

Time-Resolved Nonlinear Spectroscopy of a Fermi Doublet: The $\{\nu_1, 2\nu_2\}$ Fermi Resonance in CO₂ Solid

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It is shown that the intramolecular Fermi doublet $\{\nu_1, 2\nu_2\}$ in crystalline CO₂ arising from resonant anharmonic coupling between a single-phonon state and a quasibound two-phonon state can be coherently driven and its dynamics determined by time-resolved nonlinear optical techniques. Coherence relaxation times for both components of the doublet are measured between 9 K and the fusion point (217 K). A mechanism for loss of coherence is proposed which involves modulation by low-lying intermolecular modes.

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Anharmonic phonon processes can have a profound influence on the spectrum of vibrational motion in condensed matter. A striking example is the bound two-phonon state which splits off the two-phonon continuum and frequently exhibits a nonnegligible infrared or Raman oscillator strength. This last feature was recently exploited^{1,2} to coherently drive these states and follow their subsequent evolution with time-resolved nonlinear optical techniques.

In this Letter we extend and apply these techniques to a quite different manifestation of phonon-phonon interactions which has an important influence on both one- and two-phonon states. It arises from hybridization of nearly degenerate single-phonon and quasibound (or bound) two-phonon states³⁻⁶ mediated by their coupling via the third-order term $H^{(3)}$ in the usual series expansion⁷ of the lattice Hamiltonian,

$$H = H_{\text{harm}} + H^{(3)} + H^{(4)} \quad (1)$$

while the fourth-order term forms the quasibound two-phonon state on top of the two-phonon continuum. This causes a transfer of infrared or Raman oscillator strength from the strong one-phonon line to the weaker quasibound two-phonon transition and results in a double peak in the vibrational spectrum whose two components split off on either side of the two-phonon continuum. At a molecular level this effect bears the joint signature of a *Fermi resonance*⁸ and a *Fano interference* and is particularly favored in molecular crystals,^{6,9,10} the CO₂ crystal offering the classic example.

It is shown here that both components of such a Raman-active doublet can be coherently driven and their dynamics investigated with time-resolved nonlinear optical pump and probe techniques, as the two hybrid states share properties of both parent states, in particular, the strong Raman line strength of the single-phonon state and its intramolecular (local) character.

The experimental demonstration reported here concerns crystalline CO₂ where Fermi resonance occurs between the symmetric Raman-active stretching mode

ν_1 and the first overtone $2\nu_2$ of the doubly degenerate infrared-active bending mode, as the overtone frequency Ω_2 falls very close to the unperturbed ω_1 fundamental frequency. These modes and their mutual interaction result from intramolecular motion, well localized on individual molecules, so that disregarding all other modes the relevant states are as follows: $|00\rangle$, the ground state; $|10\rangle$, the first excited state of mode 1; and $|02\rangle$, the quasibound two-phonon state or overtone mode 2. We denote by q_1 and $Q_{22} = q_2^2$ the vibrational coordinates of mode 1 and overtone mode 2, and by ω_1 and Ω_2 their transition frequencies, respectively. These two states interact through the third-order anharmonic term $h_{12} = \beta_{122} q_1 q_2^2 = \beta_{122} \times q_1 Q_{22}$ whose only nonvanishing matrix element is $\hbar\beta = \langle 10 | h_{12} | 02 \rangle$.

Coupling of the vibrations q_1 and Q_{22} with the total light field $E = E_L \cos(\omega_L t) + E_S \cos(\omega_S t)$, with $\omega_L - \omega_S$ supposed near resonance, is mediated by the first-order Raman tensor of mode 1, $\alpha_1^{(1)}$ and the second-order Raman tensor of mode 2, $\alpha_2^{(2)}$, through $h' = -\frac{1}{2}\alpha E^2$ with $\alpha = \alpha_0 + \alpha_1^{(1)} + \frac{1}{2}\alpha_2^{(2)} q_2^2$.

The evolution of the system is described by the equation of motion of the density matrix operator:

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} [h_0 + h_{12} + h', \rho] + \left. \frac{\partial \rho}{\partial t} \right|_R \quad (2)$$

As a consequence of (2) the coordinates q_1 and Q_{22} build up amplitudes

$$\langle q_1 \rangle = \text{Tr} \rho q_1 = \langle 00 | q_1 | 10 \rangle (\rho_{01} + \rho_{10}),$$

$$\langle Q_{22} \rangle = \text{Tr} \rho Q_{22} = \langle 00 | Q_{22} | 02 \rangle (\rho_{02} + \rho_{20})$$

where the relevant matrix elements of ρ satisfy

$$i\rho_{01} = -\omega_1 \rho_{01} - \beta \rho_{02} - \alpha_1 E^2 - i\rho_{01} \gamma_1,$$

$$i\rho_{02} = -\Omega_2 \rho_{02} - \beta \rho_{01} - \alpha_2 E^2 - i\rho_{02} \gamma_2$$

and their Hermitian conjugates, where γ_1 and γ_2 are phenomenological damping factors for ρ_{01} and ρ_{02} , respectively, and $\alpha_n = \alpha_n^{(n)} \langle 0 | q_n^n | n \rangle / n$ ($n = 1, 2$).

The observable hybrid mode frequencies Ω_+ and

Ω_- and amplitudes Q_+ and Q_- , respectively, are obtained by a unitary (rotational) transformation u defined by

$$\begin{pmatrix} Q_+ \\ Q_- \end{pmatrix} = u \begin{pmatrix} \langle q_1 \rangle \\ \langle Q_{22} \rangle \end{pmatrix} \equiv \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \langle q_1 \rangle \\ \langle Q_{22} \rangle \end{pmatrix} \quad (3)$$

which is equivalent to a rotation by an angle θ such that

$$u \begin{pmatrix} \omega_1 & \beta \\ \beta & \Omega_2 \end{pmatrix} u^{-1} = \begin{pmatrix} \Omega_+ & 0 \\ 0 & \Omega_- \end{pmatrix}$$

or $(\Omega_2 - \Omega_1)\sin 2\theta + 2\beta \cos 2\theta = 0$ so that Q_+ and Q_- satisfy

$$\begin{aligned} Q_+ + \Gamma_+ Q_+ - \Gamma' Q_- + \Omega_+^2 Q_+ &= A_1 E^2, \\ Q_- + \Gamma_- Q_- - \Gamma' Q_+ + \Omega_-^2 Q_- &= A_2 E^2 \end{aligned} \quad (4)$$

which equations are coupled by Γ' and,

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = u \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}; \quad \begin{pmatrix} \Gamma_+ & \Gamma' \\ \Gamma' & \Gamma_- \end{pmatrix} = u \begin{pmatrix} \gamma_1 & 0 \\ 0 & \gamma_2 \end{pmatrix} u^{-1}. \quad (5)$$

The frequencies Ω_+ and Ω_- are the same as those obtained by Green's-functions methods^{3,5,9} when the phonon-branch width is small, a common situation for optical modes in the molecular crystals under consideration here.

The coupled equations (4) provide an intuitively simple picture of the coherent excitation of the two hybrid modes. Their coupling is provided by dissipative terms with $2\Gamma' = (\gamma_1 - \gamma_2)\sin 2\theta$. In the frequency domain solutions of (4) are approximately those of harmonic oscillators¹⁰⁻¹² with frequency-dependent damping. The amplitudes Q_+ and Q_- can be probed

with a field E' at frequency ω_p to yield anti-Stokes signals at $\omega_A^+ = \omega_p + \Omega_+$ and $\omega_A^- = \omega_p + \Omega_-$ through the nonlinear polarization term $P_{NL} = N(A_+ Q_+ + A_- Q_-)E' + P_{nr}$ in exact analogy with one-vibron processes.

We have performed the first demonstration of such time-resolved picosecond coherent anti-Stokes scattering on the $\{\tilde{\nu}_+, \tilde{\nu}_-\}$ Fermi doublet of crystalline CO_2 which arises from anharmonic coupling of the nearly degenerate ν_1 and $2\nu_2$ states^{8,13,14} leading to hybrid frequencies $\tilde{\nu}_+ = 1383 \text{ cm}^{-1}$ and $\tilde{\nu}_- = 1276 \text{ cm}^{-1}$ bracketing the two-phonon continuum. The CO_2 crystals, which were grown by a seeding technique in a specially adapted cryostat, were of sufficiently high quality to allow cooling down to at least 77 K without severe optical degradation of the sample.

The experimental system shown in Fig. 1 is driven by a single 5-ps pulse produced by a cavity-dumped, passively mode-locked Nd^{3+} -doped phosphate-glass oscillator and subsequently amplified to a 2-GW power level and doubled in frequency to 527 nm. This green beam is then split into three parts, the first of which is rotated in polarization by 90° and serves as a probe of the vibrational overtone coherence. The other two parts pump two Raman generators, Stokes 1 and Stokes 2, employing deuterated methanol and water, respectively, to provide a suitable frequency difference, $\omega_{S1} - \omega_{S2}$ with ω_{S2} broad band, for excitation of the relevant CO_2 vibrations Ω_- and Ω_+ . This method has the advantage of pushing excitation-related noise into the red and allowing additional frequency-selective noise discrimination, especially important for cryostat work.

Figure 2 shows the experimental results for the Ω_+ line of CO_2 solid at 215 K. The dynamic measurement

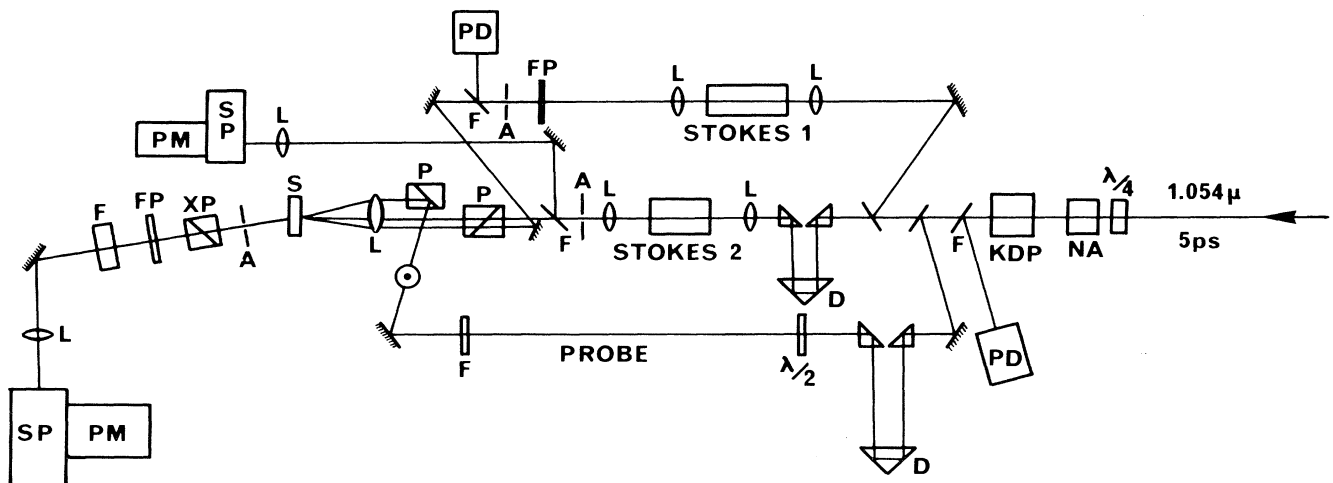


FIG. 1. Experimental setup: $\lambda/4$, quarter-wave plate; NA, nonlinear absorber; KDP (potassium dihydrogen phosphate), frequency doubler; F, filter; PD, photodiode; D, delay line; L, lens; FP, Fabry-Perot; A, aperture; $\lambda/2$, half-wave plate; P, Glan polarizer; S, cooled sample; XP, crossed polarizer; SP, monochromator; and PM, photomultiplier.

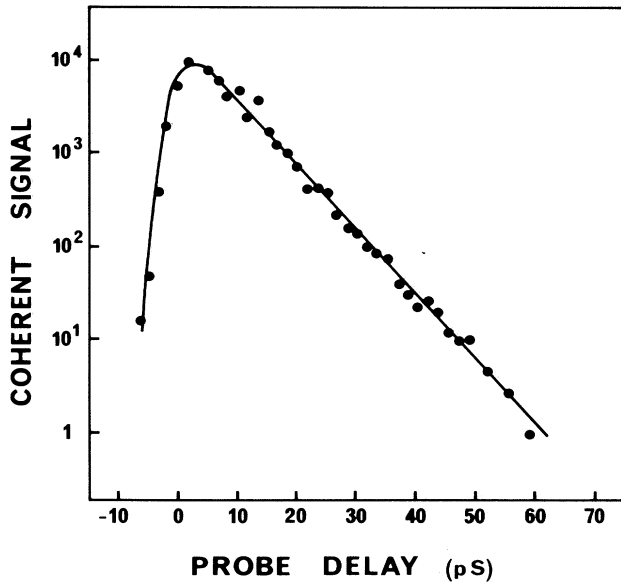


FIG. 2. Coherent anti-Stokes signal plotted on a logarithmic scale vs probe delay in picoseconds, for the Ω_+ component of the Fermi doublet in CO_2 solid at 215 K.

range of 10^4 for an *in situ* grown cryogenic solid is noteworthy, and the observed exponential decay of the vibrational coherence yields $\Gamma_+^{-1} = T_2^+ = 12.5$ ps. Exponential decay is maintained for both components Ω_+ and Ω_- over the whole temperature range considered from 9 to 245 K where CO_2 is liquid ($T_M = 217$ K).

Figure 3 depicts the temperature dependence of Γ_+ and Γ_- for the components Ω_+ and Ω_- of the Fermi doublet up to and across the solid/liquid phase transition, where we plot the observed decay rate $2\Gamma_{\pm}$ as a function of temperature. Both lines exhibit a strong temperature variation of more than a factor of 2. Another striking feature to remark is that the Γ_+ and Γ_- curves appear parallel and exhibit two regimes.

At low temperatures the loss of coherence of these coupled modes may occur through their mixing with the free two-phonon continuum states^{1,2} or isotope-induced disorder, but at higher temperatures a new mechanism becomes dominant; that is, the time fluctuations of the transition frequencies of the intramolecular modes ω_1 and Ω_2 , or equivalently Ω_+ and Ω_- , as a result of the intermolecular degrees of freedom of the lattice. The CO_2 crystal belongs to the space group T_h^6 with four molecules in the unit cell on S_6 sites and there is a large number of low-frequency modes representing the rotational, librational, and translational intermolecular motions. As the reduced Hamiltonian actually depends on the relative configurations of the molecules in a unit cell it can be written to a good approximation $h(q_1, Q_{22}, Q_i)$, where we explicitly introduce the functional dependence on the

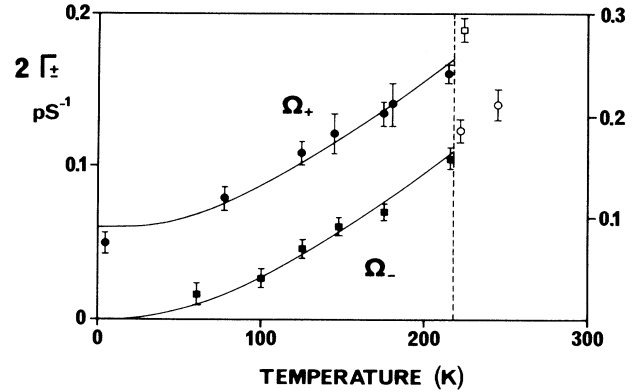


FIG. 3. Variation of the measured relaxation rates $2\Gamma_+$ and $2\Gamma_-$ with temperature for the Ω_+ line (full circles, solid; open circles, liquid) and Ω_- line (full squares, solid; open square, liquid) of the Fermi doublet in CO_2 , respectively. The dashed line indicates the phase transition. Note the scale change between solid and liquid. The solid lines are theoretical curves calculated using $\Gamma_{\pm} = k_{\pm} + kn(n+1)$ where n is the Bose factor for a low-frequency phonon ($< 100 \text{ cm}^{-1}$) and k_{\pm} represent the temperature independent residues (see text).

amplitudes Q_i of these intermolecular modes. This produces a parametric dependence on Q_i of the intramolecular frequencies ω_1 and Ω_2 which become time dependent, since the Q_i are dynamical variables. Taking into account the symmetry of the crystal and the fact that ω_1 and Ω_2 were calculated at the equilibrium configuration of the intermolecular positions we may set $\omega_1(Q_i) = \omega_1 + \delta\omega_1(Q_i)$ where to lowest order $\delta\omega = \sum k_{ij} Q_i Q_j$ and similarly for Ω_2 . Assuming Markovian processes one finds

$$\gamma_1 = \int_{-\infty}^{\infty} \langle \delta\omega(\tau) \delta\omega(0) \rangle d\tau \sim \sum_{ij} n_i (n_j + 1) |k_{ij}|^2, \quad (6)$$

where n_i is the phonon occupation number for intermolecular mode i at a temperature T and the modes i and j are such that $\Omega_i - \Omega_j \approx 0$. Thus uniquely energy-conserving mechanisms are involved and the above expressions only describe pure dephasing of the states. The predicted temperature variation is very insensitive to the frequency of the intermolecular modes involved in (6) and a single-parameter fit, the same for both curves, explains well the observed Γ_+ and Γ_- results and in particular the long coherence times at low temperatures. Clearly for very low temperatures additional mechanisms must be taken into account providing a temperature-independent residue.

In conclusion, we have shown for the first time that anharmonically coupled single-phonon and quasibound two-phonon states can be coherently driven with high efficiency and their dynamics selectively studied in the time domain using nonlinear optical techniques. This

also provides a flexible method for creating phonon pairs as the coupling can be modified by temperature, frequency, pressure, or other physical variables and a wide range of conditions in the parametric interaction of phonons can be accessed, and polariton effects⁴ should also be observable. Furthermore, the above considerations are not limited solely to intramolecular vibrations¹⁵ but should apply equally to acoustic phonons.

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