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COHERENT EXCITATION AND EVOLUTION OF TWO-PHONON STATES IN MOLECULAR CRYSTALS

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Abstract - Picosecond coherent excitation and probing techniques are employed to measure the temperature dependence of the dephasing times \( T_2 \) of the very weak \( 2\nu_2 \) two-vibron bound states in solid nitrous oxide and of the composite \( \{\nu_2 + \nu_4\} \) bound state in crystalline ammonium chloride. These results highlight the importance of the strength of Fermi resonance on two-phonon dynamics in crystals.

The recent demonstration of coherent excitation of two-phonon states in molecular crystals [1-4] offers some attractive possibilities to selectively study and exploit anharmonic interactions in crystals. Although optical transitions to these states as a general rule are much weaker than to one-phonon states their number is much larger: indeed optically accessible two-phonon states are formed by pairing phonons with opposite wave vectors all over the Brillouin zone in contrast to the one-phonon states that are restricted in the center of the Brillouin zone. Even so these two-phonon states as a general rule form a continuum over an energy range \( 2W \) where \( W \) is the phonon branch width and their coherent excitation is in general not feasible. However under certain conditions the anharmonic terms of the third and fourth order, \( h^{(3)} \) and \( h^{(4)} \) respectively, in the usual expansion of the lattice hamiltonian [5-6]

\[
h = h^{(0)} + h^{(3)} + h^{(4)}
\]

cause a spectral condensation into narrow regions [7] leaving behind a residual weaker continuum of the free two-phonon states. Because of their relatively narrow line-width and nonnegligible oscillator strength these local states can be coherently driven with high efficiency [2-3] and their subsequent evolution and decay process observed. Below, we review briefly the main results obtained with the CAHORS technique and present some more recent ones in \( N_2 O \) and \( NH_4Cl \).

The above mentioned spectral condensation occurs as a consequence of a subtle interplay of the intermolecular and intramolecular forces. Thus if the strength \( \Gamma \) of the fourth order term \( h^{(4)} \) which is mainly intramolecular is larger than the phonon branch width \( W \) a bound two-phonon state splits off the continuum. If a one-phonon state couples with the two-phonon continuum and is nearly degenerate with such a bound or quasibound two-phonon state then a "Fermi doublet" appears [7] with its two components on either side of a much weaker residual continuum of free two-phonon states [8,9,10].

In the CAHORS technique these "local" states are coherently driven by two time coincident picosecond pulses of frequencies \( \omega_L \) and \( \omega_S \) respectively with \( \omega_L -\omega_S = \Omega_o \),

\[
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\]
the "local" compound phonon frequency, and the coherence evolution of this state is followed by delayed antistokes scattering at \( \omega + \Omega \) of a probe pulse at frequency \( \omega_p \). The experimental setup is described elsewhere [3]; the high sensitivity of our experimental system which allows a dynamic measurement range of \( 10^3 \) for a strong Raman scatterer, means that previously inaccessible weak Raman features may now be studied and that the coherent exclusion of narrow Raman lines in a cluttered region of the spectrum may be isolated.

The description of this technique is most conveniently presented in terms of the optically accessible two-phonon coordinate

\[
\langle q_+ q_- \rangle = \text{Tr} \rho q_+ q_-
\]

where \( q_+ \) and \( q_- \) are the simple phonon coordinates with wavevector \( k \) and \(-k\) respectively and \( \rho \) is the density matrix operator in the optically accessible two-phonon state space. The definitions and properties of this coordinate are given elsewhere [11].

We present below a simple description of the dynamics of the two-phonon states and for simplicity we limit ourselves to the dynamics of the \( 2v_2 \) state coupled with the \( v_1 \) state in a crystal with triatomic molecules (\( \text{CS}_2 \), \( \text{CO}_2 \),...); this situation actually is quite general and encompasses many other cases with minor changes. In order to include Fermi resonances we assume that the \( v_1 \) single phonon state (state, \( |10> \), coordinate \( q_1 \) and frequency \( \omega_1 \)) and the \( 2v_2 \) bi-phonon or resonance (state \( |02> \), coordinate \( q_{22} = q_2^2 \) and frequency \( \Omega_2 \)) interact through the third order anharmonic term

\[
h_{122} = \delta_{122} q_1 q_2^2
\]

where only non vanishing matrix element is \( h_{12} = \langle 10 | h_{12} | 02 \rangle \); the main effect of the fourth order term \( h_{4} = \gamma q_4^4 \) is taken into account in the formation of the bound or quasibound two-phonon state but a residual term is still left which can couple the biphonon with the parent free two-phonon states or the low lying intermolecular modes.

The coupling of the above states with the total field \( E = E_L \cos(\omega_L t) + E_S \cos(\omega_S t) \) in a Raman excitation process, with \( \omega_L - \omega_S \) near resonance, is mediated by the first order Raman tensor of mode \( 1 \), \( \alpha_1(1) \) and the second order Raman tensor of order 2 \( \alpha_2^2 \), through \( h' = -\frac{1}{2} \alpha E^2 \) with \( \alpha = \alpha_0 + \frac{1}{2} \alpha_1(2) \). The anharmonic interaction between \( \omega_1 \) and \( \Omega_2 \) leads to mixing of the wavefunctions and the production of two new states [3] whose frequencies \( \Omega_+ \) and \( \Omega_- \) are given, for small \( \Omega_2 \) phonon branch width by a unitary transformation \( u \),

\[
\begin{bmatrix}
\Omega_+ \\
\Omega_-
\end{bmatrix} = u \begin{bmatrix}
\omega_1 & \beta \\
\delta & \Omega_2
\end{bmatrix} u^{-1}
\]

with

\[
u = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{bmatrix}
\]

and \( \theta = \frac{1}{2} \tan^{-1}(2\delta \alpha \omega_1 - \Omega_2) \). The coherent amplitudes \( \Omega_+ \) and \( \Omega_- \) at \( \Omega_+ \) and \( \Omega_- \) are driven by Raman interactions \( A_+ E^2 \) and \( A_- E^2 \) respectively according to the equations

\[
\begin{align*}
\ddot{\Omega}_+ + \Gamma_+ \dot{\Omega}_+ - \Gamma' \dot{\Omega}_- + \Omega_+^2 \Omega_+ &= A_+ E^2 \\
\ddot{\Omega}_- + \Gamma_- \dot{\Omega}_- - \Gamma' \dot{\Omega}_+ + \Omega_-^2 \Omega_- &= A_- E^2
\end{align*}
\]

with the transformed Raman tensors defined by

\[
\begin{bmatrix}
A_+ \\
A_-
\end{bmatrix} = u \begin{bmatrix}
\alpha_1 \\
\alpha_2
\end{bmatrix}
\]

where \( \alpha_n = \langle \alpha_n | q_n \rangle / n \) and
and \( \gamma_1 \) and \( \gamma_2 \) are the damping of the undressed mode amplitudes \( q_1 \) and \( q_2 \) respectively. Clearly for \( \beta/(\Omega_2 - \omega_1) \ll 1 \) equation (1b) reduces to

\[
\begin{bmatrix}
\gamma_1 \alpha' \\
\gamma_2 \alpha'
\end{bmatrix} = u \begin{bmatrix}
\gamma_1^0 \\
0
\end{bmatrix} u^{-1}
\]

the equation also derived in (1).

The solution in time domain of the two equations (1a-b) is fairly complex but some insight can be gained by their solution in frequency domain. Thus keeping only the term \( E^2 \) which is near resonance with \( \Omega_+ \) and \( \Omega_- \) one gets

\[
Q_+ = \frac{\frac{i\Gamma_A (\omega_L - \omega_S)}{\Omega_+^2 - (\omega_L - \omega_S)^2 - i\Gamma_+ (\omega_L - \omega_S)} E_L E_S}{[\Omega_+^2 - (\omega_L - \omega_S)^2 - i\Gamma_+ (\omega_L - \omega_S)] + (\omega_L - \omega_S)^2 \Gamma_{+2}/\Omega^2_{+} - (\omega_L - \omega_S)^2 - i\Gamma_+ (\omega_L - \omega_S)}
\]

and similarly for \( Q_- \). For \( \beta/(\Omega_2 - \omega_1) \ll 1 \), (2) reduces to

\[
Q = Q_0 = \frac{1}{4} \alpha'' E_L E_S \frac{\Omega_0^2 - (\omega_L - \omega_S)^2 - i\Gamma_0 (\omega_L - \omega_S)}{\Omega_0^2 - (\omega_L - \omega_S)^2 - i\Gamma_0 (\omega_L - \omega_S)}
\]

which is the solution of an harmonic oscillator with constant damping. To a certain extent expression (2) is similar to (3) with an effective damping constant that may strongly depend on frequency. In particular one mode may grow as a consequence of the driving of the other mode. Note that for \( \gamma_1 = \gamma_2 \) one has \( \Gamma_+ = \Gamma_- \) and \( \Gamma' = 0 \) and the modes amplitudes are completely decoupled harmonic oscillators.

For large coupling \( \beta/\omega_1 - \Omega_2 \gg 1 \) the \( \omega_1 \) and \( \Omega_2 \) states are almost completely mixed and displaced in energy by approximately \( \pm \beta \). Both states have comparable Raman strength \( A_+ \sim A_- \sim \alpha_0/\sqrt{2} \) on the order of that of first order transitions. The above situation arises in CO\(_2\), the classic example of strong Fermi resonance.

For weak coupling and considering \( \omega_1 > \Omega_2 \), the one phonon state moves up by \( \beta/(\omega_1 - \Omega_2) \) and the bound state down by the same amount. For the bi-phonon the Raman coupling becomes

\[
A_+ = a_2 - a_1 \beta/(\omega_1 - \Omega_2)
\]

The first term creates two-phonon states directly through the electrical anharmonicity and the second indirectly through mechanical anharmonic coupling between \( \omega_1 \) and \( \Omega_2 \). Notice that these two terms may interfere destructively.

The amplitudes \( Q_+ \) and \( Q_- \) modulate the polarization set up by \( E \) and in the probing stage the electromagnetic field of frequency \( \omega \) is scattered off the vibrational overtone shifted in frequency by the compound state frequency, \( \omega^{\pm} = \omega - \Omega_{\pm} \) and \( \omega^\pm = \omega + \Omega_{\pm} \) the Stokes and antistokes frequencies respectively. The nonlinear polarisation source term may be written

\[
P_{NL} = N (A_+ Q_+ + A_- Q_-) E^4 + P_{nr}
\]

in analogy with one-vibron processes.

We have studied the coherent relaxation of the 2\( \nu_2 \) two-vibron bound state at \( 1165 \text{ cm}^{-1} \) in solid nitrous oxide as a function of temperature from 77 K to 177 K, just below the crystal melting point \( 141 \). As N\(_2\)O is asymmetric (symmetry group \( C_3 \)) and in the crystal (T group) there are 4 molecules per unit cell on \( C_3 \) sites, this mode should be split into two components of A and F symmetry. Because nitrous oxide is an orientationally disordered crystal (with respect to the direction of the
molecule NNO or ONN) there are no rigorous Raman selection rules and both the A and F modes should give coherent signals in our experiment, similarly to the observations in spontaneous Raman spectroscopy for the $v_1$ one-vibron mode [12].

Fig. 1 shows the observed coherent signal (full circles) plotted on a logarithmic scale as a function of probe delay in picoseconds for the $2v_2$ 1165 cm$^{-1}$ mode in solid $N_2O$ at 177 K. Due to the weakness of the coherent diffusion the signal around $t = 0$ is dominated by non-resonant scattering from the cell windows as can be seen from the measurements in an empty cell (open circles - dashed line). After the initial fast rise and fall—in this case essentially limited by the system response—the coherent signal exhibits a pronounced dip, near 10 ps probe delay, followed by a broad maximum and subsequent exponential decay with a $T_2 = 10.9 \pm 0.5$ ps.

This behaviour may be explained in terms of the coherent interference of the A and F symmetry components of this line. We may fit the experimental points using the values $T_2(A) = 4$ ps, $T_2(F) = 10.9$ ps (determined from the long delay slope), $T_2(A) = 10.9$ ps, and the splitting $\Delta v = 1.7$ cm$^{-1}$. Although the calculated curve (full line, Fig. 1) is insensitive to the ratio of the Raman intensities and the exact value of $T_2(A)$ a splitting within 10% of 1.7 cm$^{-1}$ is required to reproduce the observed oscillation. Only a single, essentially destructive, interference beat is seen because of the large difference between the $T_2$ values of the two closely spaced A and F components of the $2v_2$ line.

We have investigated the effect of temperature on $2v_2$ down to 77 K. No significant qualitative change in the shape of the curves is observed and quantitatively, only a small increase, of about 30%, of coherent decay times occurs in the 177-77 K range. No change in the 1.7 cm$^{-1}$ splitting of the 1165 cm$^{-1}$ $2v_2$ doublet could be detected in this temperature range.

We may interpret the $2v_2$ measurement in terms of an intrinsic relaxation mechanism. As $2v_2$ is only in very weak Fermi resonance with $v_1$, exemplified by its very small Raman line strength, its spectral position is not significantly perturbed and the 1165 cm$^{-1}$ $2v_2$ doublet is found only about 10 cm$^{-1}$ below the top of the $v_1 + v_2$ free two-phonon quasi-continuum, into which it may decay. This mechanism leads to a coherent decay time $T_2$ inversely proportional to the density of free two-phonon states and essentially independent of temperature as observed in the present case.
The fact that the A symmetry component always relaxes about three times faster than the F component is indicative of the role of mode symmetry in coherent relaxation processes in solids. We note that a similar result has been observed for the A and F modes of both the $v_3$ and $2v_3$ bands of the $\{v_1, 2v_3\}$ dyad in crystalline CO$_2$, where A$^g$ relaxation is always about 1.6 times more efficient than that of F. Ammonium chloride belongs to the interesting class of crystals which exhibit an order/disorder phase transition. For NH$_4$Cl this transition (at $T = 242.5$ K) is associated with the relative ordering of the NH$_4^+$ ions in the cubic Cl$^-$ cage. Although this crystal is not molecular, the optical vibrations of the NH$_4^+$ ions, like the molecules in a molecular crystal, interact relatively weakly with each other and hence similar considerations to those developed for molecular crystals may be applied. Below $T_A$, in the non-centro-symmetric phase, one observes not only polar two-particle bands but also bound states, enhanced by polariton Fermi resonance with polar internal vibrations of the ammonium ion [14].

We have investigated the temperature dependence of the dephasing time of the $\{v_2 + v_{41}\}$ composite bound state at 3070 cm$^{-1}$ which is in strong Fermi resonance with the $v_3$ one-vibron mode.

Fig. 2 shows the variation of the measured relaxation rate ($2/T_2$) of $\{v_2 + v_{41}\}$ between 20 and 180 K. A strong temperature dependence of more than a factor of 7 is observed in this range, in sharp contrast to the results in N$_2$O solid. Although our interpretation of these very new results is not yet definitive we point out the remarkable similarity between the present observations and those for the $v_3$ line of CO$_2$ solid [3] another example of strong Fermi resonance between one and two-phonon states.

In conclusion we have seen that time resolved coherent techniques may be usefully exploited to measure previously unavailable relaxation times of two-phonon bound states in a wide variety of experimental conditions and crystal structures. The capability of studying bi-phonons directly substantially enriches our potential knowledge of the vibrational dynamics of solids and we anticipate extension to other many-particle states and manifestations of anharmonicity in crystal physics.

![Fig. 2. Measured coherent relaxation rates ($2/T_2$) for the $\{v_2 + v_{41}\}$ composite two-vibron bound state in NH$_4$Cl as a function of temperature for $T < T_A$ (243 K)](image-url)
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