_0$, initial momentum $\overline{P}(0) = i\hbar/2Q_0$, and the auxiliary variables $\varepsilon_1^1 = \varepsilon_2^1 = -\varepsilon_3^1 = -\varepsilon_4^1 = 1$, $\varepsilon_1^2 = -\varepsilon_2^2 = -\varepsilon_3^2 = \varepsilon_4^2 = -1$. According to Eqs. (3.1) – (3.4) only the center of each wavepacket evolves in time while its shape remains Gaussian. Different phase-space trajectories (Eqs. (3.2)–(3.4)) coincide if $\overline{P}(0) = 0$ and in both semiclassical expansions these four wavepackets are approximated by a single wavepacket which represents the total density matrix.

Acknowledgements. We gratefully acknowledge the support of the National Science Foundation and the United States Air Force Office of Scientific Research.

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