Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Ultrafast Dephasing Measurement by Transient Four-Wave Mixing

K. Misawa [a] & T. Kobayashi [a]
[a] Department of Physics, University of Tokyo, 7-3-7 Hongo, Bunkyo-ku, Tokyo, 113, Japan
Version of record first published: 04 Oct 2006.

To cite this article: K. Misawa & T. Kobayashi (1990): Ultrafast Dephasing Measurement by Transient Four-Wave Mixing, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 182:1, 125-137

To link to this article: http://dx.doi.org/10.1080/00268949008047794

Mol. Cryst. Liq. Cryst., 1990, Vol. 182A, pp. 125–137
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Ultrafast Dephasing Measurement by Transient Four-Wave Mixing

K. MISAWA and T. KOBAYASHI

Department of Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

(*Received June 21, 1989; in final form November 1, 1989*)

Transient four-wave mixing has been applied to dephasing measurements in the picosecond or femtosecond range using coherent short pulses or incoherent light. The dephasing time is a key parameter in the investigation of coherent interactions of light and matter. Measurements of electronic (excitonic) and vibrational dephasing time are reviewed together with our results using incoherent light.

Keywords: ultrafast, dephasing, four-wave mixing, coherent transients, incoherent light

1. INTRODUCTION

Lasers have been extensively used for the study of light-matter interaction to obtain information on the physical properties of materials. The interactions have also been utilized for the characterizations of laser light. This paper concentrates on the relaxations of the states in condensed-phase materials prepared by the interaction with laser light. There are two relaxation processes of the prepared states, namely depopulation and dephasing. The former is the decay of the population change induced by the absorption of light to the thermal equilibrium state (sometimes called energy relaxation or longitudinal relaxation). The latter is the disappearance of the macroscopic polarization (sometimes called transverse relaxation). Coherently induced microscopic polarizations constructively interfere with each other resulting in finite macroscopic polarization. The phases of these microscopic polarizations become gradually random because of scattering between carriers or excitations so that they destructively interfere and the macroscopic polarization decays. The dephasing time (T_2) is the decay time constant of the macroscopic polarization.

From the physical point of view, dephasing time T_2 is a very important parameter because optical coherent transients, which hold promise for applications such as optical switching or optical data communication, are effective within a time comparable to T_2. Thus investigations of dephasing processes in various materials have attracted the interest of many scientists. In order to measure T_2 in the time domain,

transient four-wave mixing (FWM) or photon echo is usually applied. However, dephasing time is in the subpicosecond range because of the strong interaction between excitations in condensed matters. Only recently has development in the generation method of ultrashort laser pulses made such measurements possible. The shortest pulse duration reported to date is 6 fs.[1]

When two beams with the same frequency ω and different wavevectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are focused at the same area on a material, signal beams at ω are emitted in the phase-matched directions $\mathbf{k}_3 = 2\mathbf{k}_2 - \mathbf{k}_1$ and $\mathbf{k}_4 = 2\mathbf{k}_1 - \mathbf{k}_2$ due to the third-order optical nonlinear effect. This process is also explained in terms of the laser-induced transient grating effect. Two beams make a transient grating with a wavevector $\mathbf{k}_2 - \mathbf{k}_1$, and one beam is self-diffracted in the direction of $\mathbf{k}_3$ or $\mathbf{k}_4$. One beam can be variably delayed with respect to the other by changing its optical pass length using a translational stage. The time-integrated energy of the generated signal is measured as a function of the relative delay time (τ) between these two beams. Yajima and Taira demonstrated that T_2 can be obtained from the signal trace for both homogeneously and inhomogeneously broadened two level systems by solving the density-matrix equations in the weak perturbation limit.[2] Here it is assumed that the material studied has a single set of T_1 and T_2. When the incident laser pulse duration τ_p is much shorter than T_2, the signal trace has a tail with a decay constant $T_2/2$ for homogeneously broadened systems. When the system has an extremely inhomogeneous broadening, this optical parametric process leads to the photon echo, and the decay constant of the signal profile becomes $T_2/4$. In the inhomogeneously broadened case, the dephasing time obtained corresponds to the reciprocal of the width of the hole-burning spectrum.

This two-beam "self-diffracted" DFWM is the simplest configuration to measure T_2, but dephasing measurements can be performed in other geometries such as three-beam DFWM[3] and pump-probe experiments.[4,5] These geometries are depicted in Figure 1. Even though the former experiment is more complicated, it has the advantage that the energy relaxation time T_1 can be also measured with the same equipment. T_2 or T_1 can be measured by changing the delay time between $\mathbf{k}_1$ pulse and $\mathbf{k}_2$ or between $\mathbf{k}_1$ and $\mathbf{k}_3$, respectively. The latter has the disadvantage that the decay curve is not only dependent on T_2, but also on T_1; however the alignment is easy and heterodyne detection can be applied because the signal and the probe beams are collinear.

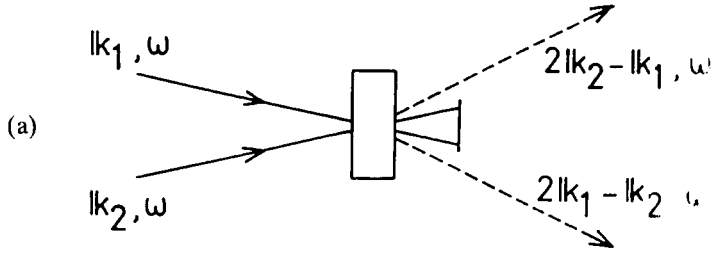

FIGURE 1 Experimental geometries for dephasing measurement by (a) ordinary two-beam DFWM; (b) three-beam DFWM; (c) pump-probe experiment; (d) Kerr-shutter configuration as a type of pump-probe experiment.

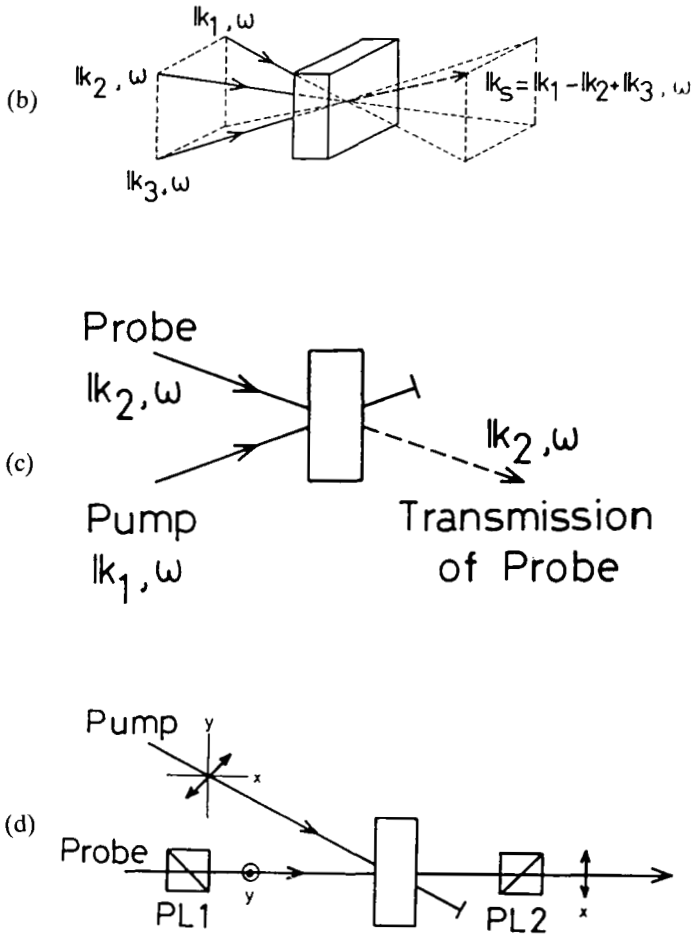

FIGURE 1 (*continued*)

Time-resolved coherent Raman scattering is applied to reveal dynamical properties of molecular vibrations or phonon dynamics in condensed matters as a type of nondegenerate FWM. At time zero, two short pulses with different frequencies excite a vibrational mode at their difference frequency through transient stimulated Raman scattering. The relaxation process of the coherently excited vibration is monitored with a probe light which is variably delayed with respect to the pump light pulse pair. Its signal intensity decays against the delay time with a time constant $T_2^{vib}/2$, where T_2^{vib} is denoted as a vibrational dephasing time. However, these techniques do not allow measurement of the vibrational dephasing time for systems with wide inhomogeneous broadening, because this coherent Raman scattering contains no rephasing process. The signal decay of homogeneous broadened systems will be exponential, and the nonexponential decay component, if any, is attributed to contribution of inhomogeneous broadening.

In this review paper, recent experimental results on dephasing measurements for several materials are discussed. Applications of DFWM to the measurements of electronic dephasing times using coherent ultrashort pulses are reviewed together with original work using incoherent light in section 2. The measurement of vibrational dephasing times by coherent Raman scattering is discussed as an application of nondegenerate FWM in section 3. Previous results using incoherent light to determine vibrational dephasing times are also summarized in section 3. This review is not intended to be comprehensive because of limitation of pages, and there are other interesting and important papers which are not mentioned in this article.

2. ELECTRONIC DEPHASING TIME MEASURED BY DFWM

2.1. Carrier density dependence of dephasing time in GaAs

Becker *et al.* made the first observations of 2-beam DFWM signal from band-to-band transitions in gallium arsenide (GaAs), and determined T_2 as a function of the carrier density with 6 fs pulses.[7] The dephasing time measured in their study provides information on momentum relaxation process.[8] At high carrier densities, carrier collisions dominate the momentum relaxation.

The pulse train at a repetition rate of 8 kHz was split into two and both parts were focused at the same point on a sample through a Michelson interferometer. The experiment of Becker *et al.*[7] was held at room temperature. Figure 2 shows the logarithmic plot of the signal intensity as a function of the delay. The carrier density was estimated from the absorbed light energy. As the carrier density is reduced, the decay time becomes longer. The decay time constant denoted as T_{echo} in the paper of Becker *et al.*[7] is plotted as a function of the carrier density in Figure 3. The data are power-law fitted and an equation $T_{echo} = 6.8\,N^{-0.3}$ was obtained, where N is denoted as the carrier density.

In a low or intermediate carrier density region, Schultheis *et al.* measured T_2 and observed the transition of dephasing property from a low- to high-density regime.[9] The excitonic dephasing time in GaAs was measured by transient DFWM with a synchronously pumped dye laser, while free carriers or incoherent excitons are additionally injected by preexcitation pulses as shown in Figure 4. The dephasing time measured by Schultheis *et al.*[9] is excitonic T_2, while that by Becker *et al.*[7] is that of free-carriers; however, the density dependence of these dephasing times are similar to each other. The decay rate increases dramatically with the density of excitons or free-carriers. At low densities, the dephasing time is independent of the exciton or carrier density, because in this region other mechanisms such as electron-phonon interaction dominate the dephasing process. As the carrier density increases, exciton collision gradually becomes predominant. Exciton-exciton scattering is efficient even at an exciton density of 5×10^{14} cm^{-3}, and scattering by free-carriers is still more efficient as shown in Figure 5.

2.2. Accumulated photon echo

A decade ago, Hesselink and Wiersma observed photon echoes stimulated from an accumulated grating in the electronic ground state.[4] The accumulation is caused

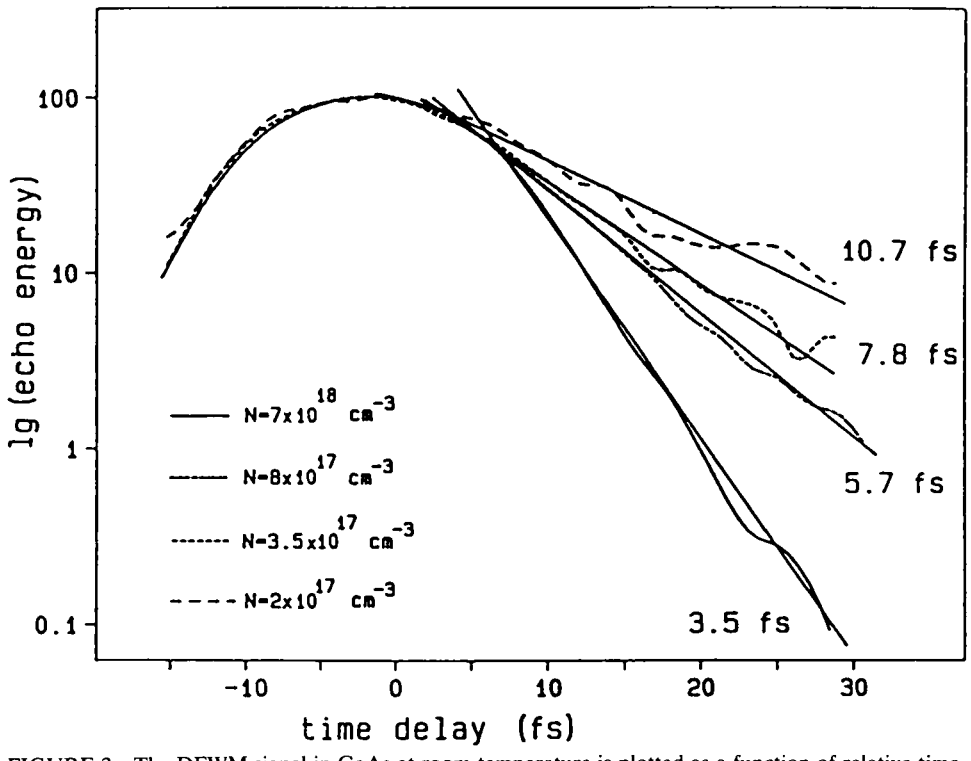

FIGURE 2 The DFWM signal in GaAs at room temperature is plotted as a function of relative time delay between the two 6-fs exciting pulses. The time constant of the exponential decay, T_{echo} is indicated for each carrier density. (modified from Reference 6)

by a bottle-neck in the optical pumping cycle or the excited state of the resonant two level system with a lifetime much longer than T_2. It results in the stationary grating amplitude, and consequently, enhancement of the self-diffracted signal. In the experiment of Hesselink and Wiersma a synchronously pumped, mode-locked dye laser at 82 MHz was used. Accumulated photon echoes can be observed in both the phase-matched directions, $\mathbf{k}_e = 2\mathbf{k}_2 - \mathbf{k}_1$ and $\mathbf{k}_e = \mathbf{k}_2$. Especially in the latter case the stimulated echo is in phase with the collinear probe beam $\mathbf{k}_2$, thus, the echo constructively interferes with the probe at the detector. The pump beam was chopped at 300 Hz and the probe intensity was phase-sensitively detected using a lock-in amplifier, which results in an improvement in the signal to noise ratio. In this heterodyne detection scheme, the observed signal is proportional to the induced macroscopic polarization, which decays as $\exp[-2\tau/T_2]$. On the other hand, for the phase match condition $\mathbf{k}_e = 2\mathbf{k}_2 - \mathbf{k}_1$, the observed signal is proportional to the squared absolute value of the polarization with a decay constant $T_2/4$, because no interference occurs. Figure 6(a)–(c) shows the echo signal from the zero phonon line of pentacene in naphthalene. The decay constants for these two phase-match conditions are different by a factor of two at the same temperature as shown in Figure 6(b) and 6(c), which verifies the theoretically expected decay times of $T_2/4$ and $T_2/2$.

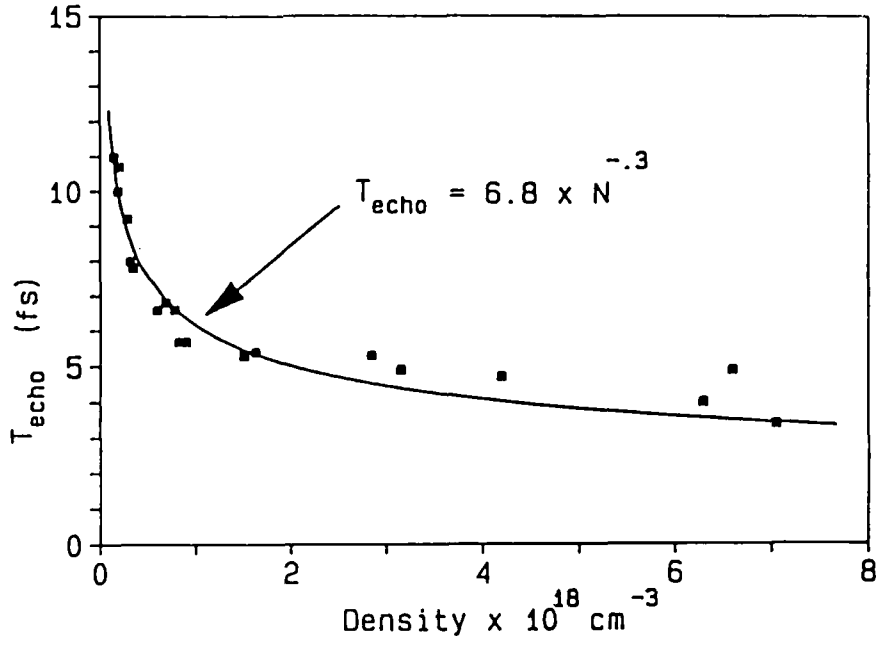

FIGURE 3 Observed decay time constant as a function of the carrier density, for GaAs at room temperature. (modified from Reference 6)

According to the same principle, Saikan *et al.* investigated ultrafast relaxation in dye molecules and observe damped oscillating decays.[5] Observed echo signals from cresyl violet and tetraphenyl-porphine (TPP) are shown in Figure 7. The quantum beats last for several picoseconds. The long decay tail corresponds to the dephasing process between the electronic ground and excited states, and the damped oscillation comes from quantum beats which correspond to interference between the wavefunctions of different vibronic levels. According to another work by Saikan *et al.*,[6] the hole-burning spectrum can be obtained from the Fourier-cosine transform of the echo signal. Figure 8 shows the Fourier-transformed spectrum compared with the persistent hole-burning spectrum measured in the frequency domain. These spectra are similar to each other and vibronic lines associated with the quantum beat are clearly observed.

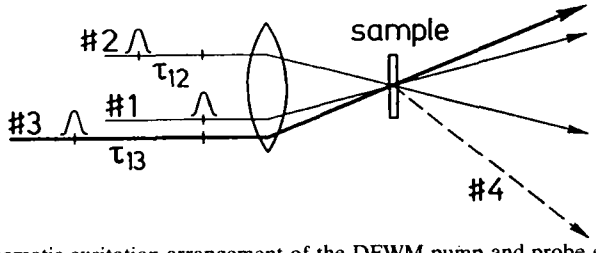

FIGURE 4 Schematic excitation arrangement of the DFWM pump and probe experiment. The self-diffracted signal No. 4 from an orientational grating formed by pulses No. 1 and No. 2 (delayed by τ_{12}) monitors the phase coherence of the excitons in the presence of additional incoherent excitons or free carriers created by the stronger pulse No. 3 (advanced by τ_{13}). (Reference 8)

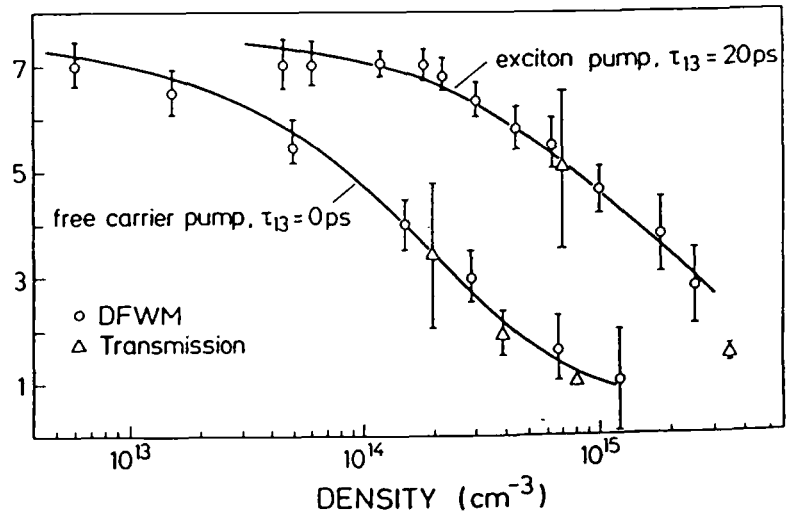

FIGURE 5 The dephasing time T_2 of a small exciton ensemble subjected to collision with additional free carriers or excitons. The presented data are from DFWM experiment (circles) and time-resolved transmission (triangles). The collision rates are .mb8 derived from the theoretical fit (full curve). (Reference 8)

2.3. Dephasing measurement using incoherent light

In ordinary time-resolved nonlinear spectroscopic techniques, the time resolution is limited by the temporal width of pulses. However, the generation of ultrashort pulses for higher time resolution requires very sophisticated apparatus. Recently incoherent light has been utilized for ultrafast time-resolved spectroscopy by means of transient DFWM.[5,6,9-16] Temporally incoherent light with a wide spectral width has a correlation time (τ_c) much shorter than its temporal duration, and incoherent light can be considered to generate macroscopic polarization in a similar manner to a train of coherent pulses with pulse duration τ_c. Here we note that a spectral diffusion causes the fast decay of the macroscopic polarization accompanied by the decay with T_2 in the measurement using incoherent light, which is not observed using coherent short pulses.[11] The time resolution of the correlation experiment such as transient DFWM previously mentioned, is determined by τ_c. According to this principle, ultrahigh time resolution can be attained much more easily by using temporally incoherent light. The incoherent light source is usually an incompletely mode-locked cw dye laser or a dye laser pumped by a nanosecond-pulselaser. Once the optics for wavelength selection are removed from these lasers, ultrahigh time resolution is obtained. In addition the incoherent light source used in the method is widely tunable for each dye laser; all visible, near UV, and near IR regions can be covered by selecting an appropriate dye. Therefore, this method can be applied to various materials.

Morita and Yajima investigated electronic T_2 measurement theoretically, under the assumptions that: the envelope function of the electric field of incoherent light is expressed by a complex gaussian random process; and that τ_c is much shorter than the relevant relaxation times.[10] Asaka *et al.* measured T_2 in Nd^{3+} doped glass

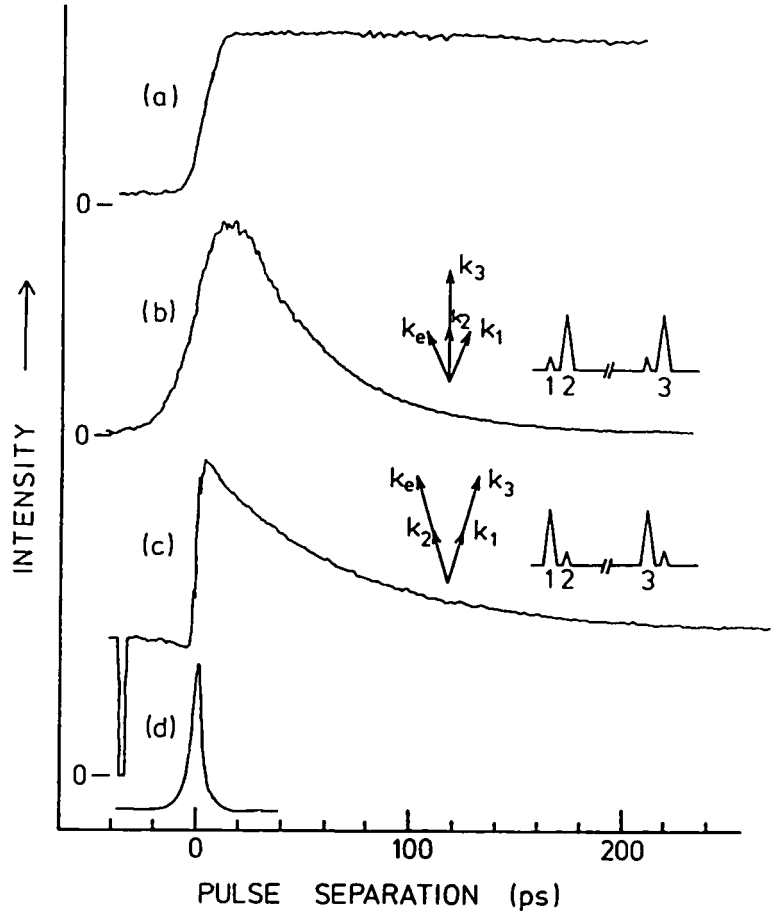

FIGURE 6 Optical coherent transients observed in pentacene in a pump-probe experiment for phase-matched conditions (a) at 1.3 K; (b) and (c) at 7.2 K for each phase-match condition; (d) pump-probe cross correlation at zero pulse separation. (modified from Reference 4)

by accumulated photon echoes with incoherent light.[11] They obtained T_2 using incoherent light in agreement with T_2 using picosecond pulses and verified the applicability of this method. Saikan *et al.*[5,6] applied the same technique to the heterodyne detection of the femtosecond photon echo with quantum beats as mentioned in section 2.2.

Incoherent light has also been used to resolve dephasing time in various materials.[12-17] Recently the dephasing time in cadmium sulfide (CdS) microcrystallites doped in a polymer film at liquid helium temperatures has been measured.[15] The measurement was performed in the Kerr-shutter configuration.[16] A single beam of linearly polarized light is divided into two. One of them (the probe beam) is variably delayed and focused onto the sample. The other (the pump beam) is polarized 45° with respect to the probe beam and focused at the same point. The incoherent light source was a broad-band dye laser pumped by a nanosecond excimer laser. The laser dye was stilbene 420, which was selected to be nearly resonant with the

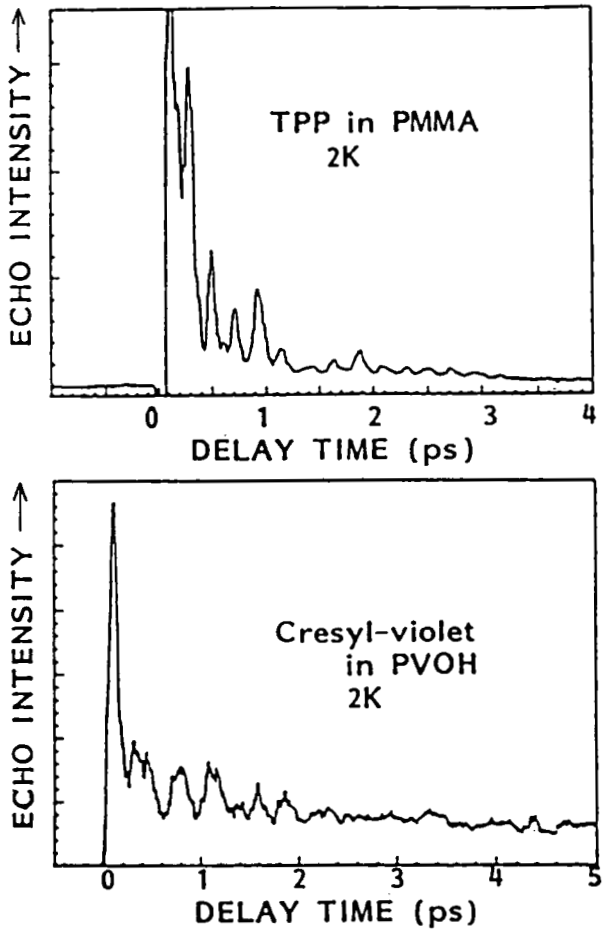

FIGURE 7 Heterodyne-detected accumulated photon echo in cresyl violet and TPP. (modified from Reference 5)

exciton energy. The peak wavelength and its spectrum width was 422 nm and 6.1 nm, respectively. The correlation time τ_c was about 120 fs. Samples were immersed directly in superfluid liquid helium. The signal transmitted through a crossed analyzer is detected as a function of the delay between the two beams. Figure 9 shows the signal obtained and the dephasing time is estimated to be 230 ± 20 fs. The reason why the dephasing is so fast may be as that the exciton absorption of the microcrystallites is inhomogeneously broadened, thus higher levels of excitons are excited and they rapidly dephase.

3. VIBRATIONAL T_2 STUDIED BY NONDEGENERATE FWM

3.1. Measurement using ultrashort coherent pulses

Zinth *et al.* and Leonhardt *et al.* have investigated the dephasing properties of vibrational Raman modes using femtosecond laser pulses.[18,19] The vibrational modes

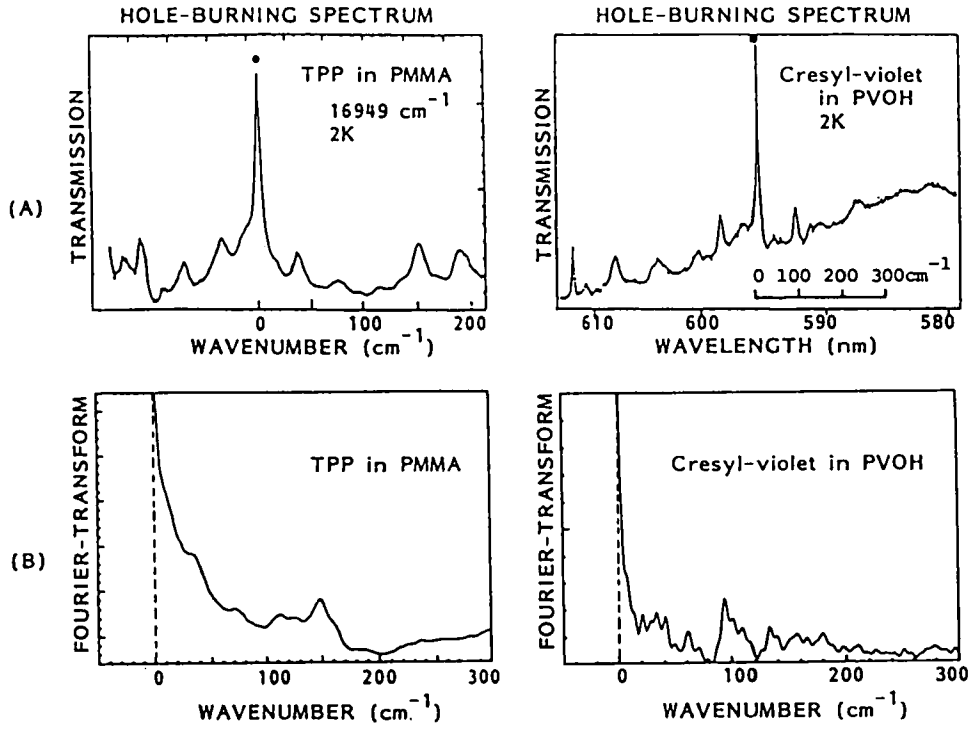

FIGURE 8 (A) Persistent hole-burning spectra. Closed circles indicate the burning laser wavelength. (B) Fourier-cosine transformed spectra of the echo signals in Figure 7. (Reference 5)

between 300 cm^{-1} and 3000 cm^{-1} can be excited using two synchronized lasers. One is a femtosecond unidirectional ring dye laser which generates pulses with a duration of about 80 fs at a wavelength of 625 nm. The pulses from this dye laser are divided into two, the pump and the probe. The other is an ordinary synchro-

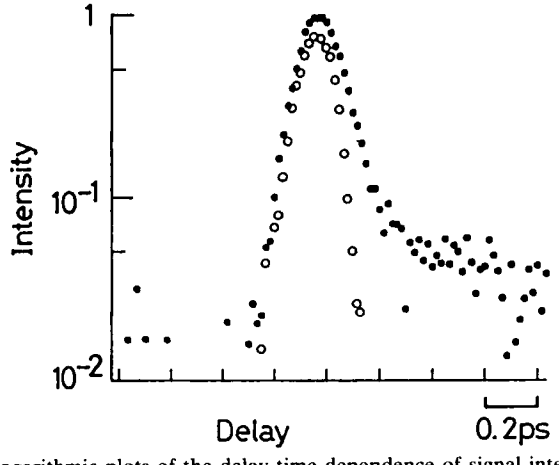

FIGURE 9 Semi-logarithmic plots of the delay time dependence of signal intensity at 2 K obtained from CdS microcrystallites; signal (closed circle); autocorrelation (open circle). (Reference 14)

nously mode-locked dye laser tuned in red or near-IR region at the Stokes frequency with a duration of 6 ps. The duration of the first excitation of the Raman modes is determined by the shorter of the two pulses, because the driving force is proportional to the product of two laser pulse amplitudes. Using a single femtosecond laser, vibrational modes whose frequencies are less than the bandwidth of the laser light can be excited by impulsive stimulated Raman scattering and consequently its dephasing process can be observed.[20]

Recently Leonhardt *et al.* observed quantum beats between different vibrational modes.[19] Several modes of the same or different molecules are excited simultaneously by a pair of excitation pulses. The signal from each Raman line decays exponentially with a time constant of $T_2^{vib}/2$. In addition, oscillation at the frequency difference of several Raman modes can be observed on the decay tail. For example liquid pyridine has two vibrational modes at wavenumbers 991 and 1030 cm^{-1}, which are assigned to two A_1 ring modes. Figure 10 shows the observed coherent anti-Stokes Raman scattering (CARS) signal plotted as a function of the delay between the pump and the probe. From the envelope of the oscillating peaks, the vibrational T_2 is obtained to be 5.1 ± 0.3 ps, which is the average value of dephasing times of two modes. Distinct oscillation can also be seen and its temporal period of the oscillation is 0.85 ± 0.01 ps. It corresponds to the frequency difference between the two modes and the difference is determined to be 39.2 ± 0.5 cm^{-1} from the measurement in the time domain.

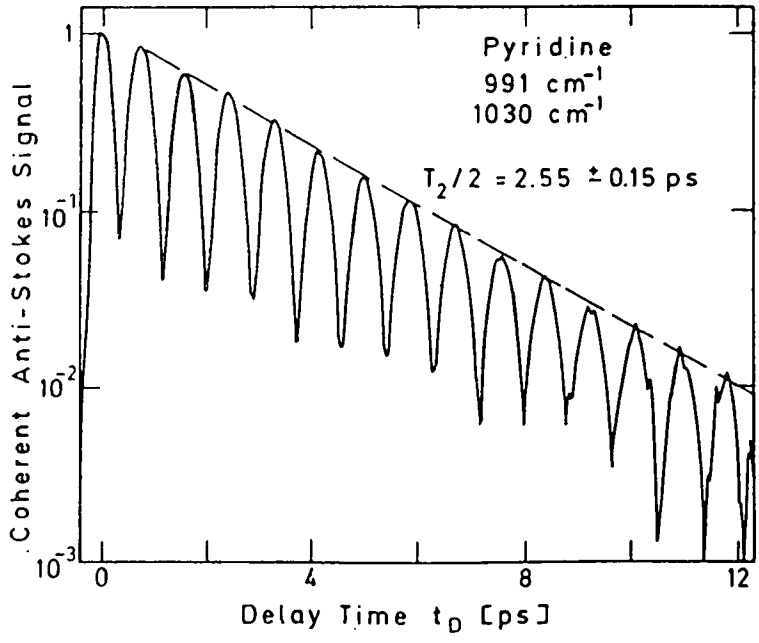

FIGURE 10 Coherent anti-Stokes Raman signal obtained for liquid pyridine. The time-resolved data exhibit the strong beating between two vibrational modes of pyridine at 991 cm^{-1} and 1030 cm^{-1}. The frequency difference can be accurately determined to be 39.2 ± 0.5 cm^{-1}. (Reference 18)

3.2. Measurement using incoherent light

Hattori *et al.* measured vibrational T_2 of symmetric CH stretching mode at 2915 cm^{-1} in dimethylsulfoxide (DMSO).[17] In this experiment, incoherent light was used instead of femtosecond laser pulses. The incoherent light is generated from a broadband dye laser pumped by the second harmonic (532 nm) of a Q-switched Nd:YAG laser at a repetition rate of 8 Hz, and divided into two. A third beam is a part of the second harmonic, which can be regarded as coherent within the time scale of observation. The incoherent light is tuned at 630 nm so that the difference frequency between 532 nm and 630 nm is resonant with the Raman mode of DMSO. The spectral width (FWHM) of the incoherent light was 7 nm which corresponds to a correlation time of about 100 fs. In Figure 11 the coherent Stokes Raman scattering (CSRS) signal intensity profile is plotted as a function of the delay, from which the vibrational T_2 is determined to be 1.4 ps. The result agrees well with that obtained using picosecond pulses.[21]

4. CONCLUSION

In this paper the ultrafast dephasing measurements in the time domain were discussed. The dephasing times discussed here are classified into two types, namely, electronic (excitonic) T_2 and vibrational T_2 assumed exponential decay properties. Many more experiments can be found in the literature. From the electronic T_2 measurements the following information can be obtained: (1) T_2 in homogeneously or inhomogeneously broadened systems; (2) dephasing mechanisms such as carrier-carrier (exciton-exciton) or carrier-phonon (exciton-phonon) scattering; and (3)

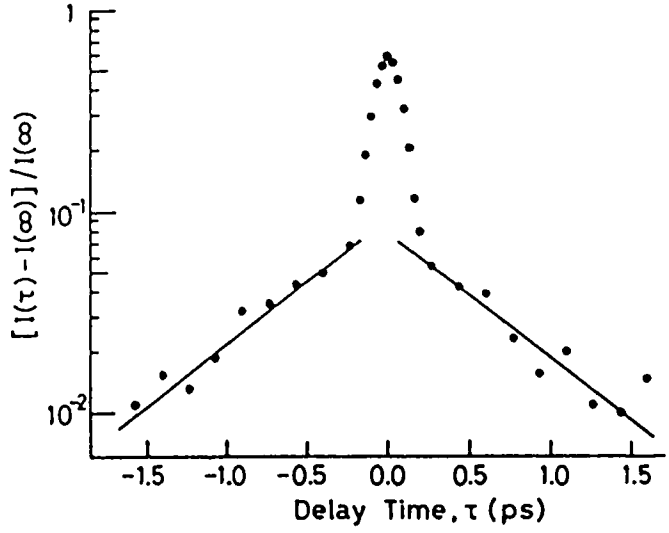

FIGURE 11 CSRS intensity normalized by the background is plotted after the latter is subtracted. (Reference 16)

the structure of the corresponding hole-burning spectra. From the vibrational dephasing measurements, not only can T_2 be determined for homogeneous broadened Raman lines but also the difference frequency of several vibrational modes.

By means of optical coherent transients, these measurements have a ultrahigh time resolution down to several femtoseconds. Investigations of such fast dynamical processes in condensed matters are quite necessary for evaluating optical nonlinear devices as well as clarifying their physical mechanisms.

Acknowledgments

We thank Prof. S. Saikan for critical reading and useful suggestions.

References

1. R. L. Fork, C. H. Brito Cruz, P. C. Becker, and C. V. Shank: *Opt. Lett.* **12**, 483 (1987).
2. T. Yajima and Y. Taira: *J. Phys. Soc. Jpn.* **47**, 1620 (1979).
3. A. M. Weiner, S. De Silvestri, and E. P. Ippen: *J. Opt. Soc. Am.* **2**, 654 (1985).
4. W. H. Hesselink and D. A. Wiersma: *Phys. Rev. Lett.* **43**, 1991 (1979).
5. S. Saikan, T. Nakabayashi, Y. Kanematsu, and A. Imaoka: *J. Chem. Phys.* **89**, 4609 (1988).
6. S. Saikan, T. Nakabayashi, Y. Kanematsu, and N. Tato: *Phys. Rev. B* **38**, 7777 (1988).
7. P. C. Becker, H. L. Fragnito, C. H. Brito Cruz, R. L. Fork, J. E. Cunningham, and C. V. Shank: *Phys. Rev. Lett.* **61**, 1647 (1988).
8. J. L. Oudar, A. Migus, D. Hulin, G. Grilon, J. Etchepare, and A. Antonetti: *Phys. Rev. Lett.* **53**, 384 (1984).
9. L. Schultheis, J. Kuhl, A. Honold, and C. W. Tu: *Phys. Rev. Lett.* **57**, 1635 (1986).
10. N. Morita and T. Yajima: *Phys. Rev. A* **30**, 2525 (1984).
11. S. Asaka, H. Nakatsuka, M. Fujiwara, and M. Matsuoka: *Phys. Rev. A* **29**, 2286 (1984).
12. T. Kobayashi, A. Terasaki, T. Hattori, and K. Kurokawa: *Appl. Phys. B* **47**, 107 (1988).
13. T. Kobayashi, T. Hattori, A. Terasaki, and K. Kurokawa: *Revue Phys. Appl.* **22**, 1773 (1987).
14. T. Kobayashi, K. Misawa, and T. Hattori: In *Lasers '88*, (STS Press), in press.
15. K. Misawa, T. Hattori, and T. Kobayashi: *Nonlinear Optics of Organics and Semiconductors* ed. by T. Kobayashi (Springer, Berlin 1989), p. 66.
16. K. Misawa, T. Hattori, and T. Kobayashi: *Opt. Lett.* **14**, 453 (1989).
17. T. Hattori, A. Terasaki, and T. Kobayashi: *Phys. Rev. A* **35**, 715 (1987).
18. W. Zinth, R. Leonhardt, W. Holzapfel, and W. Kaiser: *IEEE J. Quantum Electron.* **24**, 455 (1988).
19. R. Leonhardt, W. Holzapfel, W. Zinth, and W. Kaiser: *Chem. Phys. Lett.* **133**, 373 (1987).
20. S. Ruhman, A. G. Joly, and K. Nelson: *IEEE J. Quantum Electron.* **24**, 460 (1988).
21. S. M. George, H. Auwester, and C. B. Harris: *J. Chem. Phys.* **73**, 5573 (1980).