Impurity perturbed domains: Resonant enhancement of bulk mode CARS by coupling to the electronic states of dilute impurities

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A new experimental method for the direct observation of electronic excitation–phonon coupling is presented. The CARS signal from the 69 cm^{-1} optical phonon mode of naphthalene crystals is resonantly enhanced by coupling to the electronic states of dilute pentacene impurities. The resonantly enhanced signal decays over three times faster than the nonresonant decay in the same crystal. This is explained in terms of impurity perturbed domains.

I. INTRODUCTION

A molecule in a condensed matter system at finite temperatures experiences a wide variety of dynamical interactions with its environment. In general, the mechanical degrees of freedom of the host medium (crystal, glass, liquid, or protein)[1-4] will couple to the electronic states of the molecule of interest. The time dependent fluctuations of this heat bath (host medium) strongly influence or dominate processes such as optical dephasing,[5] chemical reactions,[3] electron transport,[6] and excitation transport.[7] In addition to random heat bath fluctuations, other time dependent mechanical perturbations, e.g., coherently excited single phonon modes or shock waves, can interact strongly with impurities and defects in a crystal lattice or other medium.

In spite of the importance of the coupling between impurity electronic states and bulk phonons (mechanical states of the host medium), there are few experiments which are able to address the coupling directly.[8] In this paper we illustrate a new approach to probing the coupling between bulk mechanical degrees of freedom and the internal electronic states of an impurity or other defect. The observable in these experiments is the time resolved coherent anti-Stokes emission[9] arising from the bulk mode of interest in a low concentration mixed molecular crystal, pentacene in naphthalene. The most striking feature of the data is its dependence upon the scenario chosen to coherently populate and probe the host phonon mode. If all wavelengths used in the CARS experiment are tuned well to the red of the impurity singlet state electronic absorption, and the pump and Stokes beams are adjusted such that $\omega_p - \omega_s$ is on resonance with the phonon, the decay of the anti-Stokes emission is identical to that of the same mode in the pure crystal (naphthalene). However, very different results are obtained when ω_p is tuned into the S_0 to S_1 electronic transition of the *impurity* molecule (pentacene) and $\omega_p - \omega_s$ is kept on resonance with the naphthalene crystal phonon. Two dramatic changes take place. First there is a substantial resonant enhancement[10] of the anti-Stokes emission from the *bulk* mode. Second, there is a threefold reduction in the decay time of the CARS signal from the bulk phonon.

The details of these observations as well as their implications about the nature of the coupling of a localized defect to the bulk modes of the crystal are discussed below. The resonant enhancement provides a direct probe of the coupling of the impurity electronic states to the bulk mode propagating in the direction determined by the wave vectors of the excitation beams. Thus it is possible to probe the selective interaction of impurity electronic states with a particular bulk phonon, and it should be possible to obtain the directional anisotropy of the coupling. Observations pertaining to the change in the CARS decay on resonance demonstrate the existance of impurity perturbed domains[11] (IPD), i.e., regions of the crystal associated with the impurity which are distinct from the bulk material.

II. EXPERIMENTAL PROCEDURES

The time resolved four wave mixing experiments were performed utilizing the output of an acousto-optically mode-locked and Q-switched Nd:YAG laser (2 mJ per pulse train at a 1 kHz repetition rate), which is frequency doubled and used to pump a pair of folded cavity, electro-optically cavity dumped dye lasers. The two dye lasers, each with a spectral bandwidth of 0.7 cm^{-1} are used to generate the pump, probe, and Stokes pulses. The pulses have a temporal width of ~ 17 ps and each has an energy of 5–10 μJ. The probe pulse is delayed relative to the pump and Stokes beams using a mechanical delay line. The pulses are focused to $\sim 200 \mu$m. The crystals are grown using the Bridgeman method. Small parallel faced slabs are cleaved from the single crystal boules. The samples are mounted in a liquid He cryostat, and the temperature is maintained at 1.5 K. The coherent anti-Stokes signal is spatially separated from the excitation beams, spectrally isolated using a 3/4 m monochromator, and detected with a 9781R photomultipler tube. The photo-tube output is measured with a lock-in amplifier which is referenced at the frequency at which one of the excitation beams is chopped. The lock-in output, as well as a voltage proportional to the probe optical delay, are digitized and recorded by an IBM PC.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the CARS decay of the 69 cm^{-1} libron mode of naphthalene in a pure crystal at low temperature. Part (b) of this figure illustrates the decay of the same mode in a pentacene and naphthalene mixed crystal having an impurity concentration of 10^{-6} m/m. The frequencies of all the beams in the CARS experiments were tuned well to the red of any impurity absorption. Within the experimental error and the variations in decay times which occur from one crystal to another, the results are identical. The observed decay times, 130 ± 10 ps, are consistent with values reported previously in the literature.[12]

As discussed briefly in the Introduction, a very different picture emerges when the pump beam frequency ω_p is tuned into the S_0 to S_1 electronic transition of the pentacene, and the difference in frequency between the pump beam and the Stokes beam $\omega_p - \omega_s$ is kept at the phonon frequency. First,
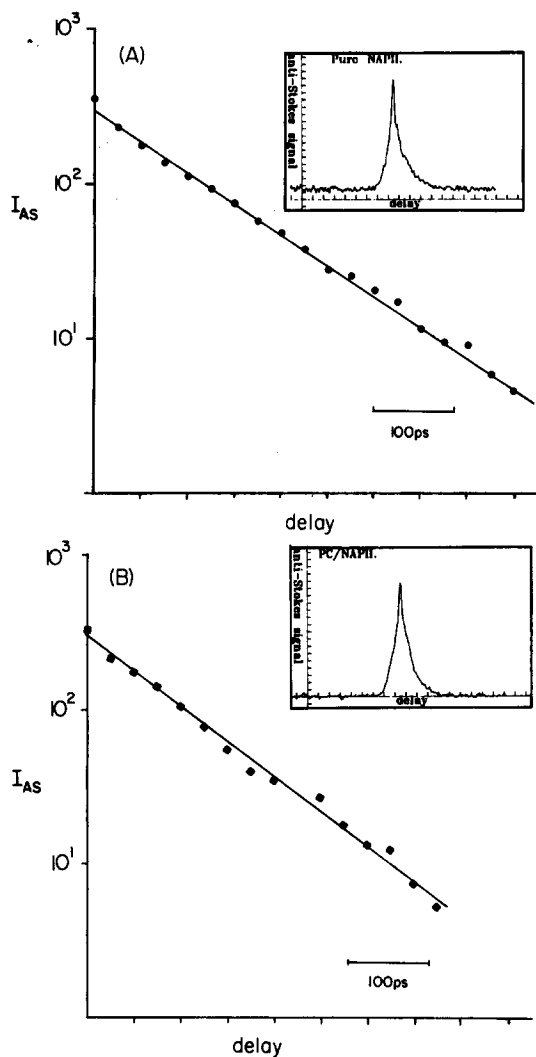
there is a large decrease in decay time as illustrated by Fig. 2. Shown is a log plot of the pure crystal decay, the mixed crystal result with ω_p tuned into the S_0 to S_1 electronic transition of the pentacene (concentration 10^{-5} m/m), and the experimental system's impulse response. The decay times are 130 ± 10 ps, 40 ± 10 ps, and 17 ps, respectively. Second, there is a substantial resonant enhancement of the CARS signal. The signal increase is approximately a factor of 10 in intensity, in spite of the large decrease in effective E-field due to crystal absorption. Typical crystal optical densities were approximately 1, which results in an order of magnitude attenuation of the pump beam and probe beam intensities. Since the signal depends on the intensities[9] $I(\omega_p)^2 I(\omega_s)$, the impurity resonant enhancement of the bulk phonon mode signal is very large. CARS spectra taken on both pure and mixed crystals verify that we are probing the same bulk mode of the host. There is no change in observed phonon frequency to within the 0.7 cm^{-1} bandwidth of the lasers, and the signal has the appropriate dependences on the pump and Stokes field intensities.

There are two primary questions which must be addressed in this investigation. (1) *How is it possible for an impurity electronic resonance to enhance the polarization generated by the bulk mode?* (2) *Why is the CARS decay faster on resonance and normal off resonance in the same mixed crystal?* First take the question of resonance enhancement. Considering the problem perturbatively, in zeroth order we have two mutually exclusive quantum mechanical systems, i.e., states of the bulk crystal and states of the impurity. In zeroth order the eigenstates of the two subsystems are completely independent, and therefore the CARS signal
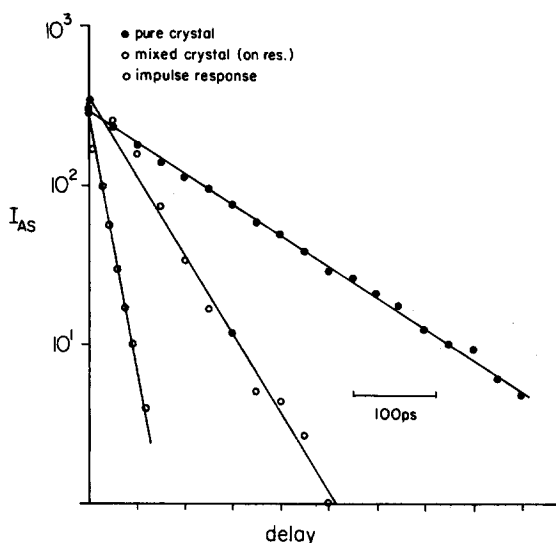

FIG. 1. (a) The decay of the anti-Stokes emission of the 69 cm^{-1} libron mode in a pure naphthalene crystal. (The contributions due to the nonresonant susceptibility is excluded from all figures.) The inset shows the raw data. The decay time ($T_2/2$) is 135 ± 10 ps. (b) The decay of the anti-Stokes emission of the 69 cm^{-1} libron mode in a pentacene and naphthalene mixed crystal at a concentration of 10^{-5} m/m. (The inset shows the raw data.) ω_p for both data sets was detuned 15 cm^{-1} to the red of the pentacene origin. The decay time ($T_2/2$) of 125 ± 10 ps is essentially identical to that of the pure crystal.

FIG. 2. Shown is a log plot illustrating the decay of the anti-Stokes emission for a pure crystal, a mixed crystal (10^{-5} m/mol) and the system impulse response. ω_p in this case was tuned on resonance with the electronic origin of the pentacene impurity (~6028 Å). The nonresonant contributions are excluded from this plot. The decay times are 130 ± 10 ps, 40 ± 10 ps, and 17 ps, respectively. The system response was measured by monitoring the time resolved anti-Stokes emission of the 992 cm^{-1} ring breathing mode in benzene liquid at room temperature.

from a bulk mode will not be affected by resonance of ω_p with an impurity electronic transition. However, in a real crystal, electronic excitation–phonon coupling admixes the impurity electronic states and the bulk phonon states. This mixing with acoustic phonon states is evident in the phonon sideband of impurity spectra.[13] The mixing introduces transition character into electronic transitions which create and annihilate phonons. Therefore the details of the excitation arrangement can become significant when coherently probing the nature of bulk phonons.

The probe pulse, which gives rise to the time resolved CARS observable, interrogates the coherent Raman polarization induced by the excitation pulses. The anti-Stokes intensity can be written as[14]

$$I_{AS}(t) = \int_{-\infty}^{t} |R(t-t')|^2 Q_1(t')dt' + Q_2(t). \qquad (1)$$

Q_1 and Q_2 are third order correlations of the three laser pulses. Q_2 arises solely from the nonresonant background. This contribution decays so rapidly that it does not influence the signal on the time scale of the CARS decay arising from the bulk phonon mode of interest. The contribution to the signal arising from the phonon and instrument function are contained in the first term of Eq. (1). The response function $R(t-t')$ in Eq. (1) is the Fourier transform of the third order susceptibility calculated in steady state treatments.[14] This susceptibility, $\chi^{(3)}$, contains all pertinent information about the field–system interaction.

$\chi^{(3)}$, and hence the observable $I_{AS}(t)$ is influenced by the excitation–phonon interaction. In a standard CARS experiment [as shown in Fig. 3(a)], the susceptibility for the case in which $\omega_p - \omega_s$ is resonant with ω_{ph} takes the form[15]

$$\chi^{(3)} = \frac{N}{\hbar^3} \frac{1}{[\omega_{ph} - (\omega_p - \omega_s) - i\Gamma_{ph}]}$$
$$\times \left(\sum_i \frac{\langle 0|\mu|E_i\rangle\langle E_i|\mu|1\rangle}{(\omega_{i0} - \omega_{AS} - i\Gamma_{i0})} + \frac{\langle 0|\mu|E_i\rangle\langle E_i|\mu|1\rangle}{(\omega_{i0} + \omega_{AS} - i\Gamma_{i0})} \right)$$
$$\times \left(\sum_j \frac{\langle 1|\mu|E_j\rangle\langle E_j|\mu|0\rangle}{(\omega_{j1} + \omega_s - i\Gamma_{j1})} + \frac{\langle 1|\mu|E_j\rangle\langle E_j|\mu|0\rangle}{(\omega_{j1} - \omega_p - i\Gamma_{j0})} \right).$$
$$(2)$$

The states $|0\rangle$ and $|1\rangle$ are the unpopulated and populated phonon levels in the manifold of the lowest electronic state. The states $\{|E_n\rangle\}$ are higher lying crystal electronic states. In Eq. (2), N is the number of oscillators, Γ_{ij} is the damping rate between levels i and j, and μ is the dipole operator. (Note $\omega_{ij} = (E_j - E_i)/\hbar$.) The states $|0\rangle$, $|1\rangle$, and $|E_i\rangle$ are as shown in Fig. 3(a). This is $\chi^{(3)}$ in the pure crystal. The dipole matrix elements in the summations induce the two-photon Raman interaction between the phonon states $|0\rangle$ and $|1\rangle$. States $|0\rangle$ and $|1\rangle$ are coupled through a virtual intermediate state $|V\rangle$ at frequency ω_p, (see Fig. 3) where the virtual state represents the polarizability of the medium. This state has no direct oscillator strength.

To illustrate the source of the CARS resonance enhancement, we will use the basis set with the smallest number of states that will reproduce the physical effect. This zeroth order basis set contains four states. The bulk phonon states in the host ground state manifold are $|0\rangle$ and $|1\rangle$, and the impurity electronic states are $|S_0\rangle$ and $|S_1\rangle$. The zeroth order states are the product states $|S_0,0\rangle$, $|S_0,1\rangle$, $|S_1,0\rangle$, and $|S_1,1\rangle$. ω_p is tuned to the frequency of the S_0 to S_1 transition of the impurity with $\omega_p - \omega_s$ still equal to the phonon frequency [see Fig. 3(b)]. The susceptibility given in Eq. (2) now contains a term which has multiple resonances in the denominator. This term is given in Eq. (3)[16]:

$$\chi_{Res}^{(3)} = \frac{N}{\hbar^3} \frac{1}{[\omega_{ph} - (\omega_p - \omega_s) - i\Gamma_{ph}]} \left(\frac{\langle S_0,0|\mu|S_1,0\rangle\langle S_1,0|\mu|S_0,1\rangle\langle S_0,1|\mu|S_1,1\rangle\langle S_1,1|\mu|S_0,0\rangle}{(\omega_{1'0} - \omega_{AS} - i\Gamma_{1'0})(\omega_{10} - \omega_p - i\Gamma_{10})} \right). \qquad (3)$$

In this expression we have excluded the host electronic state index and $\omega_{1'0} = (E_{1,1} - E_{0,0})/\hbar$. However, in the absence of the excitation–phonon coupling, Eq. (3) vanishes because the dipole matrix elements are zero. For example, the matrix element $\langle S_1,0|\mu|S_0,1\rangle = \langle S_1|\mu|S_0\rangle\langle 0|1\rangle$ is zero. The susceptibility in this case becomes identical to that of Eq. (2), the pure crystal $\chi^{(3)}$, since the terms in the summations with resonances in the denominators arising from the impurity electronic transitions have vanishing dipole matrix elements.

Now consider the coupling among the four product states of the zeroth order basis because of the impurity electronic state-phonon interactions [see Fig. 3(b)]. Limiting the terms in the interaction Hamiltonian H_{ep} to those linear in the phonon operators H_{ep} takes the form[1]

$$H_{ep} = \hbar g_1(b^\dagger + b)a^\dagger a, \qquad (4)$$

where $b^\dagger$ (b) and $a^\dagger$ (a) are the phonon and excitation creation (annihilation) operators, respectively, and g_1 is the

coupling matrix element for the phonon under consideration. Treating the linear excitation phonon coupling term to first order in perturbation theory, it becomes evident that there will be a resonant enhancement of the anti-Stokes signal. For example, by mixing the zeroth order states $|S_1,0\rangle$ and $|S_1,1\rangle$, H_{ep} induces dipole transition character into the $S_0,1$ to $S_1,0$ transition, which is forbidden in zeroth order. Excitation and deexcitation of the electronic state can now be accompanied by the creation or annihilation of a bulk phonon.

As shown in Fig. 3(b), of the four transitions which are involved in the CARS experiment, two are allowed in zeroth order and two are allowed in first order. (The transition $S_0,1$ to $S_1,1$ will have essentially the same transition frequency as the $S_0,0$ to $S_1,0$ transition provided there is not very strong quadratic excitation–phonon coupling. Given the inherent bandwidth of a picosecond laser pulse, both transitions can be simultaneously resonant.) Therefore, a multiresonant term of the form
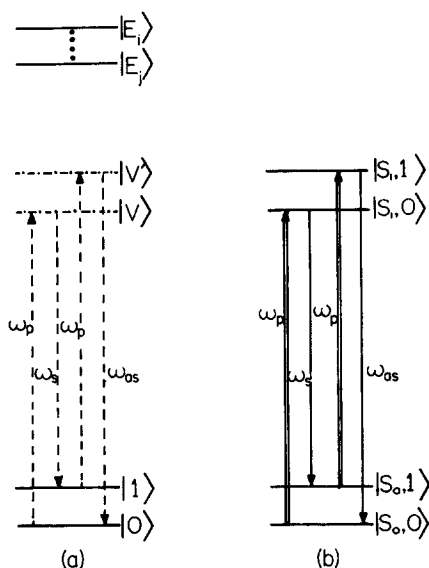
FIG. 3. (a) Field configuration for a standard CARS experiment. The phonon modes $\{|0\rangle, |1\rangle\}$ are populated and depopulated via a two-photon interaction coupled through the virtual levels $|V\rangle$ and $|V'\rangle$. Transition between real and virtual levels are represented by dashed line arrows. The set of states $\{|E_n\rangle\}$ are the high lying crystal electronic states. (b) Effective four level basis for the coupled impurity-phonon system. The states $|S_1,1\rangle$, etc., are the product states $(|S_1\rangle, |1\rangle)$ of the zero order basis set. In zeroth order the matrix elements $\langle S_0,1|\mu|S_1,0\rangle$ and $\langle S_1,1|\mu|S_0,0\rangle$ vanish and there is no modification of the anti-Stokes emission. Upon inclusion of the linear excitation–phonon coupling, the matrix elements become nonzero and multiresonant contributions to the susceptibility become significant. In the figure the double line arrows represent transitions between levels allowed in zeroth order while the single line arrows are transitions allowed in first order perturbation theory.

$$\chi_{\text{Res}}^{(3)} = \frac{Ng_1^2}{\hbar^3 \omega_{\text{ph}}^2} \frac{1}{[\omega_{\text{ph}} - (\omega_p - \omega_s) - i\Gamma_{\text{ph}}]}$$
$$\times \left(\frac{\langle S_0|\mu|S_1\rangle \langle S_1|\mu|S_0\rangle \langle S_0|\mu|S_1\rangle \langle S_1|\mu|S_0\rangle}{(\omega_{1'0} - \omega_{\text{AS}} - i\Gamma_{i0})(\omega_{10} - \omega_p - i\Gamma_{10})} \right) \quad (5)$$

dominates $\chi^{(3)}$. In this expression all matrix elements are nonzero. g_1/ω_{ph} is the excitation–phonon coupling matrix element scaled by the phonon frequency. This is the first order perturbation theory coefficient for the admixture of the basis states.

It is important to note that this treatment is not complete. It is used to display the basic features of the phenomenon. A full calculation would include all electronic and internal vibrational states of the impurity molecule or defect, as well as all host electronic and mechanical degrees of freedom.[13] In many instances the states discussed here would be expected to provide the dominant contribution to the resonant enhancement. The degree of resonant enhancement is a direct measure of the excitation–phonon coupling matrix element g_1 for the specific phonon mode and electronic transition under investigation. By generating the phonon in different propagation directions, the directional anisotropy of the coupling can be studied.

The discussion given above illustrates the nature of the resonant enhancement of the bulk mode CARS signal by

coupling to the impurity electronic states. We will now turn our attention to the change in the CARS decay time when ω_p is tuned into resonance with the impurity electronic transition. There are several reasons why a change in decay time could occur. The population relaxation pathways available to bulk phonon modes can be modified by inclusion of impurities or defects in a mixed crystal system. Impurities can increase the extent of anharmonicity of the phonon potential. Cubic anharmonicity has been shown to dominate phonon population dynamics in pure crystals.[17] Another possibility is the formation of phonon traps, a mechanism which has been observed in very highly concentrated isotopically substituted crystalline systems.[18]

However, these mechanisms are inconsistent with the data. They would produce a single decay time on and off resonance (which would be different from that of the pure crystal). The resonance condition would only affect the magnitude of the signal. The data clearly shows a fast decay and one indicative of the pure crystal result in the on and off resonance cases, respectively. These results suggest the possibility that two distinct oscillating polarizations are being observed, one being identical to that generated in the pure crystal, the other being associated with an ensemble of domains of bulk molecules substantially coupled to an impurity molecule. These will be referred to as impurity perturbed domains (IPD).

A number of experimental observations support the idea of IPDs. Crystals with impurity concentrations on the order of 10^{-6} m/m when examined on resonance, or higher concentration crystals (10^{-5} m/m) examined with ω_p detuned somewhat to the red of the impurity electronic transition, exhibit nonexponential decays. In the IPD model, there are two contributions to the nonlinear susceptibility which are resonant with the phonon frequency, i.e.,

$$\chi_{\omega\text{ph}}^{(3)} = \chi_{\text{bulk}}^{(3)} + \chi_{\text{IPD}}^{(3)}. \quad (6)$$

The first is the $\chi^{(3)}$ measured in the neat material which is labeled $\chi_{\text{bulk}}^{(3)}$. This term has a form identical to Eq. (2). Next there will be a contribution from the multiresonant impurity perturbed domains which is labeled $\chi_{\text{IPD}}^{(3)}$. This term is given by Eq. (5) In IPD regions, the impurity eigenstates are mixed with the bulk degrees of freedom. All the matrix elements of $\chi_{\text{IPD}}^{(3)}$ have true transition character unlike the bulk susceptibility where the dipole matrix elements represent the coupling of the states of interest to virtual levels. $\chi_{\text{IPD}}^{(3)}$ characterizes the nature of the phonon in the vicinity of the impurity, and in some sense $\chi_{\text{IPD}}^{(3)}$ is a site selective contribution to the susceptibility.

The total $\chi_{\text{tot}}^{(3)}$ can be written as

$$\chi_{\text{tot}}^{(3)} = (\chi_{\text{bulk}}^{(3)} + \chi_{\text{IPD}}^{(3)} + \chi_{\text{NR}}^{(3)}), \quad (7)$$

where the terms not resonant with the phonon have been combined in χ_{NR}. This form of the susceptibility makes it clear why the CARS time dependences differ when ω_p is tuned on and off the impurity electronic transition. When ω_p is well off resonance, $\chi_{\text{tot}}^{(3)}$ is dominated by $\chi_{\text{bulk}}^{(3)}$. There are orders of magnitude more bulk oscillators than IPD oscillators so the contribution of $\chi_{\text{IPD}}^{(3)}$ to the signal is negligible. When ω_p is on resonance with the impurity electronic transi-

tion $\chi_{\rm IPD}^{(3)}$, because of its multiresonant nature, enhances the signal by several orders of magnitude. Its contribution to $\chi_{\rm tot}^{(3)}$ now dominates the observable. Therefore, if the IPDs and the bulk have distinct time dependences, the time dependence of the signal will change when ω_p is tuned into the impurity electronic transition.

The above discussion implies that well off the electronic transition a single exponential will be observed (the decay of the bulk phonon) and that on the electronic transition in a crystal with concentrated impurities, a distinct single exponential decay will be observed. (This is ignoring the very short time contribution from the nonresonant background.) This is in fact what is displayed in Fig. 4. For mild detuning from the impurity electronic transition, or in crystals with moderate impurity concentrations, so that even on resonance the enhancement is not too great, both the bulk and the IPDs will contribute to the signal. Nonexponential behavior would be expected, and is observed (Fig. 5). Ignoring the short time contribution from $\chi_{\rm NR}$, the signal will be proportional to the square of Eq. (7), a triexponential.

The data can be fit to a triexponential decay of the form[19]

$$I_{\rm AS} = A_1^2\, e^{-2t/T_{\rm bulk}} + A_2^2\, e^{-2t/T_{\rm IPD}}$$
$$+ 2A_1 A_2 \cos\phi\, e^{-t(1/T_{\rm bulk} + 1/T_{\rm IPD})}, \qquad (8)$$

where A_i are the amplitudes of the individual contributions to the polarizations. The two decay times are the off resonance decay (bulk phonon decay) $T_{\rm bulk}$ and the single exponential decay measured on resonance in a concentrated crystal, $T_{\rm IPD}$. The ratios of the two contributions change with

FIG. 5. Example of a nonexponential CARS decay of the 69 cm^{-1} libron mode in a mixed crystal (10^{-6} m/m). The data was obtained on a moderately concentrated crystal with ω_p tuned to the impurity electronic transition.

the degree of detuning from the impurity electronic transition and with the impurity concentration. The solid line through the data in Fig. 6 was obtained using Eq. (8) with the decay constants fixed at the values for the bulk phonon decay and the on resonance (high concentration) decay. Since the polarizations generated by two sources do not necessarily add in phase,[19] there is an adjustable phase factor ϕ in Eq. (8). The agreement between the experiment and the calculation is quite reasonable. The residuals of the fit show no systematic trend.

These observations support the two domain, two oscillator picture. This picture is further supported by observations from two crystals with the same optical densities (and therefore the same number of impurity molecules) but different concentrations. The IPD model predicts that a high concentration thin crystal on resonance will exhibit a single exponential fast decay, while a low concentration thick crystal will exhibit a nonexponential decay on resonance since the number of bulk oscillators is significantly larger. This behavior is displayed in Fig. 7. In principle, if one detunes the
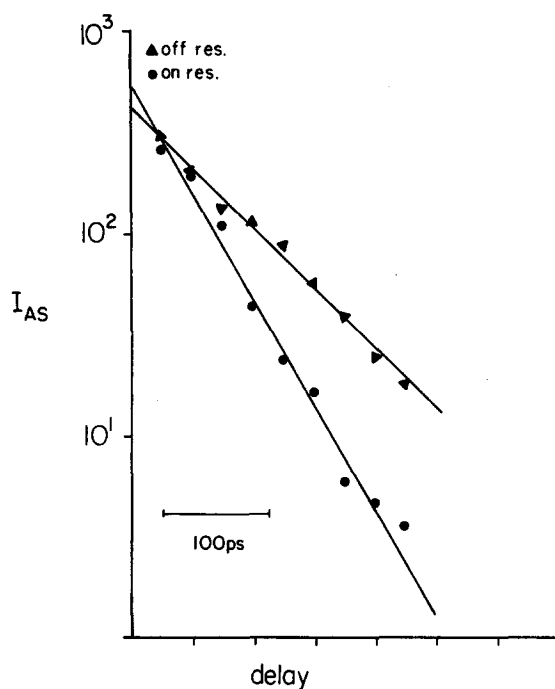

FIG. 4. The decay of the anti-Stokes emission for a pentacene and naphthalene mixed crystal(10^{-5} m/m). Purely exponential decays are obtained with ω_p on and well off resonance with the impurity electronic transition in the same sample. $\omega_p - \omega_s$ is tuned to the bulk phonon resonance in each case.
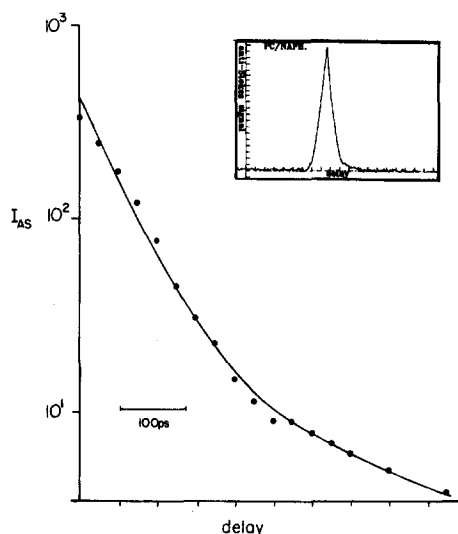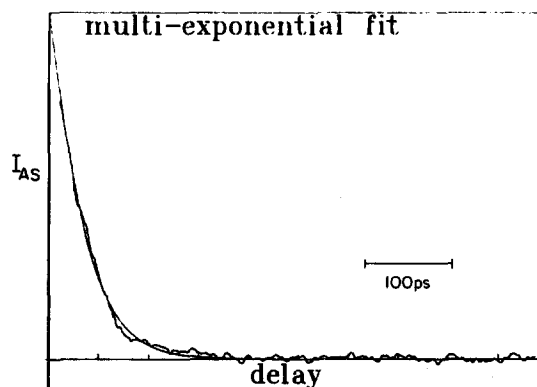

FIG. 6. Fit of nonexponential CARS decay using the two domain model. The data was fitted to Eq. (8). The fit parameters were the values of A_1 and A_2 and the phase angle ϕ which were 20 units, 70 units, and 1.5 rad, respectively.
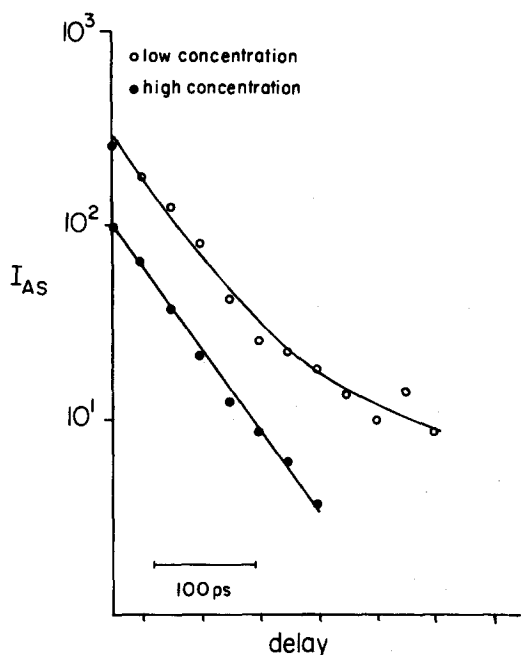
FIG. 7. The figure illustrates the decay of a high concentration thin mixed crystal and low concentration thick mixed crystal with ω_p on resonance with the impurity electronic origin. The samples have the same optical density (≈ 1), and therefore contained the same number of impurity molecules. The differences between the decays arise due to the greater number of bulk oscillators in the low concentration sample.

pump beam sufficiently from the impurity electronic transition, only the bulk oscillators should be observed with their characteristic decay time. This limit was easily reached in the low concentration crystal. In the thin high concentration sample, the decrease in crystal thickness makes signal detection difficult off resonance. The anti-Stokes emission is proportional to l^2, where l is the length of the sample.[9] For the pair of crystals under discussion, the high concentration thin crystal is approximately a factor of 10 thinner. I_{AS} from the bulk oscillators will be down two orders of magnitude and was not observed. With the addition of more sophisticated signal averaging techniques we should be able to observe this signal in future work.

There are several reasons why the decay arising from the IPDs can be different from the decay of the CARS signal from the bulk phonon mode. Since the IPD phonon is intimately connected to the impurity, the impurity can act as a scattering center increasing the rate of population relaxation. In a pure crystal such as naphthalene at low temperature, the CARS decay is temperature independent. It is attributed to population relaxation arising from cubic anharmonicity of the phonon potential. The formation of the IPDs suggests that these regions of the crystal are mechanically distinct from the bulk. An increase in the cubic anharmonicity in the IPDs could result in an increased rate of population relaxation.

The time resolved CARS experiment is essentially an observation of a Raman optical free induction decay. Qualitatively, one can think of the phonon excitation as a wave packet, and we are observing the evolution of the initially prepared packet via its interaction with the probe pulse. In

the pure crystal, optical excitation of the phonon selectively populates a very narrow distribution of k states about $k = 0$ since these are the states that satisfy the momentum conservation requirement associated with the excitation process. In principle, this initially prepared distribution of k states will lead to inhomogeneous dephasing and contribute to the decay of the CARS signal. However, in a pure crystal the inverse of the width of the initially prepared inhomogeneous distribution is negligible compared to the phonon population relaxation time, and does not contribute to the decay of the CARS signal.[20]

The coupling of the impurity degrees of freedom with the phonon in the IPDs could to some extent relax the wave vector selection rule. Therefore, the wave packet initially prepared in the IPDs by excitation resonant with the impurity electronic transition could contain a significantly wider distribution of k states. In some sense the impurity eigenstates might serve as doorways to phonon states of different k vectors. If the spread in k states became large enough, inhomogeneous dephasing would contribute to the CARS decay. The decay would become faster than the bulk phonon lifetime decay even though there was no change in the rate of population relaxation in the IPDs. It is also possible that there is a wave vector dependence to the degree of resonance enhancement. In the perturbation treatment of the resonance enhancement phenomenon given above, the phonon was taken to be a single state. However, there is actually a band of phonon states each labeled by its wave vector k. If the phonon-impurity coupling is wave vector dependent, i.e., H_{ep} is wave vector dependent, then the extent of resonant enhancement would vary with k. In Eq. (5), g_1 would become $g_1(k)$. This combined with a relaxation of the wave vector selection rule could also contribute to inhomogeneous dephasing and therefore a fast CARS decay which is not related to an increased rate of population relaxation. At this time it is not possible to distinguish between the various mechanisms. Detailed theory and experiment will be required to determine the nature of the fast IPD CARS decay.

IV. CONCLUDING REMARKS

In this paper we have presented a preliminary investigation of a new phenomenon, the resonant enhancement of a phonon CARS signal arising from the interaction of the phonon with the electronic states of an impurity molecule. While we have discussed crystals, it is reasonable that a similar effect should occur in other types of systems such as glasses, liquids, or proteins. The impurity enhancement of the phonon CARS signal is in some sense like the phonon sideband observed in the absorption spectrum of impurities or defects in crystals. The phonon sideband arises because of the interaction of the impurity electronic states with the acoustic phonons of the crystal. The coupling gives transition character to transitions which involve changes in the impurity electronic state and the creation or destruction of an acoustic phonon. The relative areas of the phonon sideband and the impurity zero phonon line give a measure of the excitation–phonon coupling.[13]

In the impurity enhanced phonon CARS experiment, the impurity electronic state-phonon coupling resonantly enhances the production and detection of an optical phonon when the excitation wavelength is on resonance with the impurity electronic transition. The extent of the resonant enhancement is a measure of the optical phonon-impurity excitation coupling. Unlike the acoustic phonon sideband which has contributions from all phonon branches and phonons propagating in all directions, the impurity enhanced optical phonon CARS signal examines a single phonon propagating in a well defined direction. By changing the phonon propagation direction it should be possible to explore the directional anisotropy of the excitation–phonon coupling. Tuning into various optical phonon modes and various electronic states will permit a range of phonon–excitation interactions to be measured.

It was observed that the CARS decay, when enhanced by the impurity electronic transition, was significantly faster than the nonenhanced decay in the same crystal. A variety of observations on the concentration dependence and the detuning dependence of the CARS decays strongly suggest the existance of impurity perturbed domains, i.e., regions of the crystal associated with the impurity in which the phonon is distinct from the bulk phonon. The impurity perturbed domains have distinct mechanical characteristics which, to some extent, decouple them from the bulk crystal. This gives rise to two decay times, one associated with the bulk phonon in the mixed crystal and one associated with the phonon in the impurity perturbed domains. The bulk phonon decay in the mixed crystal is indistinguishable from the pure crystal decay, while the IPD phonon decay is considerably faster.

These experiments provide a new approach to the examination of the interactions of the internal electronic degrees of freedom of a molecule with the mechanical degrees of freedom of its environment. Since these interactions are fundamental to understanding a wide variety of phenomena, impurity resonant enhancement of bulk mode CARS experiments can add to our understanding of condensed matter systems.

ACKNOWLEDGMENTS

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