

Temperature-dependent vibrational relaxation in isotopically mixed molecular crystals by picosecond CARS

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Temperature-dependent dephasing of 511, 766 and 1385 cm^{-1} modes in the mixed crystals of naphthalene and perdeuterio-naphthalene at various isotopic levels have been studied by picosecond CARS in the region of 6–130 K. In general, adding the isotope shows a significant effect on the low-temperature decay time. However, a small effect on the temperature dependence is observed in the Arrhenius plots of $\ln[\Delta\nu(T) - \Delta\nu(6\text{ K})]$ versus $1/T$ for all three modes. This behavior is described by a large change of the thermally activated phonon density of states at low temperature, but by a small change as temperature increases.

1. Introduction

Picosecond (ps) CARS has been employed to investigate the vibrational dynamics in crystalline benzene (BZ) [1,2] and naphthalene (NPH) [3–8] for a better understanding of the vibrational dynamics in solid state chemistry. The advantage of this method is its ability to provide a direct measurement of vibrational dephasing if the decay of coherence is long relative to the pulse width. Three possible mechanisms, vibrational relaxation, pure dephasing, and inhomogeneity, are responsible for the dephasing. Hochstrasser and co-workers [9] performed the first measurement of the relaxation time for the 1385 cm^{-1} mode of NPH by frequency domain CARS. They noted that the inhomogeneous effect is negligible due to the motional narrowing. Furthermore, the pure dephasing is frozen at low temperature [1,3]. It is likely that the vibrational relaxation is the dominant mechanism for the dephasing processes. Since the static inhomogeneous broadening must yield nonexponential decays, the exponential decays measured in the molecular crystals by ps CARS were attributed to vibrational relaxation.

Temperature-dependent vibrational dephasing on

three totally symmetric vibrations, 511, 766 and 1385 cm^{-1} , in NPH was studied by Dlott and co-workers [5,6]. The decay times measured by ps CARS are nearly temperature independent below ≈ 40 K and decrease above this temperature. Their decay times from 40 to ≈ 150 K were mainly due to the vibrational relaxation. They further found that the Arrhenius plots for temperature-dependent linewidths were concave upward at all temperatures. This feature was attributed to more vibrations participating in the dephasing with increasing temperature. Therefore, the slope is steadily increasing.

Dlott and co-workers [7,8] have further investigated the isotope dependence of vibrational relaxation at low temperature to examine whether the intermolecular anharmonic coupling provides additional decay channels. They reported that adding the isotope increased the decay rates for the 511 and 766 cm^{-1} modes significantly, but had little effect on the 1385 cm^{-1} mode. They suggested that the fast decay rate is attributed to the energy relaxation from excited NPH vibrons to the counterpart of perdeuterio-naphthalene (NPD) vibrons [7,8]. For example, the 511 cm^{-1} mode of NPH can decay to the 493 cm^{-1} mode of NPD and a phonon mode at 18 cm^{-1} through the cubic anharmonic term.

The objective of this study is to investigate the temperature-dependent vibrational dephasing on the isotopically mixed crystals. We use ps CARS to mea-

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suming an equal value for the cubic coefficients from the V state to each possible A state, eq. (1) can be written as

$$[T_1(T)]^{-1} = \frac{36}{\hbar^2} \langle V_{VAP}^{(3)} \rangle^2 \times \{ [n_P(T) + 1] \rho^P(\omega - \omega_A) + n_P(T) \rho^P(\omega_A - \omega) \}, \quad (2)$$

where $\rho^P(\omega - \omega_A)$ is the phonon density of states at $\omega - \omega_A$ which was known for NPH and NPD [16]. n_A and n_P are the thermal occupation numbers of acceptor and phonons states, where $n_P(T) = [\exp(\hbar\omega_P/k_B T) - 1]^{-1}$ and $n_A(T)$ is negligible at low temperature. $V^{(3)}$ is a cubic anharmonic coefficient, which is given as

$$V^{(3)} = \frac{1}{3!} \left. \frac{\partial^3 V(Q_i)}{\partial Q_V \partial Q_A \partial q_P} \right|_{Q=0} Q_V Q_A q_P, \quad (3)$$

where $V(Q_i)$ is the crystal potential. Q is a vibrational coordinate and q is a phonon coordinate.

In the mixed crystals, the cubic anharmonic terms involve the coupling terms of $Q_V Q_h q_P$ and $Q_V Q_g q_P$ if the phonon density of states is less affected by the guest, where Q_h represents host vibrons and Q_g represents guest vibrons. Velsko and Hochstrasser [17] have derived the decay rate for binary mixed crystals, which is given as

$$k = k^{(0)} + N^2(k_{AA} C_A^2 + k_{AB} C_A C_B) + N(k_{AB} C_B^2 + k_{AA} C_A C_B), \quad (4)$$

where $k^{(0)}$ is the single site relaxation rate. k_{AA} and k_{AB} are the rate constants for energy transfer from A molecule to adjacent A and B molecules, respectively. C_A and C_B are the mole fractions of A and B. N is the number of nearest neighbors. If $N=1$, eq. (4) can be simplified to

$$k = k^{(0)} + k_{AA} + C_B(k_{AB} - k_{AA}). \quad (5)$$

In this case, a linear concentration dependence for the decay rate should be observed in the mixed crystals.

4. Results and discussion

We have measured temperature-dependent vibra-

tional lifetimes for the 511, 766 and 1385 cm^{-1} modes of NPH in the neat and in the isotopically mixed crystals of NPH at various isotopic levels in the region 6–130 K. Our measurements of their lifetimes in NPH at 6 K for more than five neat crystals are 135 ± 15 , 66 ± 4 and 97 ± 3 ps respectively, which agree with the literature values [3]. Fig. 2 shows the semilog plots of ps CARS decay for the 511 cm^{-1} mode in the mixed crystal of NPH and NPD with 12:1 by weight at different temperatures. The decays are exponential in each case over a range of three factors of e , which suggests that the vibration is delocalized. Further, although NPD was used without further purification, the non-exponential decay resulted from impurity scattering and inhomogeneous broadening was not observed. It is indicated that the contribution to the decay time from impurity scattering can be ruled out.

Temperature-dependent lifetimes for these three modes in the mixed crystals of NPH and NPD with 12:1 by weight are listed in table 1. It is found that adding the isotopes causes a small increase for the decay rate of the 1385 cm^{-1} mode, but leads to a significant increase for the decay rate of 511 and 766 cm^{-1} modes at low temperature. The fast decay rate for the 511 and 766 cm^{-1} modes in the mixed crys-

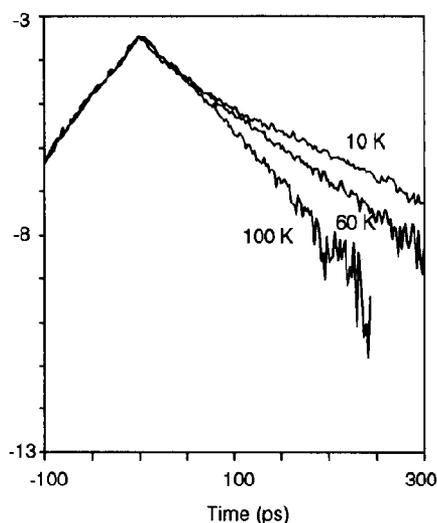


Fig. 2. The semi-log plots of picosecond CARS decay for the 511 cm^{-1} mode in the mixed crystal of NPH and NPD with 12:1 by weight at different temperatures.

Table 1

Lifetimes of mixed crystals at 511, 766 and 1385 cm^{-1} vibrational modes

511(12:1)		766 (12:1)		1385 (12:1)	
temp. (K)	lifetime (ps)	temp. (K)	lifetime (ps)	temp. (K)	lifetime (ps)
6	100±2	6	46±1	6	88±2
32	91±2	21	45±2	32	84±4
40	85±1	34	41±2	42	80±2
50	78±1	44	37±2	50	73±3
61	65±1	57	33±1	58	63±3
79	52±3	73	26±2	71	57±3
90	47±2	87	24±3	81	58±2
102	40±2	112	20±2	90	49±2
116	33±2			117	33±2

tals at 10 K has been examined by Dlott and co-workers [7,8]. Since the phonon densities of states for NPH and NPD are similar to each other [16] and the intramolecular anharmonic coupling is independent of the isotopic concentration, the fast decay rate is attributed to the process of intermolecular anharmonic coupling. The energy relaxation from NPH vibrons to the counterpart of NPD vibrons should play a dominant role because of the larger nuclear overlap for the same normal coordinates than for two different normal coordinates [7]. Therefore, the mechanism for the increase of decay rate in the mixed crystals is interpreted by a strong cubic anharmonic coupling of the excited NPH vibrons to the counterpart of NPD vibrons and a low-frequency phonon mode. This interpretation is further supported by the phonon density of states of NPH or NPD, which is higher at 65 and 18 cm^{-1} than that at 5 cm^{-1} .

The Fourier transform of the time-resolved CARS signal can provide the spontaneous Raman lineshape. Thus, the vibrational linewidths can be calculated by

$$\Delta\nu (\text{cm}^{-1}) = \Gamma / 2\pi c = 5.3 / \text{lifetime (ps)}. \quad (6)$$

Fig. 3 shows the Arrhenius plots of $\ln[\Delta\nu(T) - \Delta\nu(T=6\text{ K})]$ versus $1/T$ for these three modes in the neat and in the isotopically mixed crystals. We found that adding the isotopes makes a little difference for the curvature and the intercept of the Arrhenius plots between the neat and the mixed crys-

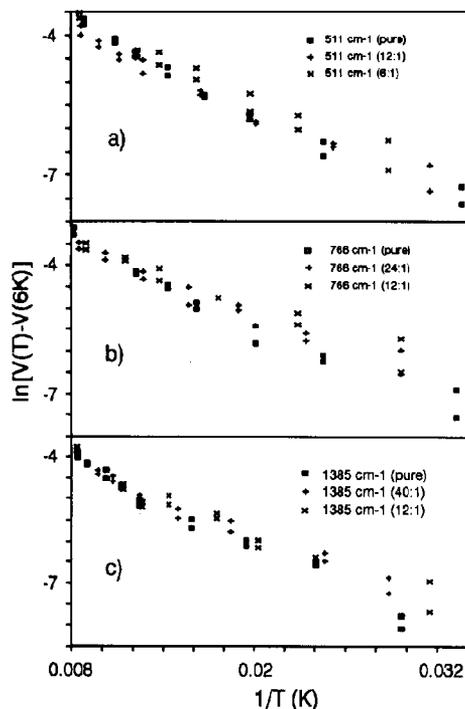


Fig. 3. The Arrhenius plots of $\ln[\Delta\nu(T) - \Delta\nu(T=6\text{ K})]$ versus $1/T$ for 511, 766 and 1385 cm^{-1} modes in the neat and the isotopically mixed crystals.

tals. Further, the change of the curvature and the intercept for the 1385 cm^{-1} mode is less than that for the 511 cm^{-1} mode and is much less than that for the 766 cm^{-1} mode. In addition, the curvature in the Arrhenius plots for each modes is nearly independent of the mixed crystals at various isotopic levels.

It is known that the dephasing processes of 766 cm^{-1} involve the down-conversion processes including the 618, 620 and 725 cm^{-1} modes at low temperature. Righini [18] has demonstrated that the up-conversion processes involving the internal modes of 786, 782 and 810 cm^{-1} also play a dominant role in the dephasing of the 766 cm^{-1} mode while increasing the temperature based on the agreement between their calculation and ps CARS results from ref. [5]. We use eq. (2) to reproduce the calculation of temperature-dependent linewidths for the 766 cm^{-1} mode in NPH, which is shown in fig. 4a. The agreement between experimental and calculated data is

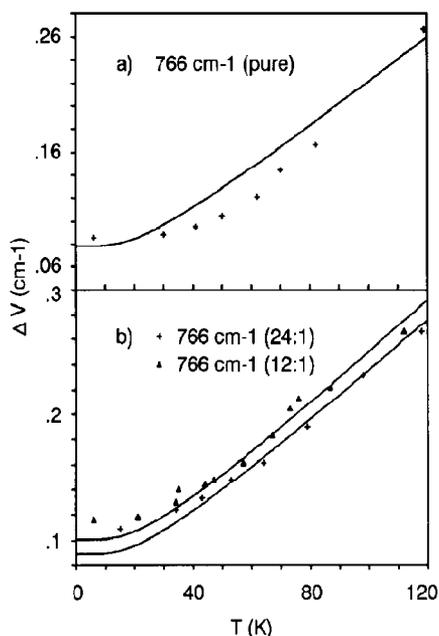


Fig. 4. Temperature dependence of the linewidths of the 766 cm^{-1} mode in the neat and the mixed crystals. Triangle and cross: experimental data; solid lines are calculated linewidths involving both down- and up-conversion processes for the pure NPH and adding the intermolecular anharmonic coupling of 766 and 701 cm^{-1} for the mixed crystals.

acceptable and can be improved if the cubic anharmonic coefficients are decreased because of the thermal lattice expansion [18]. In the mixed crystals, the main additional decay channel is the anharmonic coupling of the 766 cm^{-1} mode in NPH with the 701 cm^{-1} mode in NPD and a low-frequency phonon mode at 65 cm^{-1} . With this additional channel, we use eq. (5) to calculate the linewidths in the mixed crystals because a linear relation has been observed for the concentration dependence of this mode in the mixed crystals [7]. Fig. 4b presents the experimental and the calculated temperature-dependent linewidths for the 766 cm^{-1} mode in the mixed crystals. Temperature-dependent phonon densities of states are calculated based on ref. [16]. The only adjustable parameter in eq. (2) is $\langle V_{\text{vib}}^{(3)} \rangle$, which is determined by the low temperature lifetime. Considering the intermolecular anharmonic coupling, we vary the parameter $\langle V_{\text{vib}}^{(3)} \rangle$ in eq. (5) to fit the rest of the temperature-dependent data. Table 2 collects

Table 2

Vibron decay pathways and the values of various parameters for the calculation

Vibron	Pathways	$\rho^p(\Delta\omega)$	$V_{\text{vib}}^{(3)}$	$V_{\text{vib}}^{(3)}$
766	725	0.22	0.08	0.2
	620	0.055		
	618	0.055		
	782	0.0067		
	786	0.01		
	810	0.23		
	701 (NPD)	0.24		
511	480	0.043	0.05	0.6
	467	0.23		
	390	0.14		
	362	0.055		
	618	0.15		
	620	0.14		
	493 (NPD)	0.012		

the parameters for the calculation of temperature-dependent linewidths for this mode. It should be noted that $\langle V_{\text{vib}}^{(3)} \rangle = 0.2$ provides the best fit as shown in fig. 4b. However, $\langle V_{\text{vib}}^{(3)} \rangle = 0.25$ yields more consistent results relative to fig. 4a. Nevertheless, the good agreement between experimental and calculated data indicates that the thermally activated phonon process, involving the anharmonic coupling of the excited NPH vibrons to the counterpart of NPD vibrons, is an essential process for the temperature-dependent linewidth in the mixed crystals.

Therefore, our calculation confirms that the significant isotope effect on the low temperature linewidths is attributed to the new channel for energy relaxation from the 766 cm^{-1} mode in NPH to the 701 cm^{-1} mode in NPD [7]. Since we have subtracted the linewidth at 6 K from temperature-dependent linewidths in the Arrhenius plots, the essential isotope effect on the linewidths due to the $Q_{\text{v}}Q_{\text{g}}q_{\text{p}}$ terms is excluded. Thus, the small change in the curvature in the plots due to the isotope effect can be described by the change of the thermally activated phonon density of states at 65 cm^{-1} . Furthermore, no discernable effect due to various isotopic levels in the curvature of the Arrhenius plots is observed in our work, which can be understood by considering the small change of isotopic concentration and the small effect of thermally activated phonon density of states.

We have further calculated the linewidths for the 511 cm^{-1} mode in the mixed crystals based on the same argument cited for the 766 cm^{-1} mode. The possible decay channels involving four down-conversion, two up-conversion, and the intermolecular coupling processes and their corresponding phonon density of states are also listed in table 2. Fig. 5 presents the experimental and calculated linewidths for the 511 cm^{-1} mode in the mixed crystals as a function of temperature. The agreement in the mixed crystals is acceptable because it is difficult to measure the phonon density of states at 18 cm^{-1} accurately. In addition, it is found that the phonon density of states at 18 cm^{-1} is larger in NPD than in NPH [16]. Nevertheless, it is further confirmed that the thermally activated phonon process is an important dephasing mechanism.

Righini [18] failed to predict the low temperature lifetime of the 1385 cm^{-1} mode because of a very small cubic coefficient obtained from an inadequate description of the eigenvector of this mode. Ranson et al. [19] suggested that the possible decay channels

involved either two vibrons, or one vibron and one phonon. Since we do not have enough information for calculating the two-vibron processes, we are not able to calculate the linewidths for this mode. In the mixed crystals, the counterpart of 1385 cm^{-1} in NPH is located at 1390 cm^{-1} in NPD. The energy transfer from 1385 to 1390 cm^{-1} is negligible because the phonon density of states is ≈ 0 at 5 cm^{-1} . Therefore, if the energy relaxation from the excited NPH vibrons to the counterpart of NPD vibrons determines the change of the Arrhenius plots, the curvature of the Arrhenius plots for the neat and the mixed crystals should be more similar for the 1385 cm^{-1} mode than for the 511 and the 766 cm^{-1} modes. Further, the plots for the 1385 cm^{-1} mode should be nearly independent of the isotopic concentration. Both predictions were consistent with our experimental results as shown in fig. 3.

In summary, we have shown that adding the isotopes causes a significant increase in the low-temperature lifetime, but has little effect on the curvature of the Arrhenius plots. The former observation is attributed to the additional channel opened by the intermolecular anharmonic coupling, $Q_v Q_h q_p$, of the same normal modes in the isotopes. The change of magnitude is also determined by the phonon density of states at q_p . The latter observation can be described by the small change of the phonon density due to the thermally activated effect at q_p .

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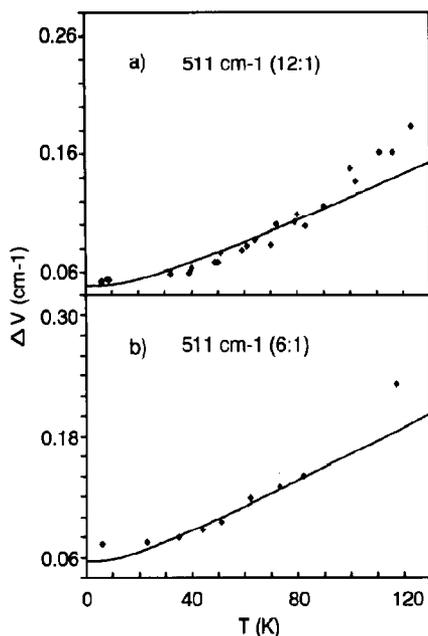


Fig. 5. Temperature dependence of the linewidths of the 511 cm^{-1} mode in the mixed crystals. Square: experimental data; solid line is calculated linewidths.

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