

# Multiplex picosecond coherent Stokes Raman spectroscopy of pentacene doped in naphthalene

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We present a study of the multiplex picosecond CSRS experiments of the mixed crystals of pentacene doped in naphthalene. By this method we are able to measure vibrational decay times from different species simultaneously. The shorter decay time measured for the  $1385\text{ cm}^{-1}$  mode of naphthalene while increasing the concentration of pentacene and tuning the pump frequency near the absorption transition may be interpreted by the model of impurity perturbed domains.

## 1. Introduction

Synchronously pumped dye lasers have been extensively applied to study a variety of pump-probe and nonlinear optical experiments because of the high pulse energy, the high repetition rates, and the broad spectral tunability [1-6]. Another advantage, not generally recognized until recently, is that variable bandwidths can be easily obtained. Using a narrow-band laser for the pump and the time-delayed probe beams and a broad-band laser for the anti-Stokes beam for generating the CSRS signals, an entire time-resolved CSRS spectrum can be taken simultaneously. This spectrum can provide unambiguous identification of multiple species and their dynamical processes. Multiplex CSRS on a fast time scale is particularly useful for the study of molecular relaxation and energy transfer processes.

Time-resolved CARS (CSRS) has been used to measure the vibrational relaxation of molecular crystals [3-9]. Wiersma and co-workers [10,11] used the multi-resonant ps CARS to study the vibrational relaxation of impurity. Multiplex CARS has been applied to measure the temperature variations

and species concentration in combustion and to study the rotational spectra in gases [12-14]. Recently, Bloembergen and co-workers [15] have used time-resolved multiplex CARS at various delay times in the nanosecond and microsecond range to study the intramolecular vibrational energy distributions in infrared multiphoton excited OCS in the collisional regime. In this work, we present the first multiplex picosecond CSRS experimental results to demonstrate that this method is able to simultaneously measure the decay times of different vibrational modes. It should be noted that the CSRS spectra instead of the CARS spectra were taken simply because it was easier to filter the laser beams for protecting the diodes in the optical multichannel analyzer (OMA).

In this work, we have measured the decay times for the  $511$ ,  $766$ , and  $1385\text{ cm}^{-1}$  modes of naphthalene (NPH) crystals at low temperature by using either a narrow-band or a broad-band anti-Stokes beam. We have performed the multiplex ps CSRS experiments of pentacene (PT) doped in naphthalene (NPH) to measure the decay times from the  $1371\text{ cm}^{-1}$  mode of PT and the  $1385\text{ cm}^{-1}$  mode of NPH simultaneously by tuning  $\omega_1$  near the absorption of PT. It is found that the decay time for the  $1385\text{ cm}^{-1}$  mode of the host decreases as the concentration of PT increases. However, the change of decay time differs from that in the isotopically mixed

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crystals, which shows very little effect even adding 10% of perdeuterionaphthalene (NPD) [7–9]. In addition, the decay time is slightly shorter when the excitation frequency is near the absorption of impurity. Similar results of shorter decay time on-resonance and normal decay time off-resonance were observed in the study of the coupling between impurity electronic states and bulk phonons [16]. The impurity-perturbed domains (IPD) model proposed by Fayer and co-workers [16] is discussed for describing our results.

## 2. Experimental

The ps CARS experimental setup is fairly conventional in design, which has been described previously [11]. In the multiplex ps CSRS experiments, a tunable dye laser with fwhm of  $2\text{ cm}^{-1}$  is obtained by tuning a dense flint glass prism and a  $100\text{ }\mu\text{m}$  étalon on the rotation stages. A broad band dye laser with fwhm of  $120\text{ cm}^{-1}$  is obtained by only tuning a thin étalon on a rotation stage. The average power is  $\approx 100\text{ mW}$  for the broad band dye laser and  $\approx 30\text{ mW}$  for the narrow band dye laser. Rhodamine 590 and rhodamine 610 dyes dissolved in methanol are employed for the two dye lasers, respectively. The dye laser emitted trains of  $\approx 10$  pulses separated by  $13\text{ ns}$  at a repetition rate of  $500\text{ Hz}$ . The pulse width for the narrow band dye laser is  $\approx 30\text{ ps}$  measured by an auto-correlation function. If one ignores a small central spike in the auto-correlation profile for the  $120\text{ cm}^{-1}$  bandwidth dye laser, the pulse width is  $\approx 45\text{ ps}$ . It is noted that the spike is not observed in the cross-correlation profile.

In the multiplex ps CSRS process, a simultaneous pulse pair of  $\omega_1$  with narrow bandwidth and  $\omega_2$  with broad bandwidth coherently excited all the vibrational modes. The subsequent decays of vibrational coherence were monitored by a time-delayed pulse  $\omega_1$ . The CSRS process generates all CSRS signals for which the frequency and phase conditions are fulfilled. The resulting CSRS signals were spatially filtered by an aperture, frequency filtered by a red-pass filter, and then dispersed in a  $275\text{ mm}$  spectrograph (Acton Research Corp.) equipped with a  $1200\text{ grooves/mm}$  grating and detected by a OMA (IRY-1024G/B Princeton Instruments). The experimen-

tal results were first collected for every  $3\text{ ps}$  by moving the optical delay line and stored in a personal computer. The changes of the CSRS intensity as a function of time for the  $1371\text{ cm}^{-1}$  mode of PT and the  $1385\text{ cm}^{-1}$  mode of NPH were simultaneously detected by the OMA. The results represent the average of 10 scans.

The PT/NPH mixed crystals with different concentration of PT were grown by Bridgman furnace using extensively zone-refined NPH. The crystal was cleaved parallel to the *ab* plane. Crystal thickness (*L*) was varied from  $0.2$  to  $1\text{ mm}$ . Since the concentration of PT is not macroscopically uniform in these samples, we have measured the optical density (OD) on the spot where the CSRS data are taken. Therefore, we use the ratio of OD/*L* instead of the molar concentration of PT for the concentration study. The OD was measured by locating a broad-band laser with fwhm of  $\approx 5\text{ }\text{Å}$  at the absorption of PT and scanning a spectrometer to find a minimum transmission and then inserting a  $100\text{ }\mu\text{m}$  étalon to narrow the width to  $1.5\text{ cm}^{-1}$ . The magnitude of OD/*L* can be deviated as large as  $\pm 30\%$  for the crystals with higher concentration of PT. The electronic transition of PT is located at  $\approx 6027\text{ Å}$ . Samples with clear transparency were mounted in a flat brass plate in a Janis liquid helium cryostat, and the temperature was maintained at  $\approx 6\text{ K}$ .

## 3. Results and discussion

We have first measured the  $511$ ,  $766$ , and  $1385\text{ cm}^{-1}$  modes of neat NPH crystals by using either a narrow band or a broad band for the Stokes beam at  $6\text{ K}$ . Our measurement of their lifetimes shows that the decay times measured by either method are approximately identical, which are listed in table 1. This result leads us to examine the feasibility of multiplex ps CARS for measuring vibrational decay times from different species simultaneously.

Fig. 1 shows an energy diagram of a four-level system for describing the multi-resonant CSRS process, 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. It is known that the intensity of the CSRS signal is mainly determined by the third-order susceptibility. The suscep-

Table 1  
Lifetimes of naphthalene vibrations at 6 K

Frequency (cm <sup>-1</sup> )	Lifetime <sup>a)</sup> (ps)	Lifetime <sup>b)</sup> (ps)	Lifetime <sup>c)</sup> (ps)	Lifetime <sup>d)</sup> (ps)	Lifetime <sup>e)</sup> (ps)
511	135 ± 10	128 ± 10		136 ± 13	128
766	69 ± 3	69 ± 3	68 ± 3	78 ± 4	62
1385	97 ± 3		97 ± 6	98 ± 9	91

<sup>a)</sup> Obtained by using a narrow band width for the Stokes beam.

<sup>b)</sup> Obtained by using a broad band width of 20 cm<sup>-1</sup> for the Stokes beam.

<sup>c)</sup> Obtained by using a broad band width of 120 cm<sup>-1</sup> for the Stokes beam.

<sup>d)</sup> Ref. [3]. <sup>e)</sup> Ref. [7].

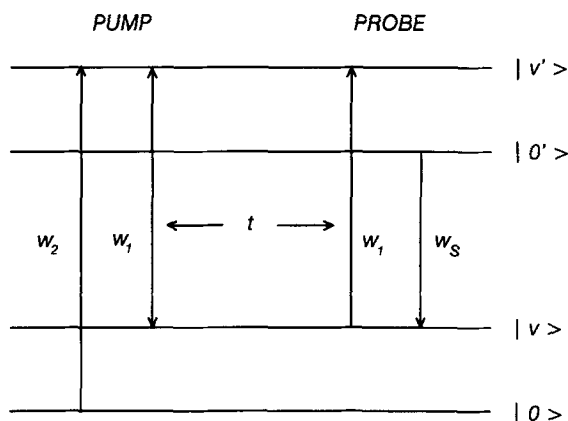


Fig. 1. Energy diagram of a four-level system for the multi-resonant time-resolved CSRS.

ibilities  $\chi^{(3)}$  for the simple CSRS and multi-resonant CSRS in a four-level system are well known [17–20] and are given by

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

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

where  $A$  and  $B$  are proportional to the transition mo-

ments.  $\Delta = \omega_1 - \omega_2$ ,  $\omega_s = 2\omega_1 - \omega_2$  ( $\omega_1 < \omega_2$ ), and  $d = \omega_{0'0} - \omega_1$ , which is the detuning parameter.  $\Gamma_{ij}$  is the damping parameter. From eq. (2), the magnitude of  $\chi^{(3)}$  (PT) can be significantly increased when  $d$  approaches either 0 or  $\Delta - \omega_{0'v}$ . The details of multi-resonant ps CSRS (CSRS) have been described by Wiersma and co-workers [10,11]. The decay time of  $46 \pm 3$  ps for the  $756 \text{ cm}^{-1}$  mode of PT measured in our work agrees with the decay time of 51 ps in their results.

We have performed the multiplex ps CSRS experiments for simultaneously measuring the decay times of the  $756 \text{ cm}^{-1}$  mode of PT and the  $766 \text{ cm}^{-1}$  mode of NPH. Unfortunately, our spectral resolution is not able to distinguish them. Fig. 2 shows the multiplex ps CSRS spectra of the  $1371 \text{ cm}^{-1}$  vibrational mode of PT and the  $1385 \text{ cm}^{-1}$  vibrational mode of NPH, which were obtained by using a narrow band at 603 nm for both the pump and the time delay probe beams and a broad band centered at 558 nm for the anti-Stokes beam at low temperature. It is clear that the signal of the  $1371 \text{ cm}^{-1}$  mode disappears much earlier than the signal of the  $1385 \text{ cm}^{-1}$  mode. Figs. 2b and 2c were simultaneously detected by scanning the optical delay time. Their decay times measured from figs. 2b and 2c are 18 ps and  $70 \pm 10$  ps, respectively. We have not found the decay time for the  $1371 \text{ cm}^{-1}$  mode of NPH in the literature. Since the instrumental response time presented in fig. 3a is 18 ps, the decay time for the  $1371 \text{ cm}^{-1}$  mode is probably shorter than 18 ps. It is known that the decay time for the  $1385 \text{ cm}^{-1}$  mode in the neat NPH crystals is  $97 \pm 10$  ps [3,7–9]. The semilog plot of the  $1385 \text{ cm}^{-1}$  peak is shown in fig. 3b. The decay time of  $70 \pm 10$  ps for the  $1385 \text{ cm}^{-1}$  mode in the PT/NPH

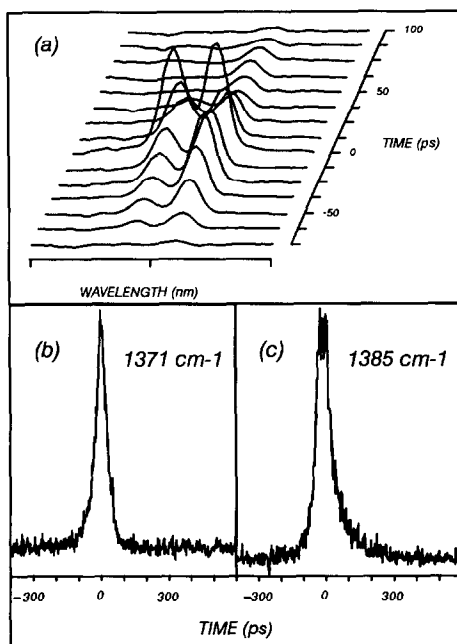


Fig. 2. (a) shows the OMA spectra obtained by moving the optical delay line for every  $\approx 13$  ps, (b) and (c) for the  $1371$  and  $1385$   $\text{cm}^{-1}$  vibrational modes, respectively, were simultaneously collected as a function of time by OMA.

crystals is shorter than that in the neat NPH crystals. This decay time is further examined by using the conventional ps CSRS method, which is shown in fig. 3c. The decay times measured in figs. 3b and 3c are  $70 \pm 10$  ps. The same results confirm that the decay time of  $70 \pm 10$  ps for the  $1385$   $\text{cm}^{-1}$  mode is real and multiplex ps CSRS is able to measure the decay times of different vibrational modes simultaneously. However, if we tuned the wavelength of the pump pulse to  $6055$  Å, the  $1371$   $\text{cm}^{-1}$  peak was absent. It indicates that multi-resonant ps CSRS (CARS) is suitable to probe the vibrations of dilute impurity.

The next question is to examine why the decay time of the host vibron is shorter in the PT/NPH mixed crystals with the impurity concentration in the order of  $10^{-5}$  m/m. Fig. 4 presents the plots of decay time versus OD/L for the  $1385$   $\text{cm}^{-1}$  mode at different excitation frequencies. It is found that the decay time for the  $1385$   $\text{cm}^{-1}$  mode decreases when the concentration of PT increases. In the isotopically mixed crystals of NPH and NPD [7–9], little effect on the vibrational decay of the  $1385$   $\text{cm}^{-1}$  mode was re-

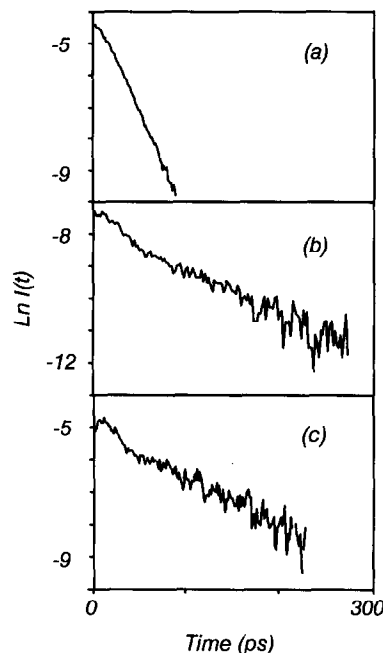


Fig. 3. The semilog plots of ps CSRS decay for the  $1385$   $\text{cm}^{-1}$  mode of neat NPH. (a) provided the instrumental response time. (b) was obtained by using a broad band for the anti-Stokes beam. (c) was obtained by using the conventional ps CSRS.

ported even for 10% NPD. The miniscule amount of PT compared to the amount of NPD suggests that the impurity concentration does not directly affect the bulk mode. In addition, the decay time is slightly shorter near the resonance than off the resonance for the crystals with higher concentration of PT. It should be noted that the intensity of the CSRS signal for the off-resonance is about half of the intensity for the near-resonance.

Recently, Fayer and co-workers [16] have examined the coupling between impurity electronic states and bulk phonons. They found that the decay time of  $69$   $\text{cm}^{-1}$  libron mode of NPH in the PT/NPH crystals at low temperature was  $130 \pm 10$  ps when all the laser beams were tuned to the red of PT absorption, which was identical to the decay time of this mode in the pure NPH crystal. However, the decay time of this mode was  $40 \pm 10$  ps when  $\omega_1$  was tuned into the PT absorption. Further, the signal was resonantly enhanced by a factor of 10 in intensity. They interpreted their results in terms of impurity perturbed domains (IPD).

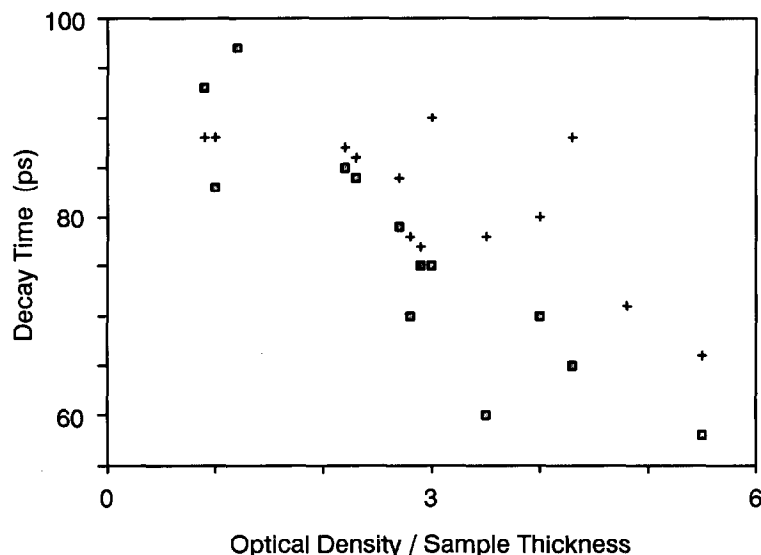


Fig. 4. Concentration dependence of the decay times of the  $1385\text{ cm}^{-1}$  mode in the PT/NPH mixed crystals at different excitation frequency, (□):  $6027\text{ \AA}$  and (+):  $6065\text{ \AA}$ . Typical deviation of the decay time is  $\pm 5\%$ .

In the IPD model [16], two Raman active oscillators contribute to the nonlinear susceptibility, which involve  $\chi^{(3)}$ (NPH) and  $\chi^{(3)}$ (IPD). Without considering the nonresonant background the  $\chi^{(3)}$  is given as

$$\chi^{(3)} = \chi^{(3)}(\text{NPH}) + \chi^{(3)}(\text{IPD}), \quad (3)$$

where  $\chi^{(3)}$ (NPH) corresponds to the measurement in the neat crystals and  $\chi^{(3)}$ (IPD) represents the measurement of the bulk vibrons admixed with impurity electronic character via electron-phonon coupling. In this case, one should observe two distinct CSRS signals characterized by their own frequencies and decay times. The form of  $\chi^{(3)}$ (IPD) is similar to the form of  $\chi^{(3)}$ (PT). However, the transition moment in  $\chi^{(3)}$ (IPD) differs from that in  $\chi^{(3)}$ (PT), which takes into account the electron-phonon coupling. This coupling is evident because of the presence of the phonon sideband. Only the coupling terms associated with the  $1385\text{ cm}^{-1}$  mode with specific wave vectors due to the coherent excitation were enhanced. Thus,  $\chi^{(3)}$ (IPD) can be dominant when  $d$  is small because of the multi-resonant enhancement and  $\chi^{(3)}$ (NPH) is dominant when  $d$  is large. Furthermore, it is reasonable that  $\chi^{(3)}$ (IPD) can be dominant when the local concentration of PT is

higher because of the increase of electron-phonon coupling.

In addition, a preliminary study of the  $766\text{ cm}^{-1}$  mode of NPH in the PT/NPH crystals shows a shorter decay time of  $\approx 30\text{ ps}$  on-resonance and a normal decay time  $\approx 60\text{ ps}$  off-resonance [21]. Furthermore, the CSRS intensity of this mode was also significantly enhanced when  $\omega_1 = \omega_{00}$ , which agrees to the IPD prediction [16]. Thus, we suggested that the shorter decay time measured near the resonance for the  $1385\text{ cm}^{-1}$  mode is attributed to the electron-phonon coupling based on the IPD model. In the crystals with high concentration of PT, the increase of the  $\chi^{(3)}$ (IPD) contribution resulting from the increase of the number of domains could significantly modify the decay. Therefore, one may estimate the magnitude of the IPD as a function of local concentration [22]. However, the possibility of a variety of impurity domain types should be considered. More detail examination on the IPD model and mode specific effect for this system in order to better understand the nature of electron-phonon coupling is in progress.

In summary, we have demonstrated that multiplex ps CSRS can be used to measure the decay times from different species simultaneously. We further find that the decay time of the vibrational mode of NPH is

shorter when the local concentration of PT increases and the excitation frequency is near the resonant transition, which is attributed to the increase of electron-phonon coupling. This behavior is tentatively described by the IPD model.

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### References

- [1] D.J. Kuizenge, D.W. Phillion, T. Lund and A.E. Siegman, *Opt. Commun.* 9 (1973) 221.
- [2] A. Laubereau and W. Kaiser, *Rev. Mod. Phys.* 50 (1978) 608.
- [3] B.H. Hesp and D.A. Wiersma, *Chem. Phys. Letters* 75 (1980) 423.
- [4] F. Ho, W.-S. Tsay, J. Trout and R.M. Hochstrasser, *Chem. Phys. Letters* 83 (1981) 5.
- [5] G. Eyring and M.D. Fayer, *J. Chem. Phys.* 81 (1984) 4314.
- [6] T.-C. Chang and D.D. Dlott, *Chem. Phys. Letters* 147 (1988) 18.
- [7] E.L. Chronister and D.D. Dlott, *J. Chem. Phys.* 79 (1983) 5286.
- [8] E.L. Chronister, J.R. Hill and D.D. Dlott, *J. Chim. Phys.* 82 (1985) 159.
- [9] T.-C. Chang, B.H. Jou, R.S. Ou, C.C. Chiang and H.W. Li, *Chem. Phys. Letters* 187 (1991) 208.
- [10] K. Duppen, D.P. Weitekamp and D.A. Wiersma, *J. Chem. Phys.* 79 (1983) 5835.
- [11] D.P. Weitekamp, K. Duppen and D.A. Wiersma, *Phys. Rev. A* 27 (1983) 3089.
- [12] W.B. Roh, P. Schreiber and J.P.E. Taran, *Appl. Phys. letters* 29 (1976) 174.
- [13] L.P. Goss, J.W. Fleming and A.B. Harvey, *Opt. Letters* 5 (1980) 345.
- [14] J.A. Shirley, R.J. Hall and A.C. Eckbreth, *Opt. Letters* 5 (1980) 380.
- [15] K.-H. Chen, C.-Z. Lu, L.A. Aviles, E. Mazur, N. Bloembergen and M.J. Shultz, *J. Chem. Phys.*, in press.
- [16] W.L. Wilson, G. Wackerle and M.D. Fayer, *J. Chem. Phys.* 87 (1987) 2498.
- [17] N. Bloembergen, H. Lotem and R.T. Lynch, *Indian J. Pure Appl. Phys.* 16 (1978) 151.
- [18] T.-C. Chang, C.K. Johnson and G.J. Small, *J. Phys. Chem.* 89 (1985) 2984.
- [19] J.R. Andrews and R.M. Hochstrasser, *Chem. Phys. Letters* 82 (1981) 381.
- [20] T.-C. Chang Ph.D. Thesis, Iowa State University (1985).
- [21] T.-C. Chang, H.W. Li and T.C. Hsieh, in preparation.
- [22] D.D. Dlott, private communication.