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# Vibrational and Rotational Dynamics of Molecules in Solution Studied by Femtosecond CARS and Raman Echo


## Abstract

Vibrational dephasing in liquids has been studied systematically by polarized femtosecond time-resolvent coherent anti-Stokes Raman scattering (CARS), using C≡N and C≡C stretchings as probe vibrations. Dependence of the inter- and intramolecular dephasing process on molecular size is examined. Reorientational motion of molecules in liquid have also been observed from anisotropic component of Raman tensor by a proper choice of polarization conditions. In addition to picosecond decay component, a faster decay component presumably due to the non-dissipative free rotation has been found in the case of neat benzonitrile. An observation of ultrafast Raman echo with a new method is reported for the C≡N stretching of benzonitrile in the liquid phase. It is found that the vibrational line broadening is mainly due to homogeneous effect.


## Introduction

Vibrational dephasing of molecules in condensed phase is a fundamental physical process and carries many important information on molecular interactions, and structure and dynamics of liquids. It gives the first step in the energy transfer pathway of chemical reaction. Since molecular vibration takes place in the femto- to picosecond timescale it is necessary to have time resolution in such a time region. Several groups have applied subpicosecond and femtosecond light pulses to time-resolved coherent anti-Stokes Raman scattering (CARS) measurements (Leonhardt et al, 1987; Bron et al, 1989; Fickenscher and Laubereau, 1990; Okamoto and Yoshihara, 1990; Joo et al., 1991). The main interests of these works have been the observation of vibrational dephasing and/or beating phenomena among several vibrational modes. We have developed an experimental apparatus for measuring femtosecond time-resolved CARS with the capability of selecting any arbitrary polarization conditions (Okamoto and Yoshihara, 1990) and have been studying systematically vibrational dephasing of C≡N stretching in series of alkanenitriles and alkanedinitriles (Inaba et al. 1991; Inba et al. 1992; Okamoto et al. 1993(a)) and of C≡C stretching in monoalkylace-

tylenes and dialkylacetylenes (Inaba et al. 1993(a)) in neat liquids as well as in mixtures with either hydrogen donating or accepting solvents. In this article we firstly describe intra- and intermolecular effects of vibrational dephasing.

One of the advantages of applying CARS is the feasibility of obtaining purely isotropic and anisotropic Raman components separately from independent experiments upon choosing proper polarization conditions (Dick, 1987). We secondly describe the anisotropic decay of $C \equiv N$ stretching mode of benzonitrile in various conditions (Okamoto et al. 1993(b)).

One extension towards exciting higher order non-linear susceptibility of the time-resolved CARS measurement is the ultrafast Raman echo experiment, and it was suggested theoretically to be a method which gives a distinct separation between homogeneous and inhomogeneous contribution to the Raman band (Loring and Mukamel, 1985). The observation of Raman echo signal has recently been reported by Vanden Bout et al. (1991) for the first time. In this article we finally describe a Raman echo experiment with high repetition rate pulses and actual observation of echo signal of $C \equiv N$ stretching of benzonitrile (Inaba et al, 1993(b)).

## Intramolecular Effects on Vibrational Dephasing

We reported that the time-resolved CARS for $C \equiv N$ stretching of relatively small alkanenitriles ($C_nH_{2n+1}CN$, $n = 1 \sim 5$) and found molecular size has significant effects on the vibrational dephasing (Inaba et al., 1991). We expected that further extensive studies on the chain length dependence might provide information on the mechanism of intramolecular relaxation.

Typical experimental results of the time-resolved CARS for the $C \equiv N$ stretching vibration ($\sim 2250\ cm^{-1}$) of neat alkanenitriles ($C_nH_{2n+1}CN$, $n = 2 \sim 17$) are given in Fig. 1. The strong peak at zero delay is due to the nonresonant background. All the observed profiles nearly fit to a single-exponential decay function.

Within the framework of Fermi's Golden Rule, the intramolecular vibrational relaxation rate of an isolated molecule should be linearly correlated with the density of states, if the other factors can be regarded as practically constant. We find that the dephasing rates for the neat alkanenitriles are approximately proportional to the logarithm of the density of vibrational states as shown in Fig. 2. If the inter-state vibrational couplings between the optically allowed state and the background dark states are equivalent, the relaxation rate is expected to be governed by an integrated strength of the inter-state couplings. The present observation suggests that an average of the inter-state matrix elements for the coupling between the $C \equiv N$ stretching and the dark states decreases as the alkyl chain becomes longer. It is interesting to note that there is no asymptotic limit for the value of $T_2$ up to $n = 17$ (Fig. 2).

In contrast to the case of nitriles, the dephasing rates of $C \equiv C$ stretching ($\sim 2120\ cm^{-1}$) of alkylacetylenes ($C_nH_{2n+1}C \equiv CH$, $n = 4 \sim 10$) are almost in-

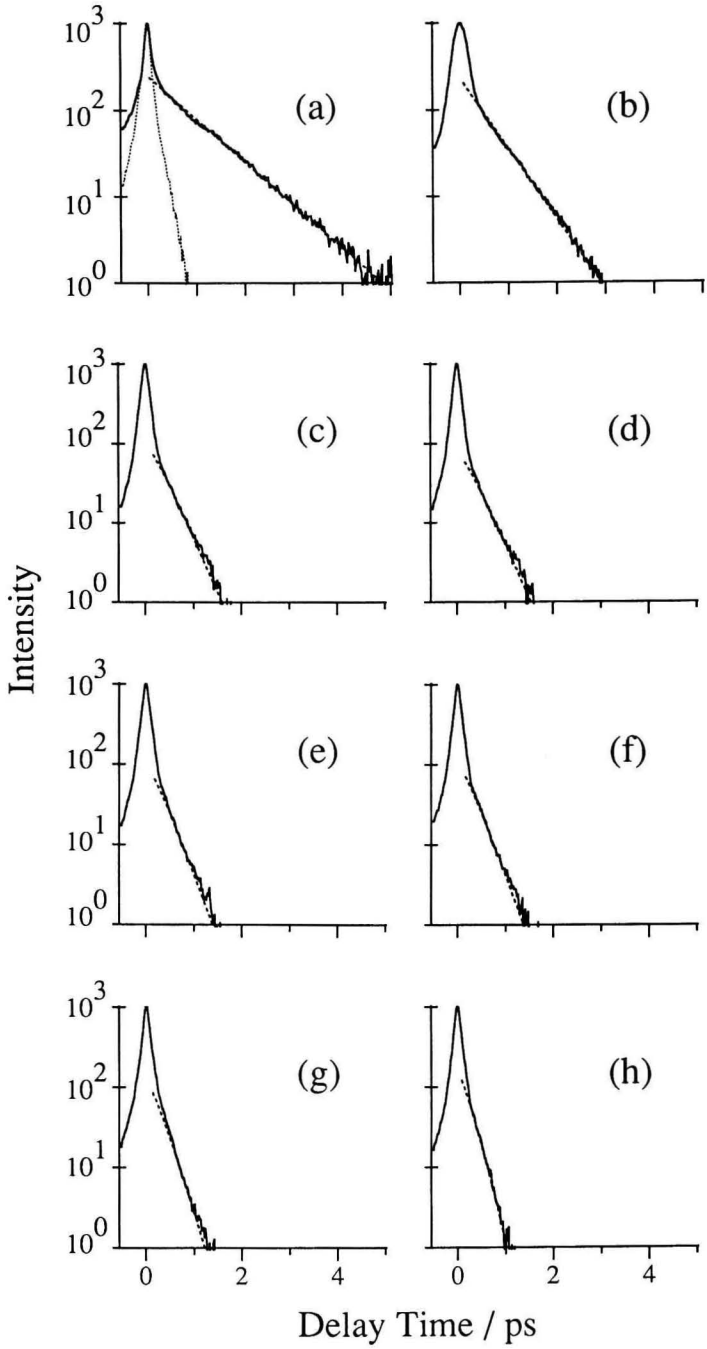


Fig. 1. Time-resolved CARS signals for the C≡N stretching of alkanenitriles. (a) $C_2H_5CN$, (b) $C_5H_{11}CN$, (c) $C_7H_{15}CN$, (d) $C_8H_{17}CN$, (e) $C_{10}H_{21}CN$, (f) $C_{11}H_{23}CN$, (g) $C_{14}H_{29}CN$, (h) $C_{17}H_{35}CN$. The dotted curve in (a) shows the nonresonant background signal from $CCl_4$.

dependent of the chain length in the region under study. Such a difference may be attributed to the presence and absence of the dipole associated with the C≡N and C≡C bonds, respectively. It is conceivable that the dephasing of C≡N stretching is affected by interactions between its own dipole and dipoles associated with the methylene groups in the same molecule but located far from the C≡N group.

## Intermolecular Effects on Vibrational Dephasing

Fig. 2 shows the dephasing time of C≡N stretching of alkanenitriles mixed with methanol (proton donating solvent) in 1:1 mole ratio. The dephasing rates in-

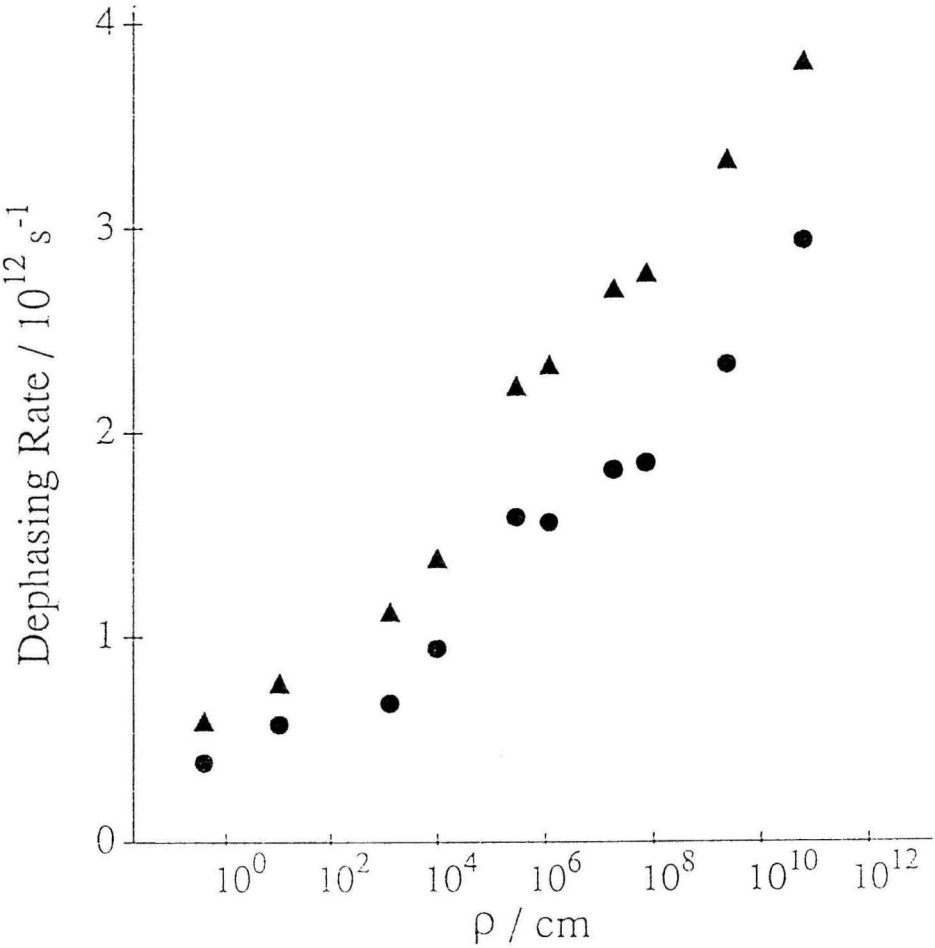


Fig. 2. Plot of the dephasing rates ($1/T_2$) of C≡N stretching of alkanenitriles ($C_nH_{2n+1}CN$, $n = 2 \sim 17$) against the density of vibrational states ($\rho$, in cm = states/cm$^{-1}$) at the C≡N stretching energy. ●: neat liquids; ▲: 50 mol% mixtures with methanol.

crease by about 30%, *regardless* of the chain length (filled triangles). This observation does not support a general expectation that the contribution of intermolecular process to the dephasing would decrease with increasing chain length. If we would divide the dephasing process into intra- and intermolecular parts, the present observation indicates that the weight of the inter-molecular dephasing due to the hydrogen bonding is independent of the molecular size. Therefore, the rate of intermolecular dissipation of vibrational coherence increases with chain length, since the total (intramolecular and intermolecular) dephasing rate also increases with the chain length. This suggests that hydrogen bond is increasingly tightened as the alkyl chain becomes longer. Such a situation may be explained by assuming the formation of a structure similar to lipid bilayer. It would be conceivable that the stability of such an aggregate is increased for longer alkyl chain.

Another explanation may be possible, if we assume that a significant part of the whole dephasing process originates from a correlation (or cross term) between intra- and intermolecular processes. If such a mechanism works, an increase in the dephasing rate of intramolecular origin (due to increasing chain length) could automatically result in greater contribution from the cross term. In the present experiment which measures the acceleration of dephasing in the mixtures with hydrogen bonding solvents, the contribution from the cross term cannot be differentiated from the purely intermolecular contribution, and both of them would appear like the contribution arising from a single origin (formation of intermolecular hydrogen bonding between the OH and CN groups, for example). These two kinds of contributions could amount to the constant degree of increases in the dephasing rate. It has been pointed out theoretically that they are generally neither independent nor simply additive when different dephasing mechanisms are simultaneously operative (Oxtoby et al., 1978). Further studies are needed in order to clarify the dephasing mechanism induced by hydrogen bonding.

## Reorientational Relaxation

One can obtain purely isotropic and anisotropic component of Raman tensor separately from independent measurements in CARS, if we adopt proper polarization conditions (Dick, 1987). We have obtained the rotational correlation function, directly in the time domain, of $C \equiv N$ stretching vibration ( $\sim 2230\ cm^{-1}$) of benzonitrile (BN) mixed with various solvents as shown in Fig. 3. In order to extract the rotational correlation function, we have divided the anisotropic signal by the isotropic signal. (Okamoto et al., 1993(a)). All the mixtures under study give exponential correlation functions. The decay time constants ($=\tau_{OR}/2$) obtained are 2.79 ps for neat BN, 2.00 ps for BN + 1-pentanol (1:1 mole ratio), and 1.87 ps for BN + benzene (1:1). A roughly linear relationship between the reorientational relaxation time and viscosity was found in the mixtures with low

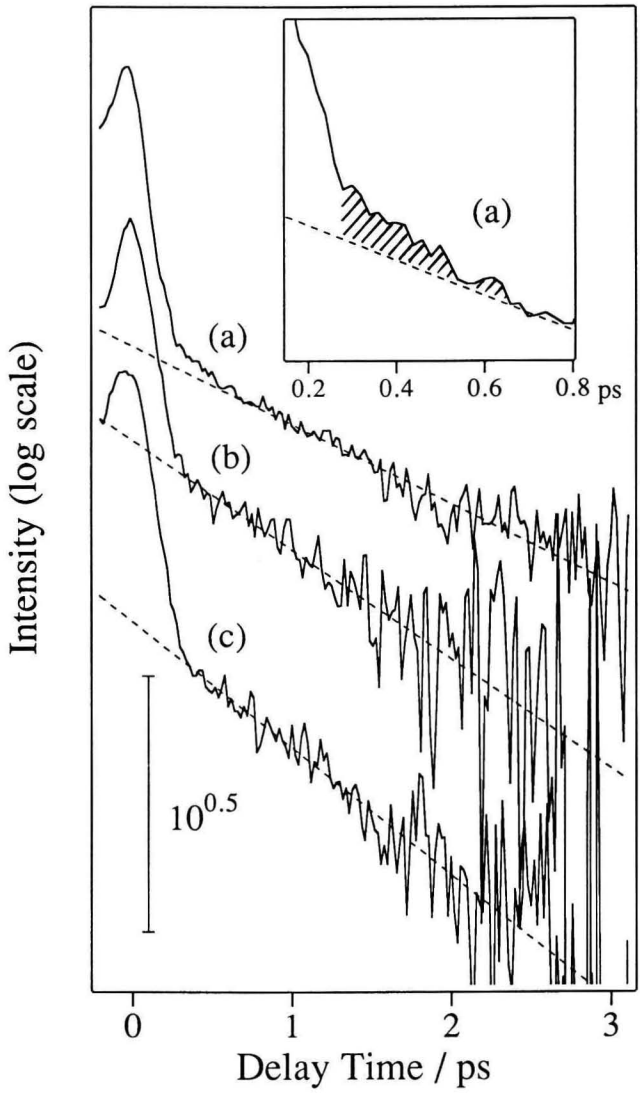


Fig. 3. Correlation functions of anisotropic component obtained by polarized CARS measurements. (a) neat benzonitrile (BN), (b) BN + 1-pentanol (1:1 mole ratio), (c) BN + benzene (1:1 mole ratio). The time constants ($=1/2\tau_{OR}$) obtained are (a) 2.79, (b) 2.00, (c) 1.87 ps.

viscosity. This observation indicates that the macroscopic Stokes-Einstein model is applicable to these mixtures.

Neat BN showed slightly non-exponential behavior in short-time region (hatches part in the inset, $<0.7$ ps). An exponential decay of the correlation function is expected when molecules undergo a number of stochastic collisions (dissipative process) in the course of the reorientational motion. On the other hand, before the molecule collides with neighboring molecules, it rotates freely

like an isolated molecule in the gas phase (non-dissipative process). Then, the rotational correlation function decays rapidly in the short-time regime before the collision occurs. Existence of the non-dissipative process has been pointed out from the band shape analysis of spontaneous Raman spectra (Gordon, 1965). The presence of the fast decay component in the rotational correlation function observed in the present time-resolved experiment may be attributed to the non-dissipative process.

Another interpretation may be possible on the basis of a recent theoretical work by Hayashi et al. (1992) who discussed intermolecular rotational coherence in liquid. They have pointed out a possibility that the interference among rovibrational Raman transitions of molecules at various sites causes the sub-picosecond decay of anisotropic part of the coherent Raman signal. The idea seems to be consistent with the present observation.

## Ultrafast Raman Echo Measurements

In time-resolved CARS or other time-resolved coherent Raman spectroscopic methods based upon the third-order nonlinear process, it is practically impossible to differentiate dephasing due to homogeneous and inhomogeneous contributions. In the previous sections, we have implicitly assumed that the dephasing is not seriously affected by the inhomogeneous contributions. In general, however, vibrational dephasing is influenced by both homogeneous and inhomogeneous contributions.

Homogeneous dephasing arises from an interaction with a bath on a very fast time scale, such as rapid fluctuation of the local environment. The resulting dephasing process usually shows an exponential decay, corresponding to a Lorentzian line shape in the frequency domain. On the other hand, inhomogeneous dephasing takes place when the frequencies of radiation field which interacts with molecules depend on local environments. In this case, the dephasing is static in nature, reflecting the spread in molecular transition energies. A Gaussian inhomogeneous distribution function is sometimes assumed in order to separate the homogeneous and inhomogeneous contributions. However, a non-Gaussian inhomogeneous contribution has been sometimes observed. Therefore, it is difficult to unambiguously determine the extent of inhomogeneous contribution to the dephasing process by means of the time-resolved coherent Raman spectroscopies or the frequency domain band shape analyses.

The homogeneous dephasing can be clearly separated from the inhomogeneous contribution by using Raman echoes, if the vibrational dephasing in liquids is described as a convolution of inhomogeneous and homogeneous contributions (Loring and Mukamel, 1985). An ultrafast Raman echo experiment in liquids has recently been reported for the dephasing of the symmetric stretching mode of methyl group of acetonitrile (Vanden Bout et al., 1991).

The Raman echo is a seventh-order nonlinear process, for which the energy diagram is shown in Fig. 4. Levels *a* and *b* represent ground and excited vibra-

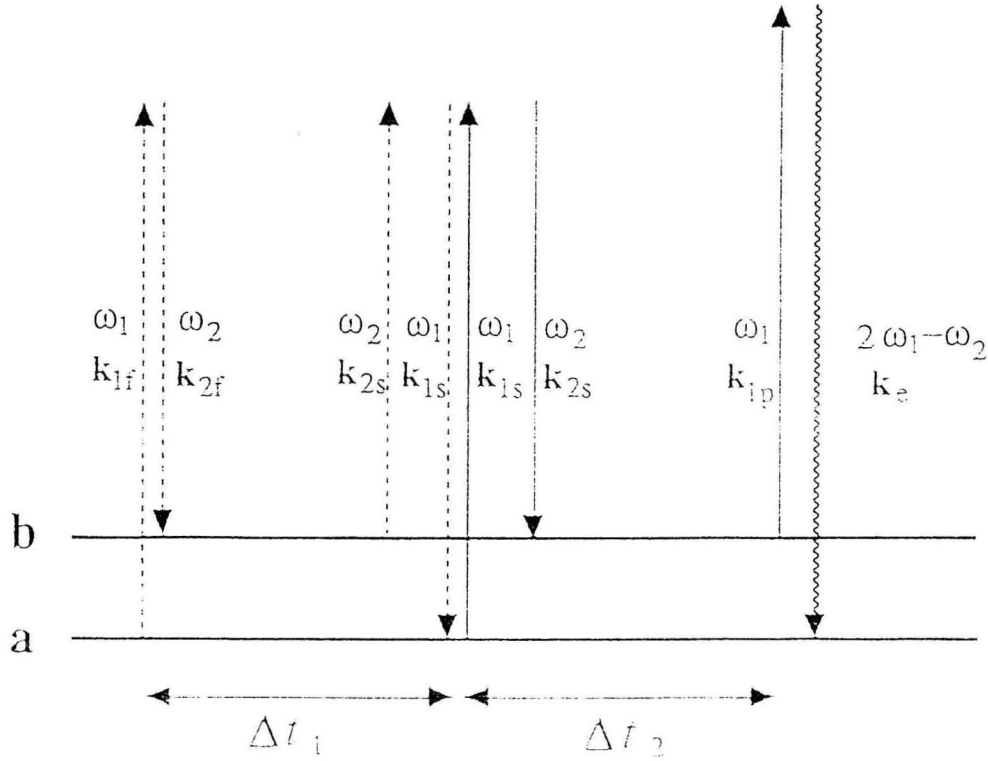


Fig. 4. Energy and time evolution diagram of the Raman echo. Time elapses from left to right. The longitudinal solid and broken arrows represent the ket- and bra-side dipole transitions, respectively. The wavy arrow indicates the light emitting transition by the induced polarization.

tional states, respectively. Initially, all the molecules in the system are assumed to be in state $a$. Coherence between $a$ and $b$ is prepared by applying simultaneously two light pulses with frequencies $\omega_1$ and $\omega_2$, where $\omega_1 - \omega_2$ is tuned to the transition from $a$ to $b$. After a delay time $\Delta t_1$, the system interacts with another pair of excitation pulses at $\omega_1$ and $\omega_2$, which induce two sequential Raman transitions. These transitions cause a rephasing of vibrational coherence partially lost due to inhomogeneity during the delay time $\Delta t_1$. After another delay time $\Delta t_2$, the system is probed with a pulse at $\omega_1$. Then, the echo signal with a frequency of $2\omega_1 - \omega_2$ is generated, reflecting the amount of the vibrational coherence, if the incident radiation fields satisfy the phase-matching condition (Loring and Mukamel, 1985),

$$\mathbf{k}_e = \mathbf{k}_{1p} + 2(\mathbf{k}_{1s} - \mathbf{k}_{2s}) - (\mathbf{k}_{1f} - \mathbf{k}_{2f}) \tag{1}$$

where $\mathbf{k}_e$ is the wave vector of the echo signal, $\mathbf{k}_{1f}$, $\mathbf{k}_{1s}$, and $\mathbf{k}_{1p}$ are those of the incident $\omega_1$ radiation, and $\mathbf{k}_{2f}$ and $\mathbf{k}_{2s}$ are those of the $\omega_2$ radiation. Subscripts '$f$', '$s$', and '$p$' denote the first and second pulse pairs, and the probe pulse,

respectively. When the signal intensity is plotted as a function of $\Delta t_2$ with a fixed value of $\Delta t_1$, the signal shows a maximum intensity when $\Delta t_2 = \Delta t_1$ for an extremely inhomogeneously broadened system. For a homogeneously broadened system, on the other hand, the echo signal decays exponentially with increasing $\Delta t_2$ regardless of $\Delta t_1$.

The ultrafast Raman echo experiment was performed using a system consisting a home-made CW mode-locked Nd:YAG laser, picosecond and femtosecond dye lasers. The pulses from synchronously pumped dye lasers were amplified by dye jet amplifiers excited by a copper-vapor laser operated at 6 kHz. The picosecond pulse was lasing at $\sim 685$ nm with $\sim 7$ ps in duration and amplified as high energy as $\sim 5\mu$J. The femtosecond pulse at $\sim 592$ nm with a duration of $\sim 200$ fs was amplified to 0.7 $\mu$J.

The amplified femtosecond radiation is divided into three portions and used as $\mathbf{k}_{1f}$, $\mathbf{k}_{1s}$, and $\mathbf{k}_{1p}$. The amplified picosecond beam is used as $\mathbf{k}_{2f}$ and $\mathbf{k}_{2s}$ without dividing into two, i.e., $\mathbf{k}_{2f} = \mathbf{k}_{2s}$. These four beams are focused onto the sample to satisfy the phase matching condition for the Raman echo shown by Eq. (1). The echo signal can be separated from the CARS signals, of which the frequency is same as that of the Raman echo, with the aperture by making use of the difference in the phase-matching conditions. However, the aperture is not effective to completely remove the CARS signals, because the difference in the wave-vector mismatch between the CARS and Raman echo is sometimes very small. In order to separate the Raman echo from the CARS signals, the $\mathbf{k}_{1f}$ and $\mathbf{k}_{1s}$ beams are mechanically chopped with frequencies of $f_f \approx 840$ Hz and $f_s \approx 700$ Hz, respectively, by a dual chopper wheel. The Raman echo signal is modulated at the frequency of $f_d = f_f - f_s \approx 140$ Hz, while the CARS signal is modulated at $f_f$ or $f_s$, except for the CARS signal which is scattered in the direction of $\mathbf{k}_{1f} + \mathbf{k}_{1s} - \mathbf{k}_{2f}$. The CARS signal in this direction is modulated at the same frequency as that of the Raman echo, but the intensity of this CARS signal is independent of $\Delta t_2$. Therefore, a plot of the $f_d$-modulated signal intensity as a function of $\Delta t_2$ reflects the decay of the Raman echo signal. The $f_d$-modulated component of the signal from the photomultiplier tube is detected by a lock-in amplifier.

In Fig. 5, the Raman echo intensities are shown for the C≡N stretching of benzonitrile as a function of $\Delta t_2$. The other delay time $\Delta t_1$ is fixed at 0 ps and 2 ps in Fig. 5 (a) and (b), respectively. A strong signal at around $\Delta t_2 = 0$ ps is due to a coherence artifact resulting from a seventh-order nonresonant response. It is found that the echo signals show exponential decay profiles with time constants of $\approx 0.6$ ps for both $\Delta t_1 = 0$ ps and $\Delta t_1 = 2$ ps, within experimental uncertainty.

If the inhomogeneous distribution in Raman transition frequency is assumed to be a Gaussian with a characteristic width (i.e., standard deviation of the transition frequencies) $\delta$, the intensity of Raman echo signal $I(\Delta t_1, \Delta t_2)$ is given by the following equation (Loring and Mukamel, 1985),

$$I(\Delta t_1, \Delta t_2) = \exp(-2(\Delta t_1 + \Delta t_2)/T_2) \exp(\delta^2(\Delta t_2 - \Delta t_1)^2) \qquad (2)$$

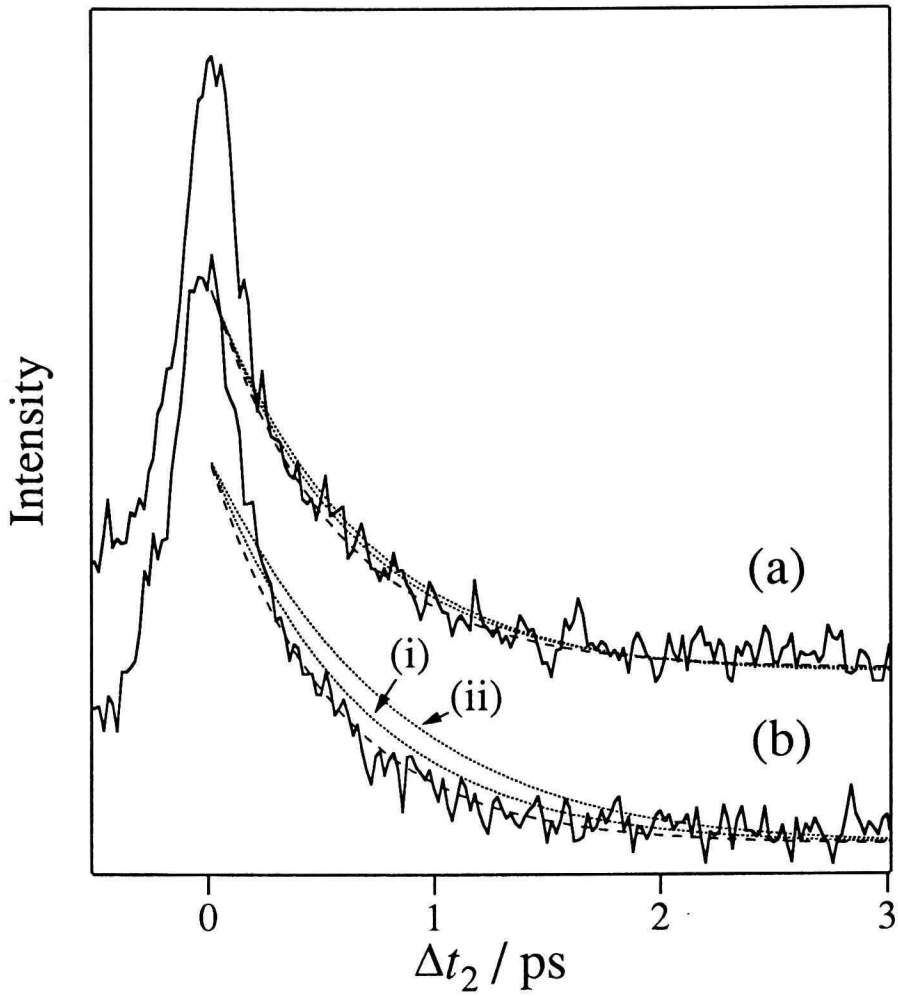


Fig. 5. Raman-echo signal intensities for the C≡N stretching of benzonitrile as functions of $\Delta t_2$. (a) $\Delta t_1 = 0$ ps. (b) $\Delta t_1 = 2$ ps. The broken curve indicates the exponential decay with a time constant 0.6 ps ($= T_2/2$). The dotted curves represent the calculated decay profiles. The parameters for the calculation are: (i) $T_2 = 1.22$ ps and $\delta = 0.92$ cm$^{-1}$; (ii) $T_2 = 1.33$ ps and $\delta = 1.41$ cm$^{-1}$.

where $T_2$ is the homogeneous dephasing time constant. Therefore, if the inhomogeneous broadening has a significant contribution to the dephasing, the decay of the signal should be retarded further as $\Delta t_1$ increases, or in an extremely inhomogeneous broadening case, the signal should show a rise-and-decay profile. The decay profile of Raman echo for $\Delta t_1 = 0$ ps corresponds to that of the time-resolved CARS signal, i.e., the Fourier transform of the isotropic Raman band shape in the frequency domain. The decay time constant of 0.6 ps obtained in this experiment for $\Delta t_1 = 0$ ps is in good agreement with that obtained in the CARS experiment of 0.74 ps (Okamoto et al., 1993).

In Fig. 5, the calculated decay profiles are also indicated for (i) $T_2 = 1.22$ ps and $\delta = 0.92\ \mathrm{cm}^{-1}$, and (ii) $T_2 = 1.33$ ps and $\delta = 1.41\ \mathrm{cm}^{-1}$. In each condition, the predicted isotropic Raman linewidth (half-width at half maximum) is $\approx 4.6\ \mathrm{cm}^{-1}$, which corresponds to 0.6 ps decay of the echo signal for $\Delta t_1 = 0$ ps. From the comparison of the observed decay profile with the calculated one, the characteristic width of inhomogeneous broadening, $\delta$, is estimated to be less than $1\ \mathrm{cm}^{-1}$. In other words, the C≡N stretching Raman band of benzonitrile is almost completely homogeneously broadened. This observation indicates either that the C≡N stretching is only weakly coupled to inhomogeneity in the local environment, or that the lifetime of the fluctuation of liquid structure which is coupled to the C≡N stretching is shorter than the homogeneous dephasing time constant ($T_2 \approx 1.2$ ps) in liquid benzonitrile.

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