

# Picosecond time-resolved CSRS study of vibrational dephasing of bulk modes perturbed by electronic state of dilute impurities

Ta-Chau Chang<sup>1</sup>, Hung-Wen Li<sup>2</sup>, Tzu-Chung Hsieh<sup>3</sup> and Shioh-Hwa Chou

*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 10764, Taiwan, ROC*

Received 14 June 1993; in final form 6 August 1993

We have found that the decays of vibrons are mode-specifically perturbed by the impurity electronic state. We observe normal decay time for the 511  $\text{cm}^{-1}$  vibron and shorter decay times for the 766 and 1385  $\text{cm}^{-1}$  vibrons of host molecules (naphthalene) when the excitation energy is tuned into the electronic transition of guest molecules (pentacene). Isotopic study elucidates that shorter decay time of the 766  $\text{cm}^{-1}$  signal, measured from the time-resolved CSRS spectra, is actually due to the vibrational dephasing of the 767  $\text{cm}^{-1}$  mode of pentacene impurity molecule. Possible mechanisms are proposed to explain the impurity perturbed domains effect on the dephasing of the 1385  $\text{cm}^{-1}$  vibron, but not of the 511 and 766  $\text{cm}^{-1}$  vibrons.

## 1. Introduction

Time-resolved CARS has been utilized to measure the vibrational dephasing in mixed molecular crystals for a better understanding of the vibrational dynamics in solids [1–5]. Wiersma and co-workers introduced the multi-resonant ps CARS to study the vibrational relaxation of impurity [6,7]. Fayer and co-workers used this resonance-enhanced method to probe the coupling between impurity electronic states and bulk photons [8]. Recently, we employed this technique to examine the effect of electron–phonon coupling on the vibrational dynamics of the host vibron in a mixed crystal [9]. The study of the electron–phonon coupling is important for understanding the fundamental nature of the following processes: the optical dephasing in molecular crystal [1–16], the cooling of hot electrons in a thin metal film [17], the relaxation of the resistance of a superconductor [18], and the functioning of proteins and membranes in biological systems [19].

In our previous work [9], we used multi-resonant time-resolved CSRS spectra to measure the decay

time of 1385  $\text{cm}^{-1}$  mode of naphthalene (NPH) in the mixed crystals of pentacene (PT) doped in NPH. We found that shorter decay times of this mode were observed when the pump pulse was tuned to the electronic transition of PT (on-resonance). Since the 1385  $\text{cm}^{-1}$  vibron of a host molecule near the impurity molecule is perturbed by the electron–phonon interaction between the impurity and host molecules, this particular host molecule would have different local modes from the bulk host molecule. The impurity perturbed domains (IPD) model was used to describe the shorter decay time on resonance [8,9]. Furthermore, a temperature dependence study on the decay time of this mode showed an inverse temperature effect; decay times observed at higher temperatures ( $\approx 25$  K) were longer than those observed at low temperatures ( $\approx 6$  K). This inverse temperature effect was interpreted by using the Born–Oppenheimer (BO) approximation model of vibrational relaxation [9,20–22]. An average phonon frequency of 20  $\text{cm}^{-1}$  obtained from the simulation using BO model implies that a decay channel from the 1385  $\text{cm}^{-1}$  vibron to the 1365  $\text{cm}^{-1}$  vibron may be important for the shorter decay time on-resonance. The enhancement of this decay channel is probably closely related to the pseudolocal phonon mode at  $\approx 18$   $\text{cm}^{-1}$  via electron–phonon coupling [12]. Therefore, we proposed that the phonon distribution

<sup>1</sup> To whom correspondence should be addressed.

<sup>2</sup> Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC.

<sup>3</sup> Present address: Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA.

of  $20\text{ cm}^{-1}$  perturbed by the impurity excitation may be responsible for the shorter decay time in the IPD model [9].

The objective of the present work is to examine the effect of the impurity excitation on the dephasing of host vibrons mode-specifically. The experiments should allow us to assess the dephasing mechanism in the IPD domains. For this purpose, we have measured the decay times on-resonance and off-resonance of the  $511$  and  $766\text{ cm}^{-1}$  vibrons of NPH in the PT/NPH molecular crystals. No significant difference on the decay times of the  $511\text{ cm}^{-1}$  mode between on-resonance and off-resonance is observed. However, it is found that the decay time of  $32 \pm 4$  ps for the  $766\text{ cm}^{-1}$  mode on-resonance is approximately twice as short as that of the neat crystal. The decay time of  $62 \pm 5$  ps measured in the off-resonance spectra is nearly identical to that of the neat crystal. Previously, Duppen and co-workers [6] reported  $60 \pm 3$  ps decay time for the  $767\text{ cm}^{-1}$  vibron of PT using time-resolved resonant CARS. In order to determine the contribution from the  $767\text{ cm}^{-1}$  mode of PT to the  $766\text{ cm}^{-1}$  signal observed in the PT/NPH crystals, we have measured the intensities and the decay times of the  $756$  and  $767\text{ cm}^{-1}$  modes of PT in the PT/NPD (deuterated naphthalene) mixed crystals. Isotopic study may allow us to elucidate dephasing processes of the  $766\text{ cm}^{-1}$  mode on-resonance and off-resonance. In the temperature dependence studies, the decay times of the  $511$  and  $766\text{ cm}^{-1}$  modes are independent of temperature, which differs from the inverse temperature behavior of the  $1385\text{ cm}^{-1}$  mode [9]. Finally, possible mechanisms for the mode specificity are discussed.

## 2. Experimental

The ps CSRS experimental apparatus was described previously [5]. An acousto-optically mode-locked and  $Q$ -switched Nd:YAG laser (Coherent Antares-76) was used to generate a pair of home-made sync pump dye lasers. The dye laser emitted trains of  $\approx 10$  pulses separated by  $13\text{ ns}$  at a repetition rate of  $500\text{ Hz}$ . The average power is  $\approx 50\text{ mW}$  and the pulse width is  $\approx 30\text{ ps}$  measured by auto-correlation function. In the ps CSRS process, a si-

multaneous pulse pair of  $\omega_1$  and  $\omega_2$  coherently excited a vibration mode at  $\omega_{v0}$ , where  $\omega_2 - \omega_1 = \omega_{v0}$ . The subsequent decay of vibration coherence was monitored by a time delayed pulse,  $\omega_1$ . The pulses are focused to  $\approx 200\text{ }\mu\text{m}$ . The CSRS signal at  $2\omega_1 - \omega_2$  was spatially filtered by an aperture and frequency filtered by a Jobin Yvon THR-1000 spectrometer. The change of intensities at the CSRS probes was detected by a photomultiplier and a lock-in amplifier. The experimental data were processed by a personal computer. The results represent the average of 10 scans. The instrumental response time of  $18\text{ ps}$  was previously reported [5].

The PT/NPH mixed crystals at various concentrations of PT were grown by Bridgman furnace. NPH was extensively zone refined and PT was only vacuum sublimed prior to use. NPD (Aldrich 98%) was used without further purification. Crystals were cleaved parallel to the  $ab$  plane. Crystal thickness ( $L$ ) was varied from  $0.2$  to  $1.0\text{ mm}$ . The samples were mounted in a flat brass plate in a Janis liquid helium cryostat. The temperature was measured by a calibrated silicon diode temperature sensor (Lake Shore Cryotronics model). Since PT may not be macroscopically uniform in these samples, it is difficult to obtain the exact values of concentration. We have measured the optical density (OD) on the spot where the CSRS data are taken. The magnitude of  $OD/L$  can vary as much as  $\pm 30\%$  for the crystals with higher concentration of PT. In every case we were very careful to examine if the sample was damaged.

## 3. Results and discussion

Fig. 1 shows the time-resolved CSRS spectra of the  $511$ ,  $766$ , and  $1385\text{ cm}^{-1}$  totally symmetric vibrons of NPH (host) in the PT/NPH molecular crystals under the influence of the electronic excitation of PT (guest). Figs. 1a–1c are measured by tuning the  $\omega_1$  away from the guest absorption (off-resonance) and figs. 1d–1f are obtained by tuning the  $\omega_1$  into the electronic transition of PT (on-resonance). The insets in fig. 1 show the semilog plots of the decay times. The decay times of  $130 \pm 10$  ps measured at off-resonance and at on-resonance for the  $511\text{ cm}^{-1}$  mode are identical to the decay time obtained in the neat NPH crystal. However, significant difference on the

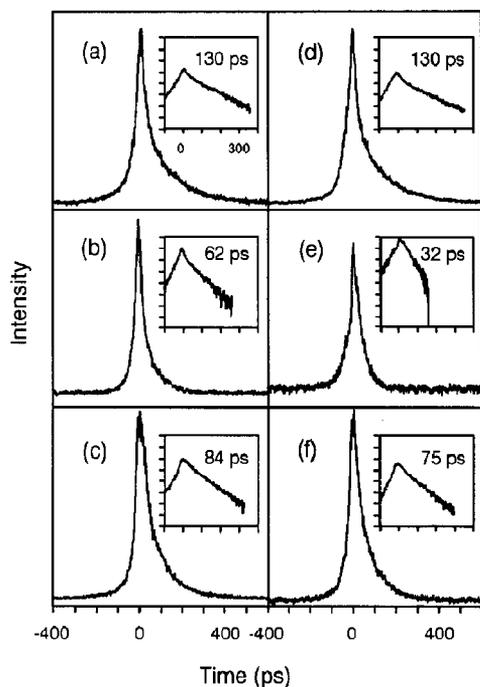


Fig. 1. Time-resolved CSRS spectra for the vibrational modes of NPH in the mixed crystals of PT doped in NPH. Spectra (a)–(c) are measured at off-resonance condition and spectra (d)–(f) are obtained at on-resonance condition. (a) and (d) present the  $511\text{ cm}^{-1}$  mode. (b) and (e) present the  $766\text{ cm}^{-1}$  mode. (c) and (f) present the  $1385\text{ cm}^{-1}$  mode. The insets show their semilog plots of ps CSRS decay. Each division in the  $y$  axis corresponds to one unit in natural log.

decay time of the  $766\text{ cm}^{-1}$  mode is observed. The decay time of  $32 \pm 3\text{ ps}$  at on-resonance shown in fig. 1e is approximately half of the decay time of  $62 \pm 3\text{ ps}$  at off-resonance shown in fig. 1b in the same crystal. In addition, the CSRS signal intensity is resonantly enhanced by one order of magnitude. It is noted that the  $62 \pm 3\text{ ps}$  measured in fig. 1b is approximately identical to the decay time measured in the neat NPH crystal [5,23,24]. The behavior of the decay time of the  $1385\text{ cm}^{-1}$  mode has been previously described [9]. The decay times are  $84 \pm 3\text{ ps}$  at off-resonance shown in fig. 1c and  $75 \pm 3\text{ ps}$  at on-resonance shown in fig. 1f, which are shorter than the decay time of  $95 \pm 5\text{ ps}$  in the neat crystal. It is found that the intensity of the  $1385\text{ cm}^{-1}$  mode on-resonance is approximately twice as strong as that off-resonance.

We first examine the origin of the shorter decay

time of the  $766\text{ cm}^{-1}$  mode on-resonance relative to off-resonance. It is known that there exists a vibrational mode of PT at  $767\text{ cm}^{-1}$ , which is near the host vibron of the  $766\text{ cm}^{-1}$  mode [6,25]. Since the width of our laser is  $\geq 2\text{ cm}^{-1}$ , the contribution from the  $767\text{ cm}^{-1}$  vibron of PT must be taken into account in the study of the  $766\text{ cm}^{-1}$  vibron of NPH. The intensity of the CSRS signal can be significantly increased for the guest vibron by resonant CSRS processes. The susceptibilities  $\chi^{(3)}$ (NPH) for a simple CSRS and  $\chi^{(3)}$ (PT) for a multi-resonant CSRS in a four-level system are given as [25–27]

$$\chi^{(3)}(\text{NPH}) = A \frac{1}{\omega_{0v} - \Delta + i\Gamma_{0v}}, \quad (1)$$

$$\chi^{(3)}(\text{PT}) = B \left[ \frac{1}{-d + \omega_{0v} - \Delta + i\Gamma_{0v}} \times \left( \frac{1}{(\omega_{0v'} - \Delta + i\Gamma_{0v'}) (d + \omega_{0v'} - \Delta + i\Gamma_{0v'})} + \frac{1}{(\omega_{0v} - \Delta + i\Gamma_{0v}) (d + \omega_{0v'} - \Delta + i\Gamma_{0v'})} + \frac{1}{(\omega_{0v'} - \Delta + i\Gamma_{0v'}) (-d + i\Gamma_{0v'})} \right) \right], \quad (2)$$

where  $|0\rangle$  and  $|0'\rangle$  correspond to the ground and excited electronic states and  $|v\rangle$  and  $|v'\rangle$  denote their vibrational states, respectively. Here  $\Gamma_{ij}$  is the damping parameter,  $\Delta = \omega_1 - \omega_2$ ,  $\omega_s = 2\omega_1 - \omega_2$  ( $\omega_1 < \omega_2$ ), and  $d = \omega_{00} - \omega_1$ , which is the detuning parameter.  $A$  and  $B$  are proportional to the transition moments. Eq. (1) indicates that  $\chi^{(3)}$ (NPH) is independent of the excitation frequency. However, eq. (2) suggests that  $\chi^{(3)}$ (PT) can be significantly enhanced when  $d$  is zero because of the multi-resonant enhancement. It has been indicated that the concentration of PT also determines the relative contribution from  $\chi^{(3)}$ (NPH) and  $\chi^{(3)}$ (PT) [28]. The shorter decay times on-resonance are normally measured by using low pulse energies. Using the same energies to repeat this experiment at off-resonance is unsuccessful; no CSRS signal is observed. It is suggested that the CSRS signal observed at low pulse energies is due to the resonant enhancement of the  $767\text{ cm}^{-1}$  vibron of PT. Therefore, the shorter decay time should be responsible for the dephasing time of the  $767\text{ cm}^{-1}$  vibron of PT.

Duppen and co-workers have measured the vibrational lifetime of dilute PT in the mixed crystals of PT/NPH [6]. They found that the decay time of the  $767\text{ cm}^{-1}$  vibron of PT is  $60 \pm 5$  ps at low temperature. In our work, the decay time of the  $766\text{ cm}^{-1}$  vibron of NPH at off-resonance is  $62 \pm 4$  ps. If the CSRS signal is only contributed by  $\chi^{(3)}$ (NPH) and  $\chi^{(3)}$ (PT), the intensity of the CSRS signal as a function of delay time can be described by [6,8]

$$I(t) = [\alpha \exp(-t/\tau_{\text{NPH}}) + \beta \exp(-t/\tau_{\text{PT}})]^2, \quad (3)$$

where  $\alpha$  and  $\beta$  correspond to the amplitudes of the contributions from host vibron and guest vibron, respectively. In eq. (3),  $\frac{1}{2}\tau_{\text{NPH}}$  is the decay time of the bulk mode and  $\frac{1}{2}\tau_{\text{PT}}$  is the decay time of the guest mode. Since their decay times of  $60 \pm 3$  and  $62 \pm 4$  ps are almost identical, the bi-exponential in eq. (3) can be simplified to a single exponential. Thus, the contribution from the  $767\text{ cm}^{-1}$  vibron of PT can be used to explain the significant enhancement of the CSRS intensity on-resonance. However, it cannot be used to describe the  $\approx 30$  ps decay time measured from the resonant spectra.

Similar results of shorter decay time on-resonance and normal decay time off-resonance were observed for the  $69\text{ cm}^{-1}$  libron mode of NPH in the PT/NPH crystals by Wilson and co-workers [8]. In addition, the signal intensity was resonantly enhanced by a factor of 10. Their results were interpreted in terms of IPD model. The existence of IPD gives rise to two distinct oscillating polarizations: one representing the phonon in the IPD with some mixing of the electronic character of impurity molecule, and the other being identical to that in the neat crystal. The lifetimes of these two types of phonons are different. The enhancement of signal is attributed to the resonantly enhanced nonlinear susceptibility of the phonon in IPD via electron-phonon coupling.

We now consider  $\chi^{(3)}$  to be the sum of the contributions from  $\chi^{(3)}$ (NPH),  $\chi^{(3)}$ (PT) and  $\chi^{(3)}$ (IPD). The form of  $\chi^{(3)}$ (IPD) is the same as that of  $\chi^{(3)}$ (PT), but the transition moment in  $\chi^{(3)}$ (IPD) takes into account the electron-phonon coupling. It is clear that both contributions from  $\chi^{(3)}$ (PT) and  $\chi^{(3)}$ (IPD) depend upon the excitation frequency and the signal should be resonantly enhanced when  $\omega_1 = \omega_{00}$ . If we assume that the single exponential decay time of  $\approx 30$  ps is attributed to

the decay time in the IPD domains, we suspect that the contribution from  $\chi^{(3)}$ (PT) should be much stronger than that from  $\chi^{(3)}$ (IPD). Otherwise, a non-exponential decay should be observed.

In order to examine the relative importance of the contributions from  $\chi^{(3)}$ (IPD) and  $\chi^{(3)}$ (PT), we have measured the intensities of  $756$  and  $767\text{ cm}^{-1}$  modes of PT in the mixed crystals of PT doped in perdeuterated naphthalene (NPD) since the corresponding vibrational mode of  $766\text{ cm}^{-1}$  in NPH is shifted to  $701\text{ cm}^{-1}$  in NPD. It is found that the ratio between the intensities of  $756$  and  $766\text{ cm}^{-1}$  signals in PT/NPH is similar to that of  $756$  and  $767\text{ cm}^{-1}$  signals in PT/NPD. It is suggested that the contribution from  $\chi^{(3)}$ (PT) to the intensity of the  $766\text{ cm}^{-1}$  signal is more dominant than that from  $\chi^{(3)}$ (IPD) in the resonant spectra of PT/NPH. The decay time of  $\approx 30$  ps measured from a single exponential decay is probably not attributed to the decay time of the  $766\text{ cm}^{-1}$  mode in the IPD domains. Furthermore, fig. 2 shows the decay times of the  $756$  and  $767\text{ cm}^{-1}$  modes of PT in NPD, which are  $60 \pm 5$  and  $30 \pm 3$  ps, respectively. The decay time of  $47 \pm 3$  ps for the  $756\text{ cm}^{-1}$

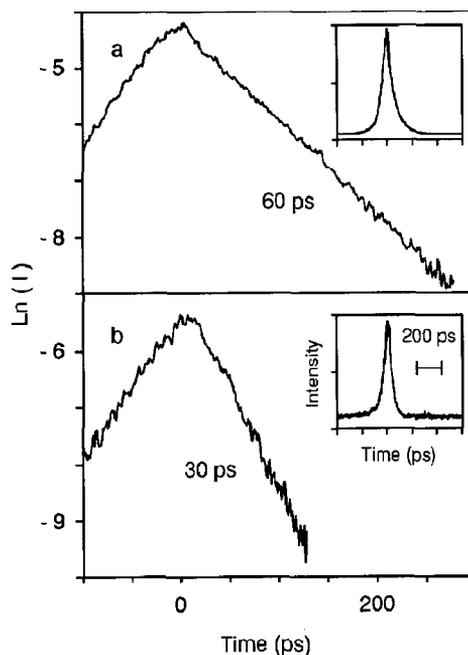


Fig. 2. Semilog plots of the decay times of  $756\text{ cm}^{-1}$  (a) and  $767\text{ cm}^{-1}$  (b) vibrons of PT in PT/NPD. The insets show their CSRS spectra.

mode of PT in NPH measured in our work agrees with the decay time of  $51 \pm 3$  ps in the literature [6,7]. Thus, we suggest that the  $\approx 30$  ps decay time is the decay time of the  $767 \text{ cm}^{-1}$  mode of PT. In addition, the power dependence study of the  $766 \text{ cm}^{-1}$  signal in PT/NPH also supports this suggestion, which will be discussed elsewhere [29].

We now turn our attention to the question why the IPD effect affects the decay of the  $1385 \text{ cm}^{-1}$  vibron but not the decay of the  $766$  and  $511 \text{ cm}^{-1}$  vibrons. Since the radiative emission processes take a longer lifetime than the radiationless processes, the contribution from harmonic term to the linewidth is negligible and the harmonic approximation is inadequate to describe the spectral linewidth. According to the many-body perturbation theory [30], the first anharmonic term contributing to the linewidth is given by

$$\Gamma = (36/\hbar^2) \sum_A \sum_P |V_{\Delta A P}^{(3)}|^2 \times [(n_A + n_P + 1)\delta(\omega - \omega_A - \omega_P) + (n_P - n_A)\delta(\omega - \omega_A + \omega_P)], \quad (4)$$

where  $V^{(3)}$  is a cubic anharmonic coefficient, and  $\delta(\omega)$  is a delta function which accounts for the phonon density of state at  $\omega_P$ . In eq. (4),  $n_A$  and  $n_P$  are the thermal occupation numbers of the acceptor and the phonon states, where  $n_P(T) = [\exp(\hbar\omega_P/k_B T) - 1]^{-1}$  and  $n_A(T)$  is negligible at low temperature. At low temperatures ( $T \leq 30$  K), the second term in eq. (4) can be neglected since it requires thermal population of the  $\omega_P$  phonons. Furthermore, eq. (4) indicates that the decay time can be shorter if the magnitudes of  $V^{(3)}$  and the phonon distribution at  $\omega_P$  are larger.

In the cubic anharmonic approximation [24,30,31], vibrational relaxation of an excited vibron,  $Q_V$ , can involve a phonon of  $q_P$  and an acceptor vibron of  $Q_A$  via the coupling terms of  $Q_V Q_A q_P$ . The energy of  $q_P$  corresponds to the energy difference between two vibrons. Table 1 collects the possible decay channels via cubic anharmonic coupling for these three vibrons [24,28,31]. In our previous study on the  $1385 \text{ cm}^{-1}$  mode [9], a lattice phonon at  $20 \text{ cm}^{-1}$  for the energy conservation of the decay channel from the  $1385 \text{ cm}^{-1}$  mode to the  $1365 \text{ cm}^{-1}$  mode is approximately identical to the  $18 \text{ cm}^{-1}$  of

Table 1  
The decay pathways via cubic anharmonic coupling for different vibrons [24]

$511 \text{ cm}^{-1}$	$766 \text{ cm}^{-1}$	$1385 \text{ cm}^{-1}$
480	725	1365
467	620	1274
390	618	1240
362		

the pseudolocal phonon mode reported by Hesselink and Wiersma [12]. It implies that the phonon distribution at  $20 \text{ cm}^{-1}$  is dramatically perturbed by the electron-phonon coupling. We believe that the increase of phonon distribution at  $20 \text{ cm}^{-1}$  due to the impurity excitation is responsible for the shorter decay time in the IPD of the  $1385 \text{ cm}^{-1}$  vibron. Table 1 lists that the nearest decay channel for the  $511 \text{ cm}^{-1}$  vibron involves a vibron at  $480 \text{ cm}^{-1}$  and a lattice phonon at  $31 \text{ cm}^{-1}$  and that for the  $766 \text{ cm}^{-1}$  vibron involves a vibron at  $725 \text{ cm}^{-1}$  and a lattice phonon at  $41 \text{ cm}^{-1}$  in the neat NPH crystal. Since both phonon energies are much larger than the pseudolocal phonon energy, the phonon distributions of these two modes are less perturbed by the impurity excitation. This is probably the reason why we do not observe the IPD effect on these two low-frequency modes.

Temperature-dependence spectra of the  $511$  and  $1385 \text{ cm}^{-1}$  modes at on-resonance are shown in fig. 3. For the  $511 \text{ cm}^{-1}$  mode, the decay time of  $124$  ps at  $7$  K is approximately identical to that of  $121$  ps at  $21$  K. It is known that the vibrational decay in the pure NPH crystal is independent of temperature until  $T \approx 40$  K [24,28]. It is confirmed that the impurity excitation does not affect the decay of the  $511 \text{ cm}^{-1}$  vibron. A similar result is observed for the  $766 \text{ cm}^{-1}$  mode. However, the  $1385 \text{ cm}^{-1}$  mode exhibits longer decay times at higher temperatures ( $\approx 17$  K) than those at low temperatures ( $\approx 6$  K) as shown in fig. 3. This inverse temperature behavior has been described by the Born-Oppenheimer approximation model of vibrational relaxation [9,20-22]. In this theory, the frequencies of the vibrons are much larger than those of the phonons so that the adiabatic type of approximation can be used to separate the Hamiltonian into the vibron motion and phonon motion. This approximation model predicts that a small value

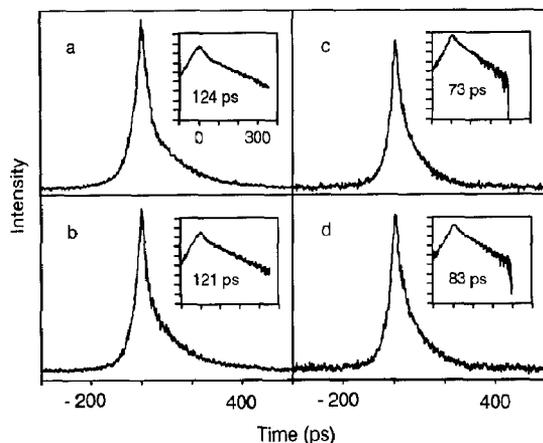


Fig. 3. Temperature-dependent time-resolved CSRS spectra of the 511 and 1385  $\text{cm}^{-1}$  vibrons of NPH in PT/NPH. (a) 511  $\text{cm}^{-1}$  mode at 7 K, (b) 511  $\text{cm}^{-1}$  mode at 21 K, (c) 1385  $\text{cm}^{-1}$  mode at 6 K, and (d) 1385  $\text{cm}^{-1}$  mode at 17 K. The insets show their semilog plots of ps CSRS decay.

of  $\omega_p$  favors the inverse temperature effect in the weak coupling limit. According to the previous study [9], an average phonon frequency of 20  $\text{cm}^{-1}$  is able to describe the inverse temperature effect of the 1385  $\text{cm}^{-1}$  mode, which is consistent with the IPD model. Therefore, it is possible that the phonon distribution of 20  $\text{cm}^{-1}$  perturbed by the electron-phonon coupling promotes the decay from the 1385  $\text{cm}^{-1}$  mode to the 1365  $\text{cm}^{-1}$  mode by stimulating phonon emission. This mechanism provides a shorter decay time for the 1385  $\text{cm}^{-1}$  vibron in the IPD.

In summary, we have studied the vibrational dephasing of the 511, 766, and 1385  $\text{cm}^{-1}$  modes of host molecule (NPH) perturbed by an electronically excited guest (PT) molecule using the time-resolved CSRS method. The decay times of the 511  $\text{cm}^{-1}$  mode are  $125 \pm 10$  ps for both on-resonance and off-resonance, which are identical to the decay time in the neat NPH crystals. Shorter decay time on-resonance of the 766  $\text{cm}^{-1}$  CSRS signal is attributed to the decay time of resonant enhancement of the 767  $\text{cm}^{-1}$  mode of PT. Therefore, we believe that the impurity excitation plays no significant effect on these two vibrons. However, shorter decay time on-resonance than off-resonance for the 1385  $\text{cm}^{-1}$  mode is observed, which can be described by the IPD model. The increase of phonon distribution at 20  $\text{cm}^{-1}$  perturbed by the electron-phonon coupling is respon-

sible for the shorter decay time in the IPD.

To the best of our knowledge, the vibrational dephasing of host vibrons affected by the electron-phonon coupling is observed for the first time. It is known that electron-phonon coupling does not determine the vibrational relaxation. In fact, no significant effects on the decay times of the two host vibrons (511 and 766  $\text{cm}^{-1}$ ) by the impurity excitation are observed in this work. However, the presence of the pseudolocal phonon mode indicates that this coupling could perturb the phonon distribution. If a lattice phonon at specific frequency (20  $\text{cm}^{-1}$  in this case) is significantly perturbed by electron-phonon coupling, which also couples to a vibrational decay channel (from 1385 to 1365  $\text{cm}^{-1}$ ) via cubic anharmonic coupling, the decay of this vibron (1385  $\text{cm}^{-1}$ ) can be shorter. Further attempts to study the IPD effect on the deuterated PT doped in NPH are planned.

#### Acknowledgement

This work was supported by Academia Sinica and the NSC of the Republic of China (Grant No. NSC-82-0208-M-001-053). TCC acknowledges Professor D.D. Dlott at the University of Illinois, Professor S.H. Lin at Arizona State University and Professor T.S. Lin at Washington University for their valuable advice and discussion. The authors also wish to thank the referee for useful suggestions.

#### References

- [1] F. Ho, W.-S. Tsay, J. Trout, S. Velsko and R.M. Hochstrasser, *Chem. Phys. Letters* 97 (1983) 141.
- [2] S. Velsko and R.M. Hochstrasser, *J. Chem. Phys.* 82 (1985) 2180.
- [3] E.L. Chronister and D.D. Dlott, *J. Chem. Phys.* 79 (1983) 5286.
- [4] E.L. Chronister, J.R. Hill and D.D. Dlott, *J. Chim. Phys.* 82 (1985) 159.
- [5] T.-C. Chang, B.H. Jou, R.S. Ou, C.C. Chiang and H.W. Li, *Chem. Phys. Letters* 187 (1991) 208.
- [6] K. Duppen, D.P. Weitekamp and D.A. Wiersma, *J. Chem. Phys.* 79 (1983) 5835.
- [7] D.P. Weitekamp, K. Duppen and D.A. Wiersma, *Phys. Rev. A* 27 (1983) 3089.

- [8] W.L. Wilson, G. Wackerle and M.D. Fayer, *J. Chem. Phys.* 87 (1987) 2498.
- [9] T.-C. Chang, S.H. Chou, H.W. Li and S.H. Lin, *J. Chem. Phys.*, in press.
- [10] D.E. McCumber and M.D. Sturge, *J. Appl. Phys.* 34 (1963) 1682.
- [11] G.J. Small, *Chem. Phys. Letters* 57 (1978) 501.
- [12] W.D. Hesselink and D.A. Wiersma, *J. Chem. Phys.* 73 (1980) 648.
- [13] V.M. Agranovich and R.M. Hochstrasser, eds., *Spectroscopy and excitation dynamics of condensed molecular systems* (North-Holland, Amsterdam, 1983).
- [14] F.G. Patterson, W.L. Wilson, H.W.H. Lee and M.D. Fayer, *Chem. Phys. Letters* 110 (1984) 7.
- [15] D. Hsu and J.L. Skinner, *J. Chem. Phys.* 83 (1985) 2107.
- [16] R.W. Olson, J.S. Meth, C.D. Marshall, V.J. Newell and M.D. Fayer, *J. Chem. Phys.* 92 (1990) 3323.
- [17] J.G. Fujimoto, J.M. Liu, E.P. Ippen and N. Bloembergen, *Phys. Rev. Letters* 53 (1984) 1837.
- [18] E.E. Aksenov, E.M. Gershenson, G.N. Gol'tsman, A.D. Semenov and A.V. Sergeev, *JETP Letters* 50 (1989) 283.
- [19] K.R. Eisenthal, ed., *Application of picosecond spectroscopy to chemistry* (Reidel, Dordrecht, 1984).
- [20] M. Born and R. Oppenheimer, *Ann. Physik* 84 (1927) 457.
- [21] S.H. Lin, *J. Chem. Phys.* 44 (1966) 3759.
- [22] S.H. Lin, *J. Chem. Phys.* 65 (1976) 1053.
- [23] B.H. Hesp and D.A. Wiersma, *Chem. Phys. Letters* 75 (1980) 423.
- [24] C.L. Schosser and D.D. Dlott, *J. Chem. Phys.* 80 (1984) 1394.
- [25] T.-C. Chang, C.K. Johnson and G.J. Small, *J. Phys. Chem.* 89 (1985) 2984.
- [26] N. Bloembergen, H. Lotem and R.T. Lynch, *Indian J. Pure Appl. Phys.* 16 (1978) 151.
- [27] J.R. Andrews and R.M. Hochstrasser, *Chem. Phys. Letters* 82 (1981) 381.
- [28] T.-C. Chang, T.Y. Liu, H.M. Wu and H.W. Li, *Chem. Phys. Letters* 197 (1992) 476.
- [29] T.-C. Chang, S.H. Chou and H.W. Li, manuscript in preparation.
- [30] S. Califano, V. Schettino and N. Neto, *Lattice dynamics of molecular crystals* (Springer, Berlin, 1981).
- [31] P. Ranson, R. Ouillon and S. Califano, *Chem. Phys.* 86 (1984) 115.