University of Groningen

Picosecond Tri-Transition and Two-Color Photon Echoes in a Doped Molecular Solid

Duppen, Koos; Weitekamp, D.P.; Wiersma, Douwe A.

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

[Link to publication in University of Groningen/UMCG research database](#)

PICOSECOND TRI-TRANSITION AND TWO-COLOR PHOTON ECHOES
IN A DOPED MOLECULAR SOLID

Koos DUPPEN, D.P. WEITEKAMP * and Douwe A. WIERSMA

Picosecond Laser and Spectroscopy Laboratory, Department of Physical Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Picosecond tri-level photon echoes are generated among vibronic transitions of pentacene doped into a naphthalene host. The echoes are generated with three excitation pulses of which the first one, at ω_1, always excites a vibronic transition in the pentacene molecule. With the second excitation pulse at ω_2 and the third at ω_1, a tri-transition echo (TTE) is formed. With the time ordering of the second and third pulse reversed, a connected two-color stimulated echo (C2CSE) is generated. It is shown that, for small pulse angles, the low-temperature decay of both echo effects is identical and that a smooth transition of one echo effect into the other occurs at the overlap in time between the second and third excitation pulse. Observation of these echoes further indicates that the inhomogeneous broadening at the selected transitions is strongly correlated.

1. Introduction

Picosecond pulse optical coherence experiments are beginning to have a considerable impact in the field of optical spectroscopy. In the past decade it was mainly through photon echo experiments and their Fourier transform (photochemical) hole burning, that the microscopic detail of optical dynamics in mixed crystals [1], ionic solids [2] and recently glasses [3] was elicited. Another new development in the field of molecular solids is the use of the one-color stimulated photon echo as a probe for population dynamics, as e.g. intersystem crossing [4]. When optical pulses of two different frequencies are used, a variety of new phenomena can be observed as two-color photon echoes [5] and time-resolved four-wave mixing [6]. When the optical fields are brought into resonance with the optical transitions of the system, in fact, the latter effects are only distinct through different time ordering of the optical pulses [7].

In a recent paper [8] we reported results of a time-resolved multi-resonant four-wave mixing (CARS) study of some vibrational transitions on the ground-state

potential energy surface of pentacene in a naphthalene crystal. One of the surprising results obtained was that these vibrational transitions showed no evidence for inhomogeneous broadening. This sharply contrasts with the situation for the electronic transitions in the molecule, which show an inhomogeneous component of about 1 cm^{-1}. The interesting implication of the CARS study was that in this system the inhomogeneous broadening at different optical (vibronic) transitions is completely correlated. The presence or absence of such a correlation is crucial to the success or failure of achieving line narrowing in dispersive four-wave mixing experiments [7,9]. In this context it is interesting to note that for the mixed crystal of pentacene in benzoic acid, the different vibronic transitions were shown *not* to be fully correlated [10]. In view of the importance of establishing the abovementioned correlation in the system pentacene in naphthalene, we decided to try and perform two-color photon echo [5] experiments on the system. A prerequisite to observation of these echoes is that full correlation exists on the excited transitions, as e.g. is the case for Doppler-broadened transitions in the gas phase.

In this paper we report observation of two distinct tri-level echoes arising from a different time ordering of the second and third excitation pulse. The appro-

* Present address: Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, USA.
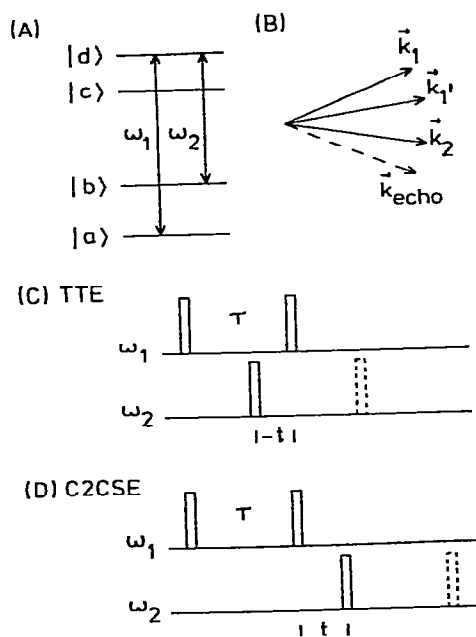
Fig. 1. (A) Level scheme. |a⟩ is the ground state of pentacene and |b⟩ a vibrationally excited state at 756 cm^{-1}. |d⟩ is the corresponding vibrationally excited state in the electronically excited manifold, 747 cm^{-1} above the vibrationless level at |c⟩. Frequency ω_1 is resonant with the vibronic transition at ω_{da} (17335 cm^{-1}) and ω_2 is resonant with ω_{db} (16579 cm^{-1}). (B) Phase matching. The angles between the beams are ≈1°. The chosen geometry gives the echo spatial separation from the exciting beams at the expense of a slight k-vector mismatch in the forward direction. (C) Pulse sequence for the tri-transition-echo (TTE). The time between the two pulses at ω_1 is τ = 60 ps. The echo appears at roughly this same time period after the pulse at ω_2, which is given a variable delay. (D) Pulse sequence for the connected two-color stimulated echo (C2CSE). The time separations between the two pulses at ω_1 and the probe and the echo at ω_2 are the same as in C.

priate level scheme and phase matching is shown in figs. 1 A and 1 B. In figs. 1 C and 1 D the different time orderings used for the second and third pulse are shown. The echo excited in case (C) we call a tri-transition echo (TTE). This rephasing effect is closely related to the tri-level echo [5] but involves three distinct dephasing times T_2^{ij}. The echo observed for case B we call a connected two-color stimulated echo (C2CSE), which of course is also a tri-level echo but it is a stimulated echo which is sensitive to other dephasing effects than the TTE.

2. Experimental

The experimental arrangement consists of two synchronously pumped dye lasers producing rains of ps pulses at a rate of 82 MHz. A Nd–YAG laser, operating at 10 Hz, was used to amplify these pulses to single-pulse energies of ≈10 μJ. The individual pulses had a duration of about 6 ps, as determined from autocorrelation traces and the jitter in time between the two pulses was found to be ≈7 ps, giving rise to a cross correlation of 11 ps. For a detailed description of the apparatus we refer to ref. [6].

The desired pulse sequence is obtained by splitting and recombining the beam at ω_1. The delay between the two pulses at ω_1 was kept fixed at 60 ps during the experiment. The pulse at ω_2 was given a variable delay by translating a stepper-motor-driven corner cube. The photon echo at frequency ω_2, which occurs ≈60 ps after the pulse at this frequency, is detected by optically mixing the echo with a probe pulse at frequency ω_1 in a KDP crystal [11].

Pentacene in naphthalene crystals were grown by the Bridgman method with a concentration of ≈10^{-5} M/M, cut to a thickness of ≈500 μm, and mounted in a temperature-variable He cryostat.

3. Results

The frequencies ω_1 and ω_2 were chosen as shown in fig. 1 A. Here ω_{da} is a vibronic transition of pentacene, 747 cm^{-1} above the electronic origin at ω_{ca}. With the chosen concentration and crystal thickness the absorption at this transition is ≈45%. Typical echo decay curves are shown in fig. 2. Zero delay (t = 0) is defined by the time coincidence of the probe pulse at ω_2 with the second pulse at ω_1. Fig. 3 shows a normalized echo intensity decay of the TTE going over to the C2CSE at low temperature (1.5 K) and at elevated temperature (8.4 K). We note that the echo decay curves shown were obtained using low-intensity excitation pulses, in the limit of small rotations of the Bloch vector. We return to this point later. The interesting feature shown in fig. 3 is that, at low temperature, there is no break in the echo decay on going from one echo branch to the other, at t = 0. The continuous exponential decay of the low-temeprature low-power signal through the region of pulse overlap
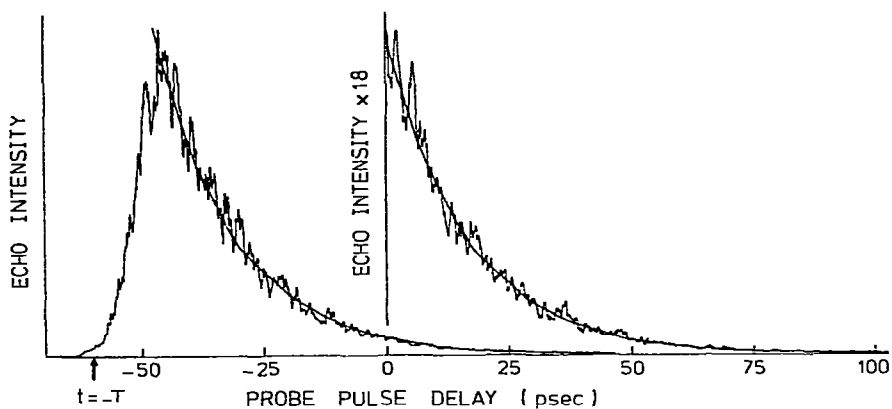
Fig. 2. Decay of the echo signal as the probe pulse at ω_2 is delayed. The enhancement of the signal at the center (upper trace) is due to the removal of neutral density filters in the echo beam. $t = 0$ is defined by the overlap in time of the second pulse at ω_1 and the probe at ω_2. The echo changes character at this point as is discussed in the text. The solid line is a fit to an exponential with a decay time of 16.5 ps $(= 1/2\Gamma_d)$.
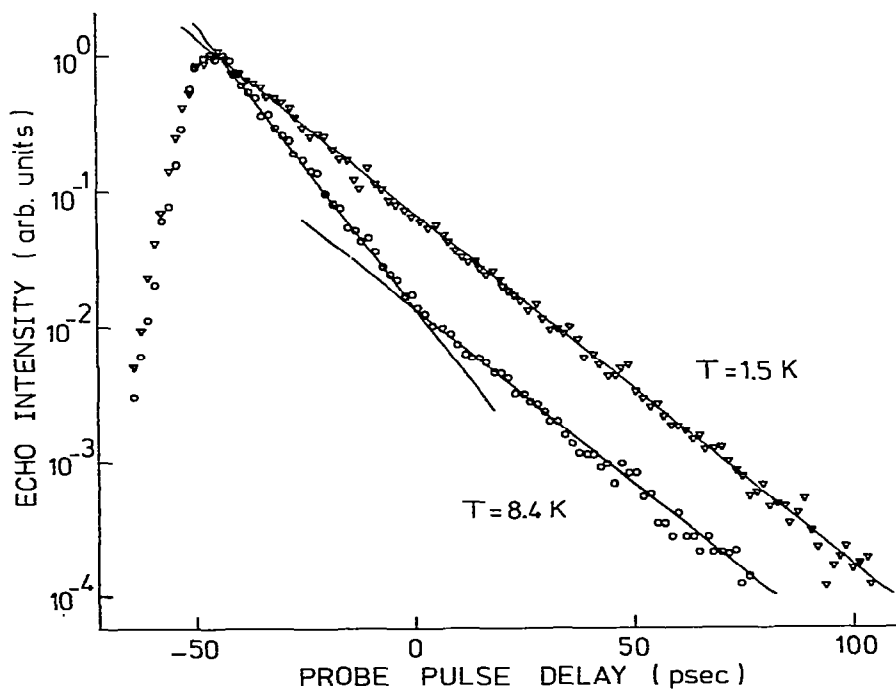

Fig. 3. Normalized logarithmic plot of the echo decay at 1.5 K and 8.4 K. A single exponential is observed at the lowest temperature, but a definite break occurs at $t = 0$ when the temperature is higher. The decay of the C2CSE has not changed (16.5 ps), but the decay of the TTE has become appreciably shorter (10.1 ps).

at $t = 0$ is remarkable in that the mechanism of echo generation is entirely different for $t < 0$ (fig. 1C) and $t > 0$ (fig. 1D).

There are two aspects of this continuity. First we calculate the dependence of the decay on the system relaxation times and establish that, in the low-temperature limit, it is the same for the TTE and the C2CSE. Then we calculate the dependence of the signal on the pulse angles for the three regimes $t < 0$, $t = 0$ and $t > 0$ and show that in the low-power limit no coherent artifact is expected in the decay as the pulse at ω_2 is scanned in time through the second pulse at ω_1 (wave vector k_1·).

4. Discussion

4.1. Calculation of TTE and C2CSE decay constants

The calculations are performed in a three-level approximation and in the doubly rotating and translating frame in which the time evolution of all points in the sample is identical. The notation parallels that of ref. [6].

The polarization near ω_2 is proportional to the off-diagonal density matrix element ρ_{bd} which at the echo maximum may be written as

$$\rho_{bd}^{echo} = \tfrac{1}{2}\sin(\theta_1)f(\theta_1·,\theta_2)R .\qquad(1)$$

The recorded signals are proportional to the square of this function. The factor $\tfrac{1}{2}\sin\theta_1$ is the efficiency with which coherence between $|a\rangle$ and $|d\rangle$ is created by the first pulse. In a square-pulse approximation the nutation angle is $\theta_1 = \epsilon_{ad}^{(1)}t_p$ where $\epsilon_{ad}^{(1)}$ is the Rabi frequency for the first pulse and t_p is its length. The factor $f(\theta_1·,\theta_2)$ (vide infra) is the efficiency of the second and third pulses at converting ρ_{ad} to ρ_{bd}.

The factor R contains the effects of the various relaxation times during the free evolution between pulses. For the tri-transition echo ($t < 0$) we can write this as a function of the (positive) interval t_{12} between pulses 1 (at ω_1) and 2 (at ω_2):

$$R(t < 0) = \exp(-t_{12}/T_2^{ad})\exp[-(\tau - t_{12})/T_2^{ab}]$$

$$\times \exp(-\kappa t_{12}/T_2^{bd}) .\qquad(2)$$

Note that three different transverse decay times enter, each weighted by the duration for which the corre-

sponding coherence exists. The inhomogeneous broadening is absent from eq. (2) since we have assumed that the dephasing occurring during the first interval t_{12} is just cancelled by rephasing during the final interval κt_{12} before the echo maximum. The assumption here is perfect correlation of the inhomogeneous distributions centered at $\bar\omega_{da}$ and $\bar\omega_{db}$. The scale factor $\kappa = \bar\omega_{da}/\bar\omega_{db}$ leads in principle to a retardation of the echo by $(\kappa - 1)t_{12}$ with respect to a three-pulse sequence on a two-level system. In the experiments this extra delay is much less than the echo width, so we can set $\kappa = 1$ in practice. During the second interval $\tau - t_{12}$ only homogeneous dephasing occurs as shown in ref. [8]. With these facts taken into account, eq. (2) reduces to

$$R(t < 0) = \exp(-t_{12}/T^{eff})\exp(-\tau/T_2^{ab}) ,\qquad(3)$$

with

$$1/T^{eff} = 1/T_2^{ad} - 1/T_2^{ab} + 1/T_2^{bd} .\qquad(4)$$

Each of the rates $1/T_2^{ij}$ can be decomposed into a lifetime and pure dephasing contribution:

$$1/T_2^{ij} = 1/2T_1^{ij} + 1/T_2^{*ij} .\qquad(5)$$

At the low temperatures of interest here the lifetime terms are

$$1/T_1^{ad} = \Gamma_d .\qquad(6)$$

$$1/T_1^{ab} = \Gamma_b ,\qquad(7)$$

$$1/T_1^{bd} = \Gamma_b + \Gamma_d ,\qquad(8)$$

where Γ_i is the total rate out of state $|i\rangle$.

All of the quantities in eqs. (4)–(8) can be deduced from previous photon echo [12], ground-state time-domain CARS [9] and transient vibrational grating [13] experiments together with excited-state time-domain CSRS experiments on the $|d\rangle \leftarrow \langle c|$ transition, which will be detailed elsewhere [14]. The picture that emerges is that for $T \leqslant 20$ K the vibrational coherence decay (T_2^{ab}, T_2^{cd}) is lifetime limited and temperature independent. The vibronic dephasing (T_2^{ad}, T_2^{bd}) is lifetime limited at the lowest temperatures, but due to uncorrelated phonon scattering in the ground and excited states has a pure dephasing contribution $T_2^{*ad} \approx T_2^{*bd}$ which is exponentially activated with temperature and significant except at pumped He temperatures [12]. Thus eq. (4) can be rewritten

$$1/T^{\text{eff}} \approx (\Gamma_d + 2/T_2^{*\text{ad}}) = 2/T_2^{\text{ad}} \qquad (T \lesssim 20 \text{ K}). \quad (9)$$

Notice that Γ_b has been cancelled out. For the C2CSE ($t > 0$) one has similarly

$$R(t > 0) = \exp(-\tau/T_2^{\text{ad}}) \exp(-t\Gamma_d) \exp(-\kappa\tau/T_2^{\text{bd}}). \quad (10)$$

This is continuous with eq. (3) at any temperature ($t_{12} \to \tau, t \to 0$) but, since τ is fixed, the effective decay time is just Γ_d^{-1} and insensitive to pure dephasing as is the ordinary stimulated echo. The effective decay times coincide at the lowest temperature, where electronic pure dephasing is absent.

Summarizing this section, we have found that, with a fixed delay between the two ω_1 pulses, the tri-level echo decay constants are as follows: for the TTE, below 20 K, it is $4/T_2^{\text{ad}}$ [eq. (9)] and for the C2CSE, at all temperatures it is $2\Gamma_d$. At *low* temperature (1.5 K) the relation $T_2^{\text{ad}} = 2/\Gamma_d$ holds which leads to an identical decay constant for the two echoes. At higher temperature, say 8 K, this relation is no longer valid as pure dephasing on the vibronic transition ω_{ad} becomes important, leading to a shortening of the decay of the TTE as observed in fig. 3. In contrast, the decay of the C2CSE, which is determined by a population relaxation constant, is unaffected; the reason being that this relaxation process exhibits no temperature dependence up to at least 20 K.

4.2. Pulse angle dependence of TTE and C2CSE

We now proceed with a discussion of the second interesting aspect of the echo formation, namely the continuous transition of the two echo phenomena at the overlap of the second and third excitation pulses.

The pulse angle dependence $f(\theta_{1'}, \theta_2)$ can now be calculated for the three regimes $t < 0$, $t = 0$ and $t > 0$ with the hamiltonian [6]

$$H_3^{(0)} = \epsilon_{\text{ad}}^{(1')} I_x^{\text{ad}} + \epsilon_{\text{bd}}^{(2)} I_x^{\text{bd}}, \quad (11)$$

where $I_x^{ij} = \frac{1}{2}(|i\rangle\langle j| + |j\rangle\langle i|)$, and ϵ_{ij} is the Rabi frequency. The only time dependence is in the ordering of the (squared) amplitude functions. The inhomogeneous offset terms are neglected in eq. (11) since the bulk of the molecules are resonant within the transform-limited width of the pulses and we are now considering only the time evolution during the pulses.

Regardless of the relative timing of pulses 1' and 2, their role in the echo formation is to convert the coherent superposition created between levels |a⟩ and |d⟩ by pulse 1 to a similar superposition between |d⟩ and |b⟩. This step in the dynamics has efficiency

$$f(\theta_{1'}, \theta) = \text{Tr}(U|\text{d}\rangle\langle a| U^{-1}|\text{d}\rangle\langle b|), \quad (12)$$

where from eq. (11) we have

$$U(t < 0) = \exp(-i\theta_{1'} I_x^{\text{ad}}) \exp(-i\theta_2 I_x^{\text{bd}}), \quad (13a)$$

$$U(t = 0) = \exp[-i(\theta_{1'} I_x^{\text{ad}} + \theta_2 I_x^{\text{bd}})]. \quad (13b)$$

$$U(t > 0) = \exp(-i\theta_2 I_x^{\text{bd}})\exp(-i\theta_{1'} I_x^{\text{ad}}). \quad (13c)$$

The two-level nutation angles are $\theta_2 = \epsilon_{\text{bd}}^{(2)} t_p$ and $\theta_{1'} = \epsilon_{\text{ad}}^{(1')} t_p$ and equal-length square pulses are assumed. The results are:

$$f(\theta_{1'}, \theta_2)$$
$$= \sin(\tfrac{1}{2}\theta_{1'})\sin(\tfrac{1}{2}\theta_2), \qquad t < 0, \quad (14a)$$
$$\tfrac{1}{2}(\theta_{1'}\theta_2/\theta_{1'2}^2)(1 - \cos\theta_{1'2}), \qquad t = 0. \quad (14b)$$
$$\tfrac{1}{4}\sin(\theta_{1'})\sin(\theta_2), \qquad t > 0. \quad (14c)$$

The new angle in eq. (14b) is $\theta_{1'2} = (\theta_{1'}^2 + \theta_2^2)^{1/2}$.

In the low-power limit ($\theta_{1'}, \theta_2 \ll \pi/2$),

$$f(\theta_{1'}, \theta_2) \approx \tfrac{1}{4}\theta_{1'}\theta_2. \quad (15)$$

irrespective of pulse ordering. In this limit, there is no additional structure in $\rho_{\text{db}}(t)$ as pulse 2 is scanned through pulse 1', but simply a switch from one exponential decay curve to another in a time comparable to the pulse cross correlation width.

4.3. Large pulse angle effects on echo decay

In the limit of large pulse angles the situation is more complex through the interference with other effects, in particular pulse amplification at ω_2 for large pulse angles at ω_1. At the highest available intensities of ω_1 the pulse amplification observed at ω_2 was a factor of 8. This effect leads to a drastic shortening of the decay of the TTE. Under the same conditions we find for the C2CSE a lengthening of the decay if $\theta_2 \approx \pi/2$ and a shortening if $\theta_2 < \tfrac{1}{2}\pi$. All experiments reported in this paper therefore were done for small pulse angles at ω_1 and ω_2 such that further lowering of the pulse intensities had no effect on the decay of either echo.

5. Conclusions

The observation of an identical decay constant, at 1.5 K, for the tri-transition echo (TTE) and connected two-color stimulated echo (C2CSE) confirms the low-temperature identity $T_2 = 2T_1$ at the vibrational and vibronic transitions in the mixed crystal of pentacene in naphthalene. At this temperature, spontaneous emission and vibrational population relaxation are the only dynamical processes that determine the electronic, vibronic and Raman lineshape in this doped solid. The possibility of generating these tri-level echoes in this mixed crystal further implies that the inhomogeneous broadenings at the excited transitions are strongly correlated. This conclusion is in agreement with the results of a recent time-resolved four-wave mixing study [8] on the same system. In this study we found no evidence for inhomogeneous broadening at vibrational transitions in the molecule, implying that the observed inhomogeneous component of the electronic (vibronic) transitions are purely electronic in nature. It is questionable whether the same situation occurs in other mixed crystals [15,16]. Particularly in the case of "floppy" molecules dispersed in solids or rigid molecules in amorphous host materials, one would expect a measurable vibrational dispersion leading to a vibration-dependent inhomogeneous optical linewidth. This letter shows that tri-level echoes can be informative on the question of possible correlations among the inhomogeneous broadenings at different transitions. At the same time the observation of this type of echo shows that two-dimensional picosecond spectroscopy [17] can be applied to the study of relaxation and cross-relaxation effects in doped molecular solids.

Acknowledgement

References

[1] W.H. Hesselink and D.A. Wiersma, in: Spectroscopy and excitation dynamics of condensed molecular systems, eds. V.M. Agranovich and R.M. Hochstrasser (North-Holland, Amsterdam, 1983).

[2] P.E. Jessop, T. Muramoto and A. Szabo, Phys. Rev. B21 (1980) 926;
R.M. Shelby, R.M. MacFarlane and R.L. Shoemaker, Phys. Rev. B25 (1982) 6578.

[3] H.P.H. Thijssen, R.E. van den Berg and S. Völker, Chem. Phys. Letters 103 (1983) 23;
J. Hegarty, M.M. Broer, B. Golding, J.R. Simpson and J.B. MacChesney, Phys. Rev. Letters 51 (1983) 2033.

[4] J.B.W. Morsink, W.H. Hesselink and D.A. Wiersma, Chem. Phys. 71 (1982) 289;
F.G. Patterson, H.W.H. Lee, W.L. Wilson and M.D. Fayer, Chem. Phys. 84 (1984) 51.

[5] T.W. Mossberg, R. Kachru, S.R. Hartmann and A.M. Flusberg, Phys. Rev. A20 (1979) 1976.

[6] D.P. Weitekamp, K. Duppen and D.A. Wiersma, Phys. Rev. A27 (1983) 3089.

[7] P. Ye and Y.R. Shen, Phys. Rev. A25 (1982) 2183.

[8] K. Duppen, D.P. Weitekamp and D.A. Wiersma, J. Chem. Phys. 79 (1983) 5835.

[9] R.M. Hochstrasser and H.P. Trommsdorff, Accounts Chem. Res. 16 (1983) 376.

[10] R. Bozio, P.L. Decola and R.M. Hochstrasser, in: Time resolved vibrational spectroscopy, ed. G.H. Atkinson (Academic Press, New York, 1983).

[11] W.H. Hesselink and D.A. Wiersma, Chem. Phys. Letters 56 (1978) 227.

[12] W.H. Hesselink and D.A. Wiersma, J. Chem. Phys. 73 (1980) 648.

[13] D.P. Weitekamp, K. Duppen and D.A. Wiersma, Chem. Phys. Letters 102 (1983) 139.

[14] K. Duppen and D.A. Wiersma, to be published.

[15] R.W. Olson and M.D. Fayer, J. Phys. Chem. 84 (1980) 2001.

[16] A.A. Gorokhovski and J. Kikas, Opt. Commun. 21 (1977) 272.

[17] K. Duppen, D.P. Weitekamp and D.A. Wiersma, to be published.