Overtone Vibrational Dephasing in Liquids Studied by Femtosecond Fifth-Order Nonlinear Spectroscopy

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We have directly observed vibrational dephasing of the first overtone bands in liquids by femtosecond fifth-order nonlinear spectroscopy for the first time to our knowledge. The overtone and fundamental dephasing processes have been studied for the C-D stretching of $CDCl_3$ and the *sym*-methyl stretching of CD_3I in neat liquid and in its binary mixture with $CHCl_3$. Simulations based on simple stochastic theory or perturbation theory for a harmonic oscillator do not explain both the overtone and fundamental dephasing simultaneously.

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Vibrational spectra in solution are sensitive probes for intermolecular interactions and microscopic dynamics in liquids [1,2]. Dependencies of vibrational bandwidths and peak frequency shifts on thermodynamic properties such as density and temperature have been investigated to study microscopic details of liquids [2]. The vibrational quantum number n is another important degree of freedom to investigate solvent effects on vibrational transitions and dephasing, since the quantum number dependence of the vibrational spectrum is significantly different with different dephasing mechanisms [3–8]. For example, the simple stochastic theory predicts that FWHM (full width at half maximum) of the vibrational band is proportional to n^2 in the case of the rapid modulation limit, whereas it is proportional to n in the case of the slow modulation limit [6].

In the frequency-domain experiments overtone bands ($n = 2$ or 3) were observed by infrared absorption [4,7] and nonresonant Raman spectroscopies [5]. Overtone transitions, sometimes up to $n = 15$, were measured in liquids by resonance Raman spectroscopy on a molecule with an electronic state having an equilibrium nuclear geometry very different from that of the ground state [3,6,8]. In these experiments the alteration of the spectral width and peak shifts were discussed as a function of the vibrational quantum number, and dependencies of the spectral widths were used as criteria to investigate whether the modes were in the rapid or slow modulation limit in some of the experiments [6,7]. Although detailed analysis of the spectral profile of the overtone band would give more detailed information, such an approach has been rather limited because of the relatively low signal level of the overtone signal, non-negligible contribution of the slit width to the spectral shape, and so on [4]. No time-domain experiment on the overtone dephasing has been reported to our knowledge [9].

The study of overtone dephasing is important also from the aspect of vibrational echo experiments [10–19]. Most recently vibrational echo experiments such as Raman echo [10–13], IR photon echo [14–16], and five-pulse correlation [17–19] experiments have been performed to unambiguously distinguish homogeneous and inhomogeneous contributions to the vibrational dephasing. In these experiments two excitation pulses are applied at different times and an echolike signal is observed in the inhomogeneously broadened case. If the vibrational mode is weakly anharmonic, the second excitation pulse creates coherence between the $n = 1$ and 2 states as well as between the $n = 0$ and 1 states. Involvement of the $n = 2$ state in the vibrational echo experiments may yield complicated phenomena in the signal, such as cancellation of the echo signal [17,20] or beating in the signal [16,21]. It is important to get detailed information of the overtone dephasing in order to develop the vibrational echo experiments further.

In this work we have developed a technique to observe time profiles of vibrational dephasing between the $n = 0$ and 2 states in liquids with a good signal-to-noise ratio using femtosecond pulses under nonresonant conditions [22]. The signal of overtone dephasing is based on fifth-order nonlinearity. This method allows one to compare experimental results and theoretical predictions of the vibrational dephasing processes of the overtone and the fundamental bands at a quantitative level.

The experiment is performed with a pair of synchronously pumped dye lasers. The first laser gives pulses with a duration of about 85 fs and a center wavelength of 592 nm, which work as pump and probe pulses. The duration of the second laser was set to be about 8 ps to avoid timing jitter between the two lasers. The wavelength of the second laser is tunable from 600 to 700 nm. The details of the oscillators [23] and the amplifier [19] for the femtosecond laser with a repetition rate of 3 kHz were already mentioned elsewhere. The picosecond pulse, which serves as a Stokes pulse, is preamplified by a six-path bow-tie dye amplifier pumped by the second harmonics of the diode-laser pumped Nd:YLF laser (Spectra Physics TFR). The preamplified pulse with an energy of about 1 μJ/pulse is power amplified in a dye solution flowing in the cell with a 10 mm optical path length, which is irradiated by a 40% output of the YAG regenerative amplifier from both sides of the cell. The final energy of the Stokes pulse is about 10 μJ/pulse. Measurements were done at room temperature (22 °C).

The two femtosecond pulses, $\mathbf{k}_L$ and $\mathbf{k}_p$, and the picosecond pulse, $\mathbf{k}_s$, are focused into the sample to generate a fifth-order response from the liquid, which corresponds to the overtone dephasing signal, $\mathbf{k}_{n=2}$. The three pulses, $\mathbf{k}_L$, $\mathbf{k}_p$, and $\mathbf{k}_s$, consist of a boxcars configuration. This signal appears at an angle which satisfies the following phase-matching condition:

$$\mathbf{k}_{n=2} = 2(\mathbf{k}_L - \mathbf{k}_s) + \mathbf{k}_p . \tag{1}$$

The signal is identified as an overtone signal from its theoretically expected power dependencies on the femtosecond (third power of the laser intensity) and picosecond (second power) pulses and its correct wavelength at the maximum intensity of the scattered light. Since the spectral width of the femtosecond pulse is broad enough ($\sim$200 cm^{-1}), the $n = 2$ level can be coherently excited by this method even though the mode is anharmonic. The polarization condition of the pulses and the signal is chosen so that the fundamental signal is not affected by the rotational motion [24]. The intensity of the overtone signal is 3 to 4 orders of magnitude weaker than that of the fundamental. The investigated vibrational modes are carefully chosen so that any combination bands or other overtone bands do not contribute to the signal.

Possible quantum pathways to generate the overtone signal based on a fifth-order nonlinear process are shown in Fig. 1. The two pathways are not exactly identical to each other, since diagram (a) involve coherence between the $n = 0$ and 1 states, which is not included in (b). However, because the probe pulse width ($\sim$90 fs) is much shorter than observed overtone dephasing times, it is safely assumed that the two pathways yield the same time dependence and the apparent overtone dephasing time is not affected by the time spent in the coherence between $n = 0$ and 1 states. Diagram (a) involves two one-quanta transitions and one two-quanta transition, which include the same vibrational transitions as the five-pulse correlation experiments proposed by Tanimura and Mukamel [17–19].

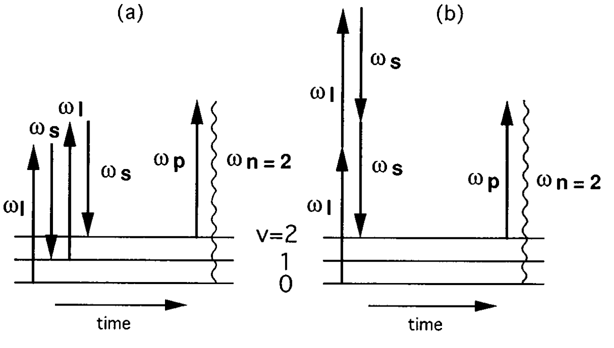

FIG. 1. Possible quantum pathways for the overtone dephasing signal. ω_L, ω_s, ω_p, $\omega_{n=2}$ denote the frequencies of the pump pulse, the Stokes pulse, the probe pulse, and the signal.

Figure 2 shows the time profiles of dephasing between the $n = 2$ and 0 states of the C-D stretching of CDCl$_3$ ($\nu_{10} = 2250$ cm^{-1}) (a) and the *sym*-methyl stretching vibration of CD$_3$I ($\nu_{10} = 2147$ cm^{-1}) (b) both together with those of the fundamentals. For these modes the anharmonicities (ν_{10}-ν_{21}) are less than 100 cm^{-1} [25]. The fundamental dephasing signals are measured with a pulse configuration which satisfies the phase-matching condition of $\mathbf{k}_{n=1} = (\mathbf{k}_L - \mathbf{k}_s) + \mathbf{k}_p$, where $\mathbf{k}_{n=1}$ is the wave vector of the signal. There are strong electronic responses in the fundamental and overtone signals around $t = 0$, which are followed by nearly single exponential decays. The time constants for the single exponential decays obtained for these transients are as follows: for CDCl$_3$ $\tau_{n=1} = 1.0$ ps and $\tau_{n=2} = 0.49$ ps, and for CD$_3$I $\tau_{n=1} = 1.6$ ps and $\tau_{n=2} = 0.66$ ps. Both of the fundamental dephasing rates are consistent with values estimated from the reported spectral widths [4,26]. Brodbeck *et al.* obtained the time autocorrelation function for the $n = 2$ mode of the C-D stretching of CDCl$_3$ by analyzing the infrared spectra of the first overtone and fundamental bands and the Raman spectrum of the fundamental [4]. They estimated the time constant of the dephasing

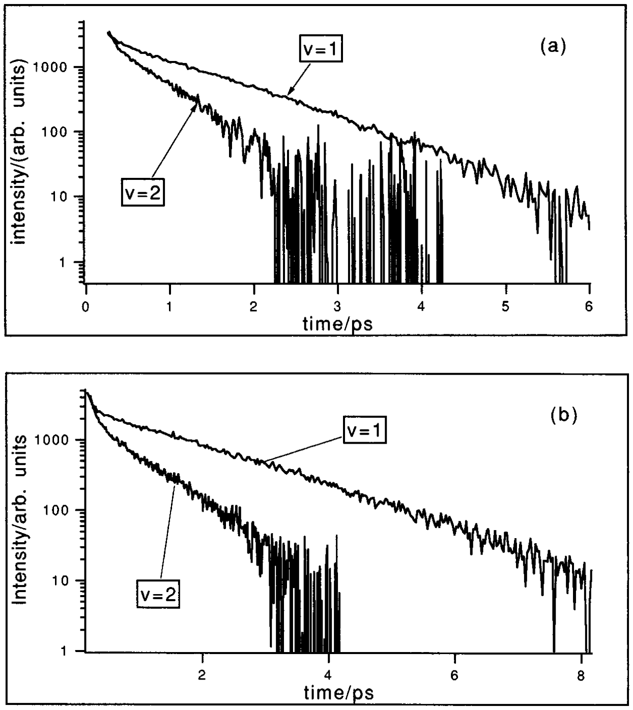

FIG. 2. Time profiles of the vibrational dephasing of the first overtone and fundamental bands of (a) the C-D stretching of CDCl$_3$ and (b) the *sym*-methyl stretching of CD$_3$I in neat liquids. The obtained exponential decay times are as follows: (a) $\tau_{n=1} = 1.0$ ps and $\tau_{n=2} = 0.49$ ps and (b) $\tau_{n=1} = 1.6$ ps and $\tau_{n=2} = 0.66$ ps.

between the $n = 2$ and 0 states as 0.7 ps, which is slightly larger than our value.

The time profiles of both the fundamental and overtone dephasings are first analyzed in terms of a one-mode model based on the stochastic theory developed by Kubo [6,7,27]. In this simple model it is assumed that the time correlation function of the deviation of the vibrational frequency from the average value for the first excited vibrational state, $\Delta(t)$, can be expressed by an exponential function with a pre-exponential factor of D and a time constant of τ,

$$\langle\Delta(0)\Delta(t)\rangle = D^2 \exp(-t/\tau), \tag{2}$$

which has been extensively used to interpret vibrational spectra [1]. The time profile of the nth overtone signal is given by [6]

$$I(t;n) \propto \exp\left(-2n^2D^2\tau t\{1 - \tau/t[1 - \exp(-t/\tau)]\}\right). \tag{3}$$

This expression predicts that the vibrational dephasing rate of the nth overtone is proportional to n^2 in the rapid modulation limit ($D\tau \ll 1$) and proportional to n in the static limit ($D\tau \gg 1$), and has been used to interpret dependencies of vibrational bandwidths on the quantum number [6,7]. Since the experimentally obtained time profiles decay single exponentially, it is natural to assume that both of the observed vibrational dynamics are in the rapid modulation limit. However, the ratio of the dephasing rates between the overtone and fundamental is 2.1 for $CDCl_3$ and 2.4 for CD_3I, which is significantly smaller than 4, the value expected for the rapid modulation case.

Figure 3 shows the time profiles of the first overtone and fundamental bands of the *sym*-methyl stretching of CD_3I in the binary mixture with $CHCl_3$ (1:1 mol/mol). Muller *et al.* performed the Raman echo experiment on the *sym*-methyl stretching of CH_3I in the binary mixture with $CDCl_3$, and found that this mode is partially inhomogeneously broadened [12]. We fitted this fundamental decay by a sum of two time correlation functions which are uncorrelated to each other,

$$\langle\Delta(0)\Delta(t)\rangle = \langle\Delta(0)\Delta(t)\rangle_{\text{fast}} + \langle\Delta(0)\Delta(t)\rangle_{\text{slow}}, \tag{4}$$

where the first and second terms are assumed in the rapid and slow modulation limits, respectively. The obtained parameters are as follows: $T_2 \equiv 1/D_{\text{fast}}^2\tau_{\text{fast}} =$ 3.4 ps and $D_{\text{slow}} = 0.18\ \text{ps}^{-1}$. We calculate the overtone dephasing with these parameters, and the result shows poor agreement with the experiment (Fig. 3). Even when we consider the finite value of τ_{slow} obtained by Muller *et al.*, the agreement is not improved.

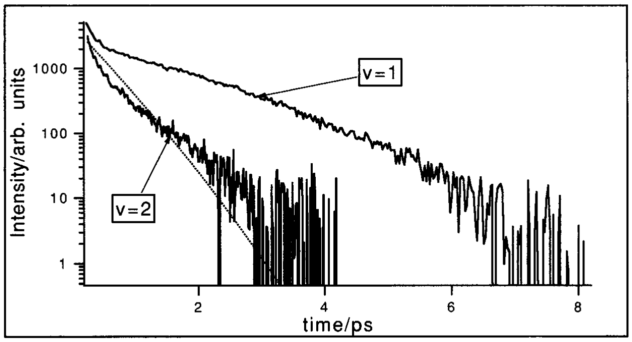

FIG. 3. Time profiles of the vibrational dephasing of the first overtone and fundamental bands of the *sym*-methyl stretching of CD_3I in a binary mixture with $CHCl_3$ (1:1 mol/mol). The obtained exponential time for the overtone band is 0.50 ps. The dotted curve is an overtone dephasing signal predicted by the stochastic theory. The fundamental dephasing shows a nonexponential behavior.

So far we have considered only the effect of pure dephasing by stochastic theory. It was shown by perturbation theory that the population relaxation rate ($1/T_1$) is proportional to n, whereas the pure dephasing rate ($1/T_2^*$) is proportional to n^2 for a harmonic oscillator [28,29]. We estimated the values of T_1 and T_2^* for the first excited vibrational state using the equation

$$1/T_{2,n} = n/2T_1 + n^2/T_2^*. \tag{5}$$

The obtained values are $T_1 = 1.1$ ps and $T_2^* = 40$ ps for $CDCl_3$ and $T_1 = 2.1$ ps and $T_2^* = 14.2$ ps for CD_3I. The value of T_1 is too small and T_2^* too large compared to commonly reported values for organic compounds in solution [30]. In order to rationalize the observed overtone and fundamental dephasing simultaneously, one possible approach may be to use a cubic term of the oscillator coordinate as a perturbation to rigorously include the effect of the anharmonicity [28,29], which is currently in progress.

The final point we wish to discuss is the possible contribution of intermolecular resonant transfer to dephasing of the higher vibrational state. As Oxtoby mentioned [1], it is normally considered that the resonant transfer contribution to an overtone band is small for greatly anharmonic modes, since the transfer of a single quantum from an $n = 2$ excited molecule to a ground state molecule ($n = 0$) requires a substantial rotational or transitional contribution to compensate the energy difference. If the anharmonicity is small, however, there may be a contribution from the resonant transfer to the overtone dephasing, and the resonant transfer effect on the overtone may be larger than that on the fundamental [1]. Since it was already found that the resonant transfer is not important in the dephasing of the fundamental bands investigated in this work by the isotopic dilution experiments [4], it is interesting to see an isotropic dilution effect on the overtone dephasing. We diluted $CDCl_3$ and CD_3I with an equimolar amount of $CHCl_3$ and CH_3I, respectively, and did not observe any noticeable change in either the fundamental or overtone dephasing. Resonant transfer does not play an important role in the overtone dephasing, probably because of the large anharmonicities of the modes investigated.

In summary, we have observed time profiles of dephasing of the first overtone bands in solution by the fifth-order nonlinear spectroscopy for the first time to our knowledge. The overtone and fundamental dephasing have been studied for the C-D stretching of $CDCl_3$ and the *sym*-methyl stretching of CD_3I in neat liquid and in its binary mixture with $CHCl_3$. Two theoretical models, which are based on simple stochastic theory or perturbation theory for a harmonic oscillator, do not explain both the overtone and fundamental dephasing simultaneously. It is found that the resonant transfer is not important in the overtone dephasing, similar to the fundamental.

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