

## Time-Resolved Spectroscopy of Vibrational Overtones and Two-Phonon States

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The authors propose the application of time-resolved nonlinear optical techniques to the selective study of the dynamics of vibrational overtones and two-phonon states in condensed media. They present the first experimental demonstration of picosecond coherent anti-Stokes higher-order Raman scattering on the first overtone and the bound two-phonon state of the  $\nu_2$  mode in liquid and crystalline  $\text{CS}_2$ , respectively, and describe its dynamics and deexcitation channel in terms of a simple effective Hamiltonian.

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Vibrational overtones and multiphonon states are related to important processes in dense molecular systems<sup>1,2</sup>; our main source of information has been the conventional infrared and Raman spectroscopy.

The purpose of this Letter is to show that nonlinear optical techniques can be extended to the selective studies of spectral and dynamical properties of vibrational overtones and multiphonon states and can be used to elucidate<sup>3</sup> previously inaccessible features of vibrational motion in condensed molecular systems and crystals in particular. In contrast to conventional spectroscopy, nonlinear techniques, and especially coherent excitation, also allow the creation of multiphonon and large-wave-vector phonon states in an off-equilibrium configuration.

From a microscopic viewpoint, the spectrum of a given mode in the overtone region arises<sup>4,5</sup> from the simultaneous excitation of the intramolecular vibration on pairs of interacting molecules (*cooperative states*) which is delocalized and distributed over a wide spectral range, as well as from the anharmonicity within a single molecule (*local states*) which carries an oscillator strength localized on individual molecules and is restricted to a narrow spectral band. The overall form of the spectrum depends<sup>6-10</sup> strongly on the relative magnitude of the strength of the anharmonicity,  $\Gamma$ , and the intermolecular coupling,  $W$ .

Thus in the infrared or Raman spectrum of crystals one observes<sup>2</sup> a quasicontinuum of two-phonon states formed from one-phonon branches  $\sigma'$  and  $\sigma''$  with wave vectors  $\vec{k}'$  and  $\vec{k}''$ , respectively, characterized by a total wave vector  $\vec{q} = \vec{k}' + \vec{k}'' \approx 0$  and an energy  $\hbar\Omega = \hbar[\omega_{\sigma'}(\vec{k}') + \omega_{\sigma''}(\vec{k}'')]$ , where  $\vec{k}' (\approx -\vec{k}'')$  varies over the entire Brillouin zone. If the anharmonic potential  $\Gamma$  is sufficiently large (comparable to or larger than the phonon branch width which reflects the intermolecular coupling  $W$ ), a localized excitation, the *bound two-phonon*

*state*,<sup>6</sup> may split off from the quasicontinuum, giving rise to a spectral feature with narrow linewidth and drastically different dynamical behavior. In ionic or covalent crystals, the forces between unit cells are as strong as inside them and  $\Gamma/W$  is small. In molecular crystals, however, the intermolecular, van der Waals type, forces are much weaker than the intramolecular ones and bound two-phonon states or large amplitude local states may appear.<sup>7,8</sup> Because of their relatively narrow linewidth and different dynamical behavior these local states can be coherently driven with high coupling efficiency by laser excitation and their subsequent time evolution and decay process observed.

For simplicity, we restrict our discussion to the first overtone (harmonic) of a Raman-inactive mode, i.e., the  $\nu_2$  mode of  $\text{CS}_2$ . Since both the overtone and the bound two-phonon state arise from vibrational motion essentially localized on individual molecules, we may momentarily neglect the distinction between a liquid and a solid and consider the coupling of the vibration with the light fields in the coherent excitation stage through

$$W = -\frac{1}{2}\bar{\alpha}\bar{E}^2, \quad (1)$$

where  $\bar{\alpha}$  is the molecular polarizability,  $\bar{E} = \bar{E}_1 \times \cos(\omega_1 t) + \bar{E}_2 \cos(\omega_2 t)$ , and  $\omega_1 - \omega_2 \sim \Omega_0$ , the overtone frequency. At this level of approximation the polarizability tensor  $\alpha$  is only modulated by the local vibrational motion and may be expanded in a power series of the local vibrational coordinate  $q_\sigma$ :

$$\alpha = \alpha_0 + (\partial\alpha/\partial q_\sigma)q_\sigma + \frac{1}{2}(\partial^2\alpha/\partial q_\sigma^2)q_\sigma q_\sigma, \quad (2)$$

where  $\alpha_\sigma^{(1)} = \partial\alpha/\partial q_\sigma$  and  $\alpha_\sigma^{(2)} = \partial^2\alpha/\partial q_\sigma^2$  are the first- and second-order Raman scattering tensors, respectively. As the  $\nu_2$  mode of  $\text{CS}_2$  is Raman inactive,  $\alpha_\sigma^{(1)} = 0$ , and the dynamics enter the calculation through the expectation value of the overtone coordinate  $Q_{\sigma\sigma} = q_\sigma q_\sigma$ ,

$$\langle Q_{\sigma\sigma} \rangle = \text{Tr} \rho_v q_\sigma q_\sigma, \quad (3)$$

where  $\rho_\nu$  is the density-matrix operator in the subspace of the overtone transition, which is spanned by the ground ( $\nu=0$ ) and the local vibrational overtone ( $\nu=2$ ), both in the ground electronic state. On the other hand, the cooperative states will serve as a reservoir of loss of coherence of the bound localized states. Two-level modeling then seems appropriate for the bound states and the evolution of  $\rho_\nu$  is governed by the equation

$$d\rho_\nu/dt = (1/i\hbar)[h_e'', \rho_\nu] + d\rho_\nu/dt|_R, \quad (4)$$

with  $h_e'' = h_0 + h_{\sigma\sigma}''$ , where  $h_0$  refers to the vibrationally undisturbed system and  $h_{\sigma\sigma}''$  is an effective interaction Hamiltonian

$$h_{\sigma\sigma}'' = -\frac{1}{4}\alpha_{\sigma\sigma}^{(2)}Q_{\sigma\sigma}E^2 \quad (5)$$

obtained with the help of (1) and (2). This set of equations completely describes the coherent excitation stage.

The expectation value (3) modulates the polarization set up by  $E$  and in the probing stage the electromagnetic field of frequency  $\omega_p$  is scattered off the vibrational overtone shifted in frequency by the overtone frequency,  $\omega_S = \omega_p - \Omega_0$  and  $\omega_A = \omega_p + \Omega_0$ , the Stokes and anti-Stokes frequencies, respectively. The nonlinear polarization source term can be written

$$P_{NL}' = \frac{1}{2}N\alpha_{\sigma\sigma}^{(2)}\langle Q_{\sigma\sigma} \rangle E' + P_E', \quad (6)$$

where  $N$  is the number density of the molecules,  $E' = E_p' \cos(\omega_p t) + E_S' \cos(\omega_S t) + E_A' \cos(\omega_A t)$ , and  $P_E'$  is the nonresonant contribution, mainly electronic. Inserting (6) in the nonlinear propagation equation<sup>11</sup> and neglecting the nonresonant contributions  $P_E'$  which are weak in the present case, we can readily calculate the coherent scattering  $S(t_D)$  from a delayed probe pulse,  $\omega_p$ , at the anti-Stokes frequency  $\omega_A = \omega_p + \Omega_0$ , in exact analogy with one-vibron processes.<sup>11</sup>

We have performed the first demonstration of time-resolved picosecond coherent anti-Stokes higher-order scattering on the  $2\nu_2$  overtone at  $795 \text{ cm}^{-1}$  in liquid  $\text{CS}_2$  and the corresponding bound two-phonon state at  $801 \text{ cm}^{-1}$  in crystalline  $\text{CS}_2$ . From available spectra<sup>12-14</sup> in the fundamental and overtone region it can be inferred that the small anharmonic shift of  $2\nu_2$  is less than the two-vibron quasicontinuum width indicating that local and cooperative states are almost degenerate.

Coherent excitation of the Raman-active  $2\nu_2$  mode of the  $\text{CS}_2$  molecule is achieved by two time-coincident optical pulses of frequencies  $\omega_L$  and  $\omega_S$  such that  $\omega_L - \omega_S = \Omega_0$ , the overtone frequency.

The time evolution of the coherent excitation of the system is followed by coherent anti-Stokes scattering of a third probing pulse delayed with respect to the excitation by a time delay  $t_D$ .

The experimental system shown in Fig. 1 is driven by a single 5-ps, 5-mJ laser pulse at  $1054 \mu\text{m}$ . Two beam splitters direct infrared energy into frequency doublers to provide the pump ( $\omega_L$ ) and probe ( $\omega_p$ ) pulses. A tunable source ( $\omega_S$ ) is obtained by amplification in a dye amplifier (pumped by an intense green pulse) of a small frequency band, selected by a Fabry-Perot filter, of the self-phase-modulation continuum generated by focusing an infrared beam into a water cell. A non-collinear  $k$ -matching geometry is used and probe polarization is crossed with the other two pulses, which allows spatial and polarization selective noise rejection. The anti-Stokes signal at  $\Omega_0 + \omega_p$  generated in the 2-mm cooled  $\text{CS}_2$  sample is detected by a photomultiplier in a 3-Å pass band. The temporal response of the system is obtained by non-resonant time-resolved coherent anti-Stokes Raman scattering in a 2-mm sample of  $\text{CH}_3\text{I}$ .

The experimental results for the  $2\nu_2$  overtone in the liquid ( $T=165 \text{ K}$ ) and crystalline ( $T=160 \text{ K}$ ) phases are shown in Figs. 2 and 3, respectively, where the coherent anti-Stokes signal is plotted on a logarithmic scale versus probe delay  $t_D$  in picoseconds. In the liquid, the experimental points (squares) are clearly distinguished from the system response function (dashed line) and follow an exponential decay curve over three orders of magnitude, yielding  $T_2 = 1.8 \pm 0.15 \text{ ps}$  at 165 K. Exponential decay is also observed in the crystalline phase but with a dramatic increase of the relaxation time to  $T_2 = 14 \pm 3 \text{ ps}$ ; the latter is also longer than

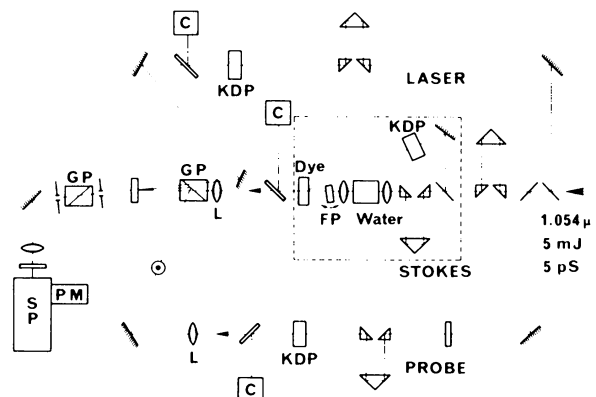


FIG. 1. Experimental setup: KDP, frequency doubler; C, photodiode; FP, Fabry-Perot filter; GP, polarizer; SP, monochromator.

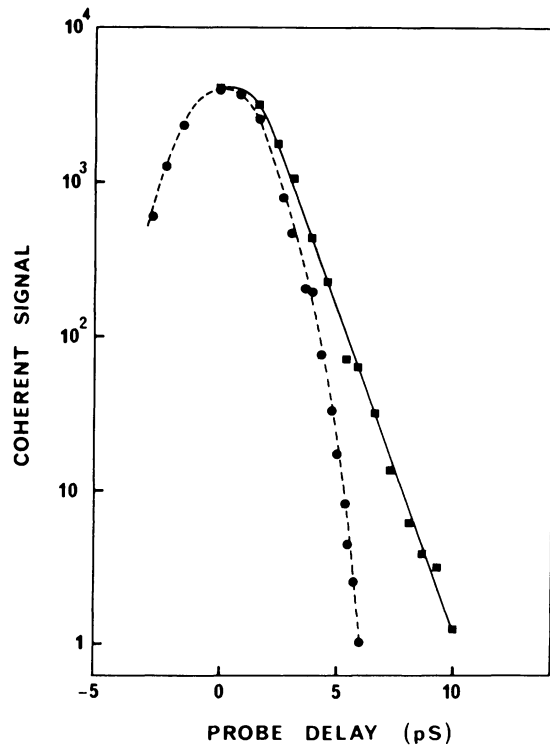


FIG. 2. Coherent signal vs probe delay for  $2\nu_2$  of  $\text{CS}_2$  liquid at 165 K (full line). The dashed line is the system response function.

the lifetime expected if independent free phonon states only are involved in the two-phonon state, which reflects the localized character of this state. The exponential behavior can be understood as follows.

In crystalline solids where the periodicity allows all movement, vibrational, translational, and orientational, to be treated quantum mechanically in terms of the delocalized phonon modes, the basic assumption<sup>3,15</sup> is that the coupling and overlap of the local (or bound) two-phonon states and the delocalized free two-phonon states mediated through an effective anharmonic Hamiltonian  $h_A' = \Gamma q_\sigma q_\sigma Q_{\sigma\sigma}$  is the primary mechanism of loss of coherence within the two-vibron subspace. Stated otherwise, the localized state finds itself mixed with free two-phonon states whose energies lie nearby and eventually disintegrates. The strength of the anharmonic interaction determines the width of the energy interval in which the mixing process occurs and therefore the degree of coherence and the lifetime of the localized state. With the use of Green's functions<sup>7,8</sup> it is shown<sup>3,15</sup> that the loss of coherence evolves exponentially in time with a time  $T_B \sim 1/\nu_0$ , where  $\nu_0$  is the density of the free two-phonon states calculated where the overlap with the

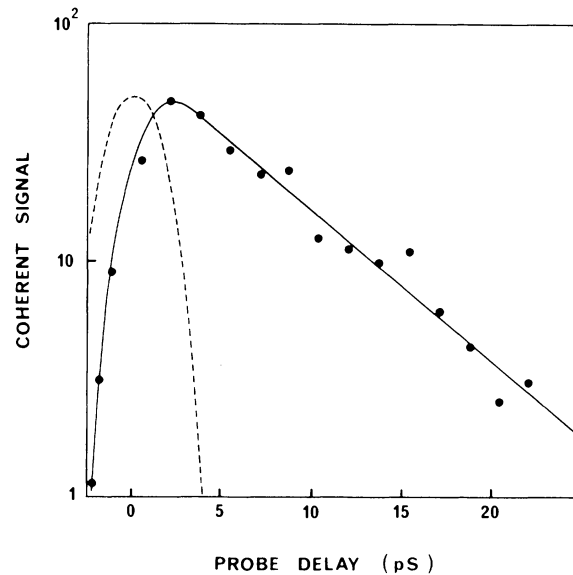


FIG. 3. Coherent response of the two-phonon bound state in solid  $\text{CS}_2$  at 160 K (full line). The dashed line is the system response.

bound state is maximal.

When this result is inserted in (4) the equation of motion of the expectation value of  $Q_{\sigma\sigma}$  can be set in the form

$$\begin{aligned} \frac{\partial^2}{\partial t^2} \langle Q_{\sigma\sigma} \rangle + \frac{2}{T_B} \frac{\partial}{\partial t} \langle Q_{\sigma\sigma} \rangle + \Omega_0^2 \langle Q_{\sigma\sigma} \rangle \\ = \frac{1}{m} F_Q(t) \end{aligned} \quad (7)$$

where  $F_Q(t)$  is the Raman force driving the coordinate  $Q$ , or with use of (5),

$$F_Q = -\nabla_a h_{\sigma\sigma}'' = \frac{1}{2} \alpha_{\sigma\sigma}^{(2)} E^2, \quad (8)$$

where  $E = E_L \cos(\omega_L t) + E_S \cos(\omega_S t)$ . Thus the expectation value behaves as the amplitude of a classical oscillator. Furthermore Eq. (7) indicates that this amplitude decays exponentially after the excitation stage has terminated and this will be reflected in the dependence of  $S(t_D)$ . Our experimental results confirm this behavior with  $T_2 = T_B$ .

In the liquid a major complication arises from the interplay of quantum and classical (stochastic) motions and the lack of long-range order. Indeed the stochastic nature of the liquid leads us to expect<sup>15</sup> additional line-broadening mechanisms which are due to random fluctuations of the environment of the oscillator, and which make intuitively plausible the observation of a shorter overtone lifetime in the liquid.

The fact stated above that in crystals  $T_2 \sim 1/\nu_0$

allows us to predict that the coherence lifetime of the bound two-phonon state should be very sensitive to structural phase transitions since in this situation the joint two-phonon density of states changes dramatically for large-wave-vector phonons at the edge of the Brillouin zone. The predicted  $T_B$  is also very sensitive to the anharmonic coupling parameter. Another important feature to notice in the crystalline phase is that the two-phonon states into which the bound two-phonon state decays and transfers its coherence may under certain conditions retain this coherence long enough to engender parametric instabilities. These points are presently under investigation in our laboratory.

In conclusion we have shown that the coherent excitation of overtone and two-phonon states is an efficient process and allows time-resolved studies of these states. In the case of the crystal one can have access to a large density of two-phonon states by coherently driving the bound two-phonon state which then transfers its coherence to the free two-phonon state.

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