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Photon Echo of Pentacene Molecules Introduced in Crystals with High Concentration

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Photon echo decay time is measured for pentacence molecules introduced in naphthalene and *p*-terphenyl crystals with rather high concentrations (10^{-6}—10^{-5} mol/mol) at temperatures between 1.6 K and 4.1 K, using a tunable picosecond laser system consisting of a mode-locked YAG laser and a parametric oscillator. In naphthalene echo decay time increases with lowering temperature approaching a constant value below 2 K, but in *p*-terphenyl it is almost constant. The phase relaxation time at very low temperature is much shorter than twice the population relaxation time in both crystals, indicating that pure dephasing processes exist. Analyzing the results it turns out that there exsists a pure dephasing process which is temperature-independent and is very probably due to interactions between pentacene molecules, in addition to the temperature-dependent dephasing process due to the scattering of pseudolocalized phonons.

Recently, with the progress of coherent transient techniques in the optical region, for example photon echo observation, much information on optical dephasing processes associated with electronic transitions has been obtained for organic molecules introduced in crystals. From the optical line shape, useful information on phase relaxation can be obtained, but usually the optical homogeneous line shape is masked by inhomogeneous line broadening. Coherent transient techniques enable to obtain homogeneous line width buried in inhomogeneous line width.

Photon echo measurements were performed recently by Wiersma and his coworkers for a number of organic molecules, such as pyrene,[1)] pentacene,[2—4)] and naphthalene[5)] introduced in organic crystals. Especially, for pentacene molecules very dilutely introduced (10^{-8}—10^{-7} mol/mol) in naphthalene and *p*-terphenyl crystals as hosts, detailed studies were made using nanosecond and picosecond lasers. It turned out[2)] in the case of *p*-terphenyl host that at very low temperature of 1.5 K where phonons are not active, the phase relaxation time (T_2) is determined by the population relaxation time (T_1), in other words T_2 is equal to $2T_1$. The temperature dependence of the phase relaxation time was measured in a wide range above 4.2 K up to 20 K.[3,4)] It was found that the homogeneous line width is exponentially activated with phonon-like activation energy. This exponential activation of the homogeneous line width was interpreted by assuming optical dephasing due to the scattering of pseudolocalized phonons,[4,6)] and the energy and the lifetime of such phonons were determined.

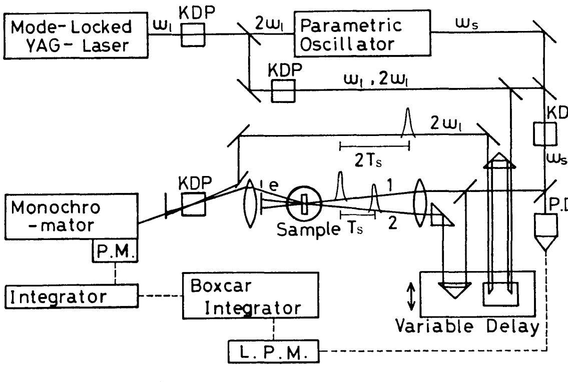

Fig. 1. Experimental set-up for photon echo measurements using a parametric oscillator (output frequency: ω_S) pumped by second harmonics of a mode-locked YAG laser (output frequency: ω_l). 1: first excitation pulse, 2: second excitation pulse, e: echo signal, T_S: separation of the first and second pulse, P.D.: photodetector, P.M.: photomultiplier, L.P.M.: laser power monitor.

If pentacene molecules are introduced in host crystals with high concentration, interactions between guest molecules would influence optical dephasing. The temperature dependence of T_2 in such cases are not yet studied. In this paper, we report picosecond photon echo measurements for pentacene molecules introduced in naphthalene and *p*-terphenyl crystals with rather high concentrations (10^{-6}—10^{-5} mol/mol) at temperatures between 1.6 and 4.2 K. As will be mentioned below, the temperature dependence of T_2 is observed, and it is found that at very low temperature, T_2 is independent of temperature, but is much shorter than $2T_1$.

Experimental

Pentacence-doped naphthalene and *p*-terphenyl crystals were grown by the Bridgman technique. In the case of naphthalene zone-refined reagent was used as the starting material. In the case of *p*-terphenyl, zone-refined reagent is not available, so ordinary reagent was vacuum-sublimed, zone-refined and then used. Crystals were cleaved in parallel to the *ab* cleavage plane to thickness of about 1 mm with a sharp razor blade.

Pentacene molecule in naphthalene has the zero-phonon absorption line of the S_0-S_1 transition at 602.7 nm. In the case of *p*-terphenyl host there exist four zero-phonon absorption lines originating from different sites. Measurements were made for the lowest energy line located at 592.2 nm. The spectral width of these absorption lines is about 1 cm^{-1} in both host crystals. The transition dipole moment for these absorption lines is known to be about 1 D.[7)] The concentration of pentacene molecules in a sample was determined combining the absorption intensity and the transition dipole moment of this value.

In photon echo experiments a tunable picosecond laser

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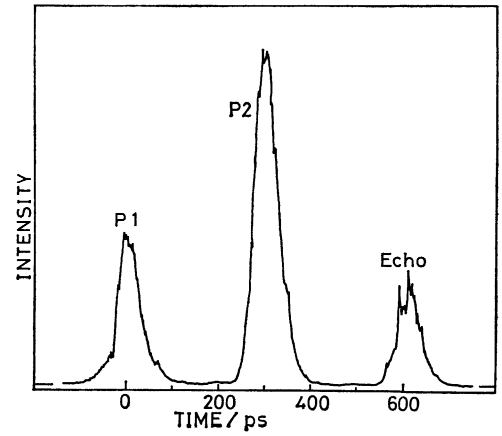

Fig. 2. Photon echo observation for pentacence in naphthalene (5×10^{-6} mol/mol) at 1.6 K. P1 and P2 are the first and second excitation pulses observed in the direction of the echo signal as leaked light. The pulse separation T_s is 300 ps.

system consisting of a repetitively mode-locked YAG:Nd^{3+} laser and a parametric oscillator was used.[8] Figure 1 shows the experimental set-up employed. The parametric oscillator using a temperature-controlled $LiNbO_3$ crystal was pumped by 532 nm second harmonic pulses of the YAG laser output. Excitation pulses tunable in the range around 600 nm were generated by the sum-frequency mixing of tunable pulses around 1300 nm produced by the parametric oscillator with 1064 nm fundamental pulses of the YAG laser by using a KDP crystal. Their characteristics are duration of about 20 ps, spectral width of about 2 cm^{-1} and peak power of about 200 kW.

The two pulses needed for the photon-echo experiments were generated by a beam splitter, and one pulse was delayed by an optical delay to obtain variable pulse separation (T_s). The intensity ratio of the first to second pulse was made to be almost 1:4 according to the standard way in photon echo experiments. Two excitation pulses were focused on the sample at an angle of about 0.5 degree. The size of the excitation spot was about 300 μm in diameter, and excitation densities of the first and the second pulses were 20 and 80 MW/cm^2, respectively. These power densities nearly correspond to the conditions of the $\pi/2$ and π pulses, respectively, since the transition dipole moment in the present case is about 1 D. The echo was emitted in a direction separated from the second pulse by the same angle as that between the first and second pulses as expected. It is sure that this configuration is useful to reduce the background by spatially separating the echo signal from the excitation pulses.

The echo signal was made to pass through a diaphragm to remove the excitation pulses as much as possible. Then the echo signal was mixed with the second harmonic pulse of the YAG laser output to generate the sum-frequency pulse. This second harmonic pulse acts as the time-gate pulse, which selects the echo signal from the excitation pulses. The gate pulse was delayed by the variable optical-delay so as to coincide with the echo in time. The optical delay consists of two prisms located on a moving stage driven by a pulse motor. The second excitation pulse passes one prism and the gate pulse passes the other prism. The gate pulse passes the delay twice, so that the time delay of the gate pulse is double that of the second pulse from the first pulse. Thus the synchronization of the gate pulse with the echo is maintained. The mixed pulse of the echo and gate pulse was made to pass through a monochromator, and then was detected by a photomultiplier. The output of the photomultiplier was integrated and held by an integrator. On the other hand, a part of excitation pulses were detected by a phototube, and the power was checked by a laser power monitor. Only when the power is within ±5% for a certain fixed value, the echo signal held in the integrator was accumulated by a Boxcar integrator.

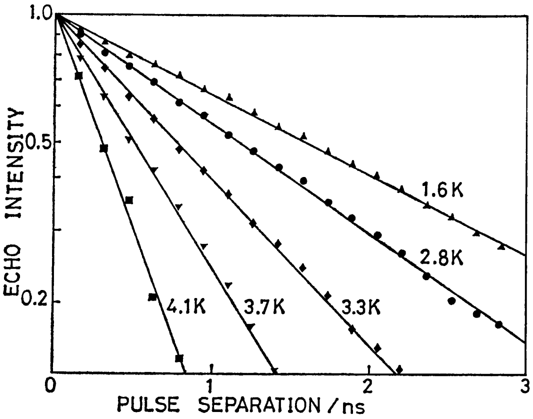

Fig. 3. Logarithmic plots of photon echo decay of pentacene in naphthalene (5×10^{-6} mol/mol) at temperatures between 1.6 and 4.1 K. Solid lines are the least square fitting to the experimental data.

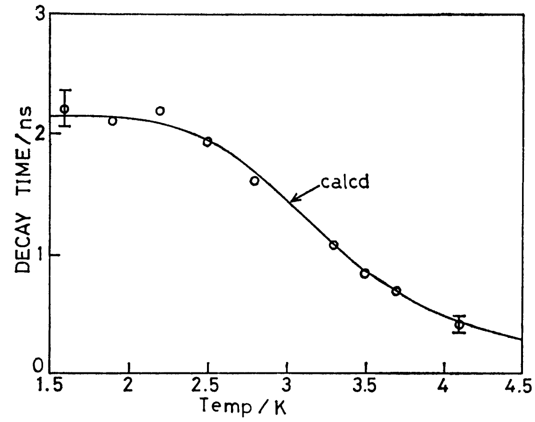

Fig. 4. Temperature change of echo decay time of pentacene in naphthalene (5×10^{-6} mol/mol). Solid line is calculated curve; see the text.

Results and Discussion

Figure 2 demonstrates an observation of photon echo for pentacene molecules in a naphthalene crystal (5×10^{-6} mol/mol) at 1.6 K. This data was obtained by changing the arriving time of the gate pulse but fixing the separation of the two excitation pulses at 300 ps. P1 and P2 are the first and second excitation pulses observed in the direction of the photon echo signal as leaked light through the diaphragm. It is seen that the photon echo appears after the second pulse with the interval the same as that between the first and second pulses.

To obtain the relaxation time of photon echo, the echo intensity was measured as a function of the separation of the two excitation pulses. The separation was changed by scanning the variable optical delay,

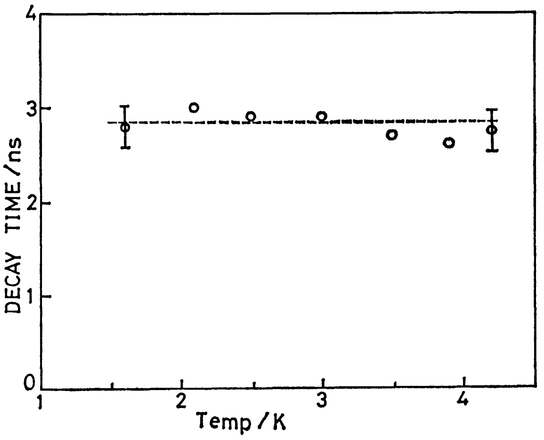

Fig. 5. Temperature change of echo decay time of pentacene in *p*-terphenyl (1×10^{-5} mol/mol).

maintaining the synchronization of the gate pulse with the echo signal. The echo intensity as a function of the excitation pulse separation is given by

$$I(T_s) = I_0\exp(4T_s/T_2). \tag{1}$$

Figure 3 shows logarithmic plots of the relative echo intensity versus the pulse separation for pentacene in naphthalene (5×10^{-6} mol/mol) at temperatures between 1.6 K and 4.1 K. The functional form of the photon echo decay is exponential at the whole temperature range. The echo decay time decreases with elevating temperature.

Decay times obtained, *i.e.* $T_2/4$, are plotted in Fig. 4 as a function of temperature. It is seen that the decay time becomes constant at temperature below 2 K. Figure 5 shows results of the echo decay time in the case of pentacene in *p*-terphenyl (1×10^{-5} mol/mol). It is found that the decay time is almost constant in the whole temperature range and is slightly longer than that in the case of the naphthalene host below 2 K.

The echo decay time is governed by the phase relaxation time T_2 given by

$$1/T_2 = 1/2T_1 + 1/T_2^*, \tag{2}$$

where T_1 is the population relaxation time and T_2^* is the pure dephasing time. T_1 in the present case was reported to be 19.5 ns in naphthalene and 23.5 ns in *p*-terphenyl.[4]

As shown in Fig. 5, the decay time of the echo in the *p*-terphenyl host is almost constant below 4.1 K and is about 2.9 ns giving the value of about 11.6 ns as T_2. This value of T_2 is much shorter than $2T_1$. This suggests that the pure dephasing process that is independent of temperature exists below 4.1 K in this host. From Eq. 2, the pure dephasing time T_2^* is obtained to be 15 ns.

In the case of the naphthalene host, T_2 increases with lowering temperature but approaches a constant value which is much shorter than $2T_1$. One may consider that the temperature-independent, pure dephasing process exists also in this host at very low temperature. As mentioned already, it is known that in dilutely doped crystals T_2 is dominated by the dephasing process due to the scattering of pseudolocalized phonons at temperature above 4.2 K.[4] Such a dephasing process dominated by phonons should exist also in highly doped crystals.

One may assume that T_2^* in the present case of the naphthalene host consists of two components, one T_{2c}^* which is temperature-independent and the other T_{2ph}^* which is temperature-dependent and is dominated by phonon scattering, that is

$$1/T_2^* = 1/T_{2c}^* + 1/T_{2ph}^*. \tag{3}$$

The temperature-dependence of T_{2ph}^* may be expressed by

$$T_{2ph}^* = \tau_{ph}\exp(E_{ph}/kT), \tag{4}$$

where τ_{ph} is the lifetime of relevant phonons and E_{ph} is their energy. The observed temperature change of the decay time in Fig. 4 was attempted to fit with the calculation based on the assumption of Eqs. 3 and 4. Adjustable parameters are τ_{ph}, E_{ph}, and T_{2c} which is the temperature-independent component of T_2 given by

$$1/T_{2c} = 1/T_{2c}^* + 1/2T_1. \tag{5}$$

The result of the calculation is shown by the solid curve in the figure. It is seen that observed decay times are well represented by the calculation. The values of the adjustable parameters used are $\tau_{ph}=7.4$ ps, $E_{ph}=16.1$ cm^{-1} and $T_{2c}=8.7$ ns. It is noted that these values of τ_{ph} and E_{ph} well coincide with those obtained in the dilutely doped naphthalene host at temperature above 4.2 K.[4] It is sure that also in the highly doped host the same kind of the pseudolocalized phonon is active for dephasing. Further from the above value of T_{2c}, T_{2c}^* is obtained to be 11.2 ns.

Also in the case of the dilutely doped *p*-terphenyl host, the values of τ_{ph} and E_{ph} are known from the temperature dependence of T_2 above 4.2 K. If T_2 is calculated using such values for temperatures below 4.2 K, it is found that T_2 becomes constant below about 3 K. Therefore, the results shown in Fig. 5 for the highly doped *p*-terphenyl host are regarded as reasonable.

From the above-mentioned discussion, it is definitely concluded that when pentacene molecules are introduced with high concentration, a pure dephasing process, represented by T_{2c}^*, exists and dominates dephasing at very low temperature where phonon-dominated processes are not active. This fact is a distinct difference of the high concentration case from the low concentration case, and allows us to consider that the origin of this pure dephasing is interactions between pentacence molecules.

Cooper *et al.*[9] observed the photon echo of pentacence molecules introduced in naphthalene crystals with rather high concentrations (10^{-7}—10^{-5} mol/mol) at 1.4 K, and found that concentration-dependent, pure dephasing takes place. Although they did not measure the temperature dependence of this process, it is certain that the same kind of origin as that of the present case dominates this process, considering the concentration and the temperature in their experiments.

They explained this concentration-dependent dephasing as caused by the fluctuation of the dipole-dipole interaction between pentacene molecules due to phonons. According to this phonon-modulated dipolar interaction model, T_{2c}^* is given by[9)]

$$1/\pi T_{2c}^* = \{(\mathrm{d}E/\mathrm{d}r)\times\Delta r\}^2/h^2\nu, \qquad (6)$$

where E is the excitation energy of molecules, Δr is fluctuation of intermolecular distance and ν is the rate of the fluctuation. The value of ν should be comparable to the thermal average acoustic phonon frequency, so that it is expected to increase linearly with temperature. On the other hand, the value of Δr is known to be almost constant in the temperature range below 4.2 K in the present case.[10)] Then T_{2c}^* given by Eq. 6 should be temperature-dependent, increasing linearly with temperature. According to our experimental results, T_{2c}^* is temperature-independent in this temperature range. Therefore, the model proposed by Cooper *et al.* can not account for the dephasing process in the case of the high pentacene concentration.

Morsink *et al.*[11)] also found concentration-dependent dephasing in photon echo measurements of naphthalene molecules in durene. This dephasing was interpreted as the effect of dipolar broadening due to energy migration among resonant molecules. However, this interpretation was based on the assumption, which has no solid experimental evidence, that the crystal consists of large domains of resonant molecules.

Anyway we need more detailed information on the temperature- and concentration-dependence of the dephasing time to discuss the mechanism of dephasing in the high concentration case as observed here. Measurements of the concentration depnedence for pentacene molecules in naphthalene and *p*-terphenyl are now in progress, and results will be reported shortly.**

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** **Note added in proof.** See: Y. Yoshikuni, A. Nakamura, S. Shionoya, and M. Aihara, *J. Phys. Soc. Jpn.*, **51**, 2604 (1982).