# Overtone Vibrational Dephasing of Chloroform Studied by Higher-Order Nonlinear Spectroscopy

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Vibrational dephasing of the overtone bands of chloroform and its deuterated analogue has been studied by higher-order nonlinear spectroscopy. The overtone signals of $v = 2$ and 3 are based on the fifth- and seventh-order optical nonlinearity, respectively. The overtone vibrational dephasing signals as well as the fundamental ones are represented well by a single-exponential function. These dephasing signals are not explained by the stochastic theory with a time correlation function having a Gaussian or exponential character. Effects of resonant transfer and population relaxation are found not to be important for the deviation from the theoretical prediction. It is suggested that polyatomic natures of the molecule such as off-diagonal anharmonicity or coupling with combination bands may be responsible for this deviation.

## 1. Introduction

The line shape of a vibrational spectrum in liquids reflects intermolecular interactions between the oscillator and surrounding molecules as well as intramolecular interactions such as anharmonic coupling.[1] It is well-known that the spectral width of the overtone vibrational band increases with the vibrational quantum number ($v$). The dependence of the vibrational line shape on the quantum number is strongly affected by underlying dynamics of the liquid molecules. Therefore, the vibrational quantum number is a good parameter for investigating the dephasing mechanism.

The overtone vibrational spectra were observed by infrared absorption and nonresonant Raman spectroscopy.[2−4] In these experiments the spectral widths of the first overtones ($\Delta\nu(v{=}2)$) of simple molecules such as $CH_3CN$ or $N_2O$ were compared with that of the fundamentals ($\Delta\nu(v{=}1)$), and the ratio of $\Delta\nu(v{=}2)/\Delta\nu(v{=}1)$ was analyzed by the stochastic theory.[5] It was found that this ratio often lies between 2 and 3. Overtone transitions, sometimes up to $v = 15$, were observed in liquids by resonance Raman spectroscopy on a molecule with an electronically excited state having an equilibrium geometry very different from that of the ground state.[6−8] Battaglia and Madden observed the vibrational progression up to $v = 11$ of $I_2$ in $CCl_4$ by the resonance Raman method, and the dependence of the overtone line width can be explained well by the stochastic theory.[7]

In the recent 5 years higher-order, fifth- and seventh-order, optical nonlinear spectroscopies have been developed to investigate the vibrational dynamics in condensed phase.[9−22] By these experiments microscopic information of liquids, especially on the molecular dynamics, is available which cannot be obtained by third-order nonresonant nonlinear spectroscopy and spontaneous Raman scattering. The examples are the seventh-order Raman echo[9−14] and the fifth-order two-dimensional Raman spectroscopy.[10,15−19,22] One of the important problems in these experiments is how to make a theoretical model to describe the vibrational dynamics of the $v = 2$ state; namely, in the higher-order nonlinear spectroscopy the contribution of the first overtone to the quantum pathway is sometimes intrinsic to generate optical nonlinearity,[15−19] and it is nessecary to obtain detailed information of the overtone dephasing in order to develop the two-dimensional Raman and vibrational echo spectroscopies further.

Recently, we have developed the fifth-order nonlinear spectroscopy to observe overtone vibrational dephasing of the intramolecular high-frequency mode in the time domain.[20,21] The first overtone bands of the C−D stretching of $CDCl_3$ and the *sym*-methyl stretching of $CD_3I$ were studied by this method, and it was found that simulations based on the simple extension of the stochastic theory or perturbation theory for a harmonic oscillator do not explain dynamics of both the overtone and fundamental dephasing simultaneously.[20] We have also demonstrated temporally two-dimensional overtone spectroscopy, which allows us to study the correlation between the fluctuations of the vibrational transition energies of two bands.[21]

In this work we have observed the $v = 2$ and 3 signals of the C−H stretching of $CHCl_3$ and its deuterated analogue by fifth- and seventh-order nonlinear methods. The results are critically compared with a couple of theoretical models for the vibrational dephasing, and it was found that none of the available theory can explain the results satisfactorily. Possible causes for the deviation from the theoretical prediction are discussed.

## 2. Experimental Section

The experiment is performed with a pair of synchronously pumped dye lasers. The first laser gives pulses with a duration of about 90 fs and a center wavelength of 597 nm. The duration of the second laser was set to be about 8 ps to avoid a timing jitter between the two lasers. The wavelength of the second laser is tunable from 600 to 750 nm. The details of the oscillators[23] and the amplifier[22] for the femtosecond laser with a repetition rate of 3 kHz were already mentioned elsewhere. An additional color filter (Schott RG610, 0.5 mm thickness) was placed after the third dye cell in the amplifier to reduce amplified spontaneous emission and get a shorter pulse. The energy of the amplified pulse is about 3 $\mu$J/pulse. A diagram

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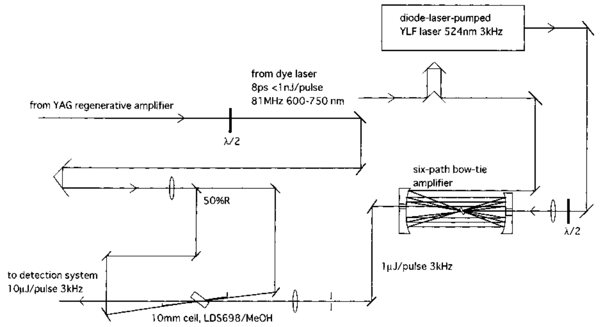

**Figure 1.** Amplifier system for the picosecond pulse. 50%R denotes a beam splitter with a reflection of 50%, and $\lambda/2$ is a half-wave plate. A six-pass bow-tie amplifier has a dye jet of a solution of LDS698 in ethylene glycol. In the power amplifier a solution of LDS698 in methanol is used.

of the picosecond amplifier is shown in Figure 1. The picosecond pulse, which serves as a Stokes pulse, is preamplified by a six-pass 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 $\mu$J/pulse is power-amplified in a dye solution of LDS698 in methanol flowing in a cell with a 10 mm optical path length, which is irradiated by a part of the output of the YAG regenerative amplifier (~600 mW) from both sides of the cell. The final energy of the Stokes pulse is about 10 $\mu$J/pulse. The samples are contained in a quartz cell with a 1 mm optical path length and a 300 $\mu$m thickness window. All of the measurements are done at ambient temperature (25 °C).

The femtosecond pulse is split into two parts with equal intensities; one serves as a pump pulse $\mathbf{k}_L$ and the other serves as a probe pulse $\mathbf{k}_p$. Before focusing the pulses by an achromatic lens ($f$ = 100 mm) into the sample, the two femtosecond pulses and picosecond pulse (Stokes pulse) $\mathbf{k}_S$ are collimated so that a diameter of the pulse is around 0.5 mm. The three input pulses and the CARS signal form a boxcars configuration. The overtone signals, $\mathbf{k}_{v=2}$ and $\mathbf{k}_{v=3}$, appear at an angle which satisfies the following phase-matching conditions:

$$\mathbf{k}_{v=2} = 2(\mathbf{k}_L - \mathbf{k}_S) + \mathbf{k}_p \tag{1}$$

$$\mathbf{k}_{v=3} = 3(\mathbf{k}_L - \mathbf{k}_S) + \mathbf{k}_p \tag{2}$$

The polarization condition of the pulses and the signal is chosen so that the fundamental signal is not affected by the rotational motion; $\mathbf{P}(\mathbf{k}_L)$ // $\mathbf{P}(\mathbf{k}_S)$, $\mathbf{P}(\mathbf{k}_P)$ // $\mathbf{P}(\mathbf{k}_{v=2})$ // $\mathbf{P}(\mathbf{k}_{v=3})$, and the angle between $\mathbf{P}(\mathbf{k}_L)$ and $\mathbf{P}(\mathbf{k}_P)$ is 54.7°, where $\mathbf{P}(\mathbf{k}_i)$ denotes the polarization vector of the $\mathbf{k}_i$ pulse.

## 3. Theoretical Background

In this section we give an expression for the quantum number dependence of the vibrational dephasing signal by the perturbation theory following Oxtoby[1] and Myers and Markel.[8] In the case where the pulse duration is shorter than the vibrational dephasing time, the time profile of the overtone signal can be expressed by

$$I(t) \propto |\exp(-i\omega_v t)\langle X(t)\, X(0)\rangle + \text{c.c.}|^2 \tag{3}$$

Here, $X(t)$ is the vibrational coordinate of interest, c.c. is the complex conjugate, and

$$\omega_v = \sum_i \epsilon_i \omega_i \tag{4}$$

where $\epsilon_i$ is +1 for the pump pulse and is −1 for the Stokes pulse. $\omega_i$ is the center frequency of the $i$th input optical pulse. The time correlation function of the coordinate is given by the fluctuation of the transition frequency between the 0th and $n$th vibrational states, $\Delta\omega_{0n}(t)$, around the average value of $\omega_0$,

$$\langle X(t)\, X(0)\rangle = Re \exp(i\omega_0 t)\langle \exp[i\int_0^t \mathrm{d}t\, \Delta\omega_{0n}(t)]\rangle \tag{5}$$

A cumulant expansion of the above equation gives

$$\langle X(t)\, X(0)\rangle = Re \exp(i\omega_0 t) \times \exp[-\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \langle \Delta\omega_{0n}(t_1)\, \Delta\omega_{0n}(t_2)\rangle] \tag{6}$$

where the double integral can be reduced to a single integral, and the overtone signal is given by

$$I(t;n) \propto \exp(-2\int_0^t \mathrm{d}\tau\, (t-\tau)\langle \Delta\omega_{0n}(\tau)\, \Delta\omega_{0n}(0)\rangle) \tag{7}$$

Hereafter, we derive an expression for the time correlation function of the transition frequency starting from a simple diatomic Hamiltonian by the perturbation theory. Most models for vibrational dephasing begin with a common perturbation approach to solvent−solute interaction.[25−29] The vibrational Hamiltonian for a molecule interacting with a bath is written as

$$H_{\text{tot.}}(t) = H_h + H_{\text{anh}} + H_c(t) \tag{8}$$

Here $H_h + H_{\text{anh}}$ is the Hamiltonian for an isolated molecule,

$$H_h + H_{\text{anh}} = \frac{1}{2M}p^2 + \frac{1}{2}M\omega^2 Q^2 + \frac{1}{6}fQ^3 \tag{9}$$

where we assume a diatomic oscillator with a weak anharmonic coupling for simplicity and $M$ is the reduced mass, $\omega$ the harmonic frequency, $Q$ the displacement from equilibrium internuclear separation, $p$ the momentum conjugated to $Q$, and $f$ the cubic anharmonicity. $H_h$ is the harmonic part of the Hamiltonian, and $H_{\text{anh}}$ is the weak anharmonic term. The solvent−solute interaction is expanded in the oscillator coordinate up to the second order,

$$H_c(t) = \frac{\partial V(t)}{\partial Q}\Big|_{Q=0} Q + \frac{\partial^2 V(t)}{\partial Q^2}\Big|_{Q=0} Q^2 \tag{10}$$

$$= F(t)Q + G(t)Q^2 \tag{11}$$

The time-dependent transition frequency between the vibrational levels $v = n$ and $m$ is expressed as

$$\omega_{nm}(t) = \frac{1}{\hbar}(\langle n|H_{\text{tot.}}(t)|n\rangle - \langle m|H_{\text{tot.}}(t)|m\rangle) \tag{12}$$

The deviation of the transition frequency between the $n$th and $m$th levels from the average value is given by[1]

$$\Delta\omega_{nm}(t) = \omega_{nm}(t) - \omega_{nm}^{\text{av}} = \frac{1}{\hbar}(\langle n|H_c(t)|n\rangle - \langle m|H_c(t)|m\rangle) \tag{13}$$

$$= (n-m)\left(-\frac{f\hbar}{2M^2\omega^3}F(t) + \frac{\hbar}{2M\omega}G(t)\right) \tag{14}$$

and finally, if $F(t)$ and $G(t)$ are uncorrelated, the following important relation for the time correlation function is obtained,

$$\langle \Delta\omega_{nm}(t)\, \Delta\omega_{nm}(0)\rangle = (n-m)^2\left[\left(\frac{f\hbar}{2M^2\omega^3}\right)^2 \langle F(t)\, F(0)\rangle + \left(\frac{\hbar}{2M\omega}\right)^2 \langle G(t)\, G(0)\rangle\right] \quad (15)$$

Oxtoby approximated that $G(t)$ is proportional to $F(t)$ in the case of the repulsive part of the intermolecular potential.[28] If the time correlation function for the fundamental band ($n = 1$ and $m = 0$) is expressed by an exponential form (Kubo form),

$$\langle \Delta\omega_{01}(t)\, \Delta\omega_{01}(0)\rangle = D^2 \exp(-t/\tau) \quad (16)$$

from eq 15 the following relation is readily obtained,

$$\langle \Delta\omega_{nm}(t)\, \Delta\omega_{nm}(0)\rangle = (n-m)^2 D^2 \exp(-t/\tau) \quad (17)$$

yielding an equation for the time profile of the signal of the $v$th vibrational state,[7]

$$I(t;v) \propto \exp(-2v^2D^2\tau t\{1 - \tau/t[1 - \exp(-t/\tau)]\}) \quad (18)$$

This is a well-known equation for the overtone dephasing derived from the Kubo form[7] and predicts that the vibrational bandwidth of the $v$th state is proportional to $v^2$ in the rapid modulation limit (homogeneous limit; $D\tau \ll 1$) for small $v$ and proportional to $v$ in the static limit (inhomogeneous limit; $D\tau \gg 1$).

It is suggested from the above derivation that eq 17 generally holds for a diatomic case, since it assumes the anharmonic coupling of the vibrational coordinate and the oscillator−bath interaction up to the second order. Actually, Battaglia and Madden used this relation to explain the vibrational quantum number dependence of the line width of the resonance Raman spectrum of $I_2$ in $CCl_4$.[7] They have shown that the effective vibrational line shape can range from having a nearly quadratic dependence on quantum number at small $v$ to a linear dependence at large $v$.

## 4. Results and Discussion

**4.1. Observation and Identification of the Signals.** Figure 2 shows the time profiles of the signals of $v = 1$, 2, and 3 of the C−H stretching of $CHCl_3$ ($\nu = 3020$ cm$^{-1}$, $\lambda_{Stokes} = 728$ nm) and of the C−D stretching of $CDCl_3$ ($\nu = 2250$ cm$^{-1}$, $\lambda_{Stokes} = 690$ nm). For these modes the anharmonicities are less than 140 cm$^{-1}$ in the gas phase.[30] There are strong instantaneous responses in the signals around $t = 0$ due to the electronic polarizability, especially in the overtone signals. These electronic responses are followed by nearly single-exponential decays. Due to the electronic response we cannot discuss the initial dynamics of the vibrational motion. The time constants of the single-exponential decays and temporal regions where the signal exponential decays are observed are summarized in Table 1. The dephasing times are equal to twice the time constants of the signal decays. In the figure the signal intensities are normalized arbitrarily. The relative intensity of the $v = 2$ ($v = 3$) signal is 3−4 (7−8) orders of magnitude weaker than that of the fundamental.

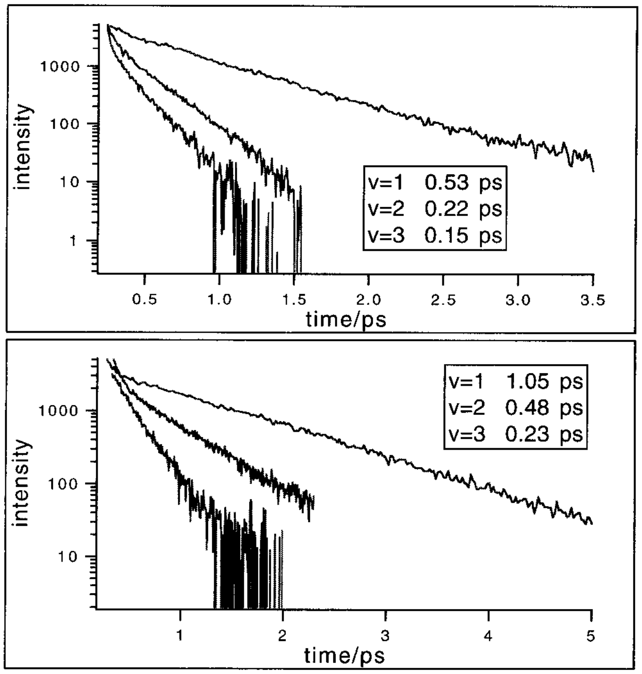

**Figure 2.** Time profiles of the vibrational dephasing of the overtones ($v = 2$ and 3) and fundamental bands of the C−H stretching of $CHCl_3$ (upper) and the C−D stretching of $CDCl_3$ (lower). The obtained exponential decay time constants are shown in the figure.

**TABLE 1: Time Constants of the Exponential Decays and Temporal Regions for the Exponential Decays**

| | time constant, ps | temporal region for the exponential decay, ps |
|---|---|---|
| | $CHCl_3$ | |
| $v = 1$ | 0.53 | 0.27−4 |
| $v = 2$ | 0.21 | 0.34−1.5 |
| $v = 3$ | 0.15 | 0.39−1.2 |
| | $CDCl_3$ | |
| $v = 1$ | 1.05 | 0.38−8 |
| $v = 2$ | 0.47 | 0.59−3 |
| $v = 3$ | 0.23 | 0.63−1.8 |

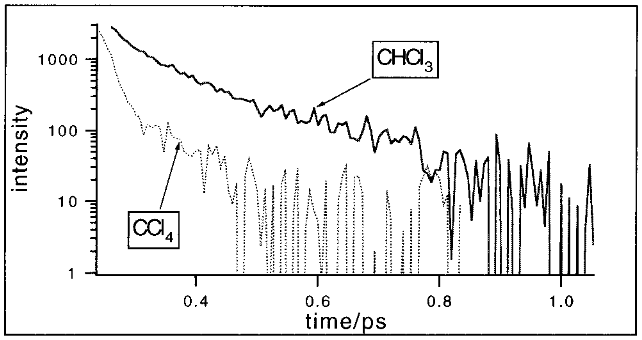

**Figure 3.** Time profiles of the seventh-order response from $CHCl_3$ and $CCl_4$.

Since there is a strong electronic response around $t = 0$ in the overtone signals, we have to carefully check that the decay we observe is not a part of the tail of the pulse but comes from a real nuclear response. We confirmed this point by using $CCl_4$ as a sample which does not have any vibrational mode whose frequency is higher than 800 cm$^{-1}$. As shown in Figure 3, $CHCl_3$ shows a delayed response compared to $CCl_4$, which clearly shows that the observed signal in $CHCl_3$ results from the nuclear response.

Possible quantum pathways to generate the fifth- and seventh-order nonlinearities are shown in Figure 4. The different pathways in the same signal are not exactly identical with each other. For example, in the fifth-order process diagram a involves a coherence between the $v = 0$ and 1 states, which is not included in b. However, because the femtosecond pulse is shorter than the observed dephasing times, it is safely assumed

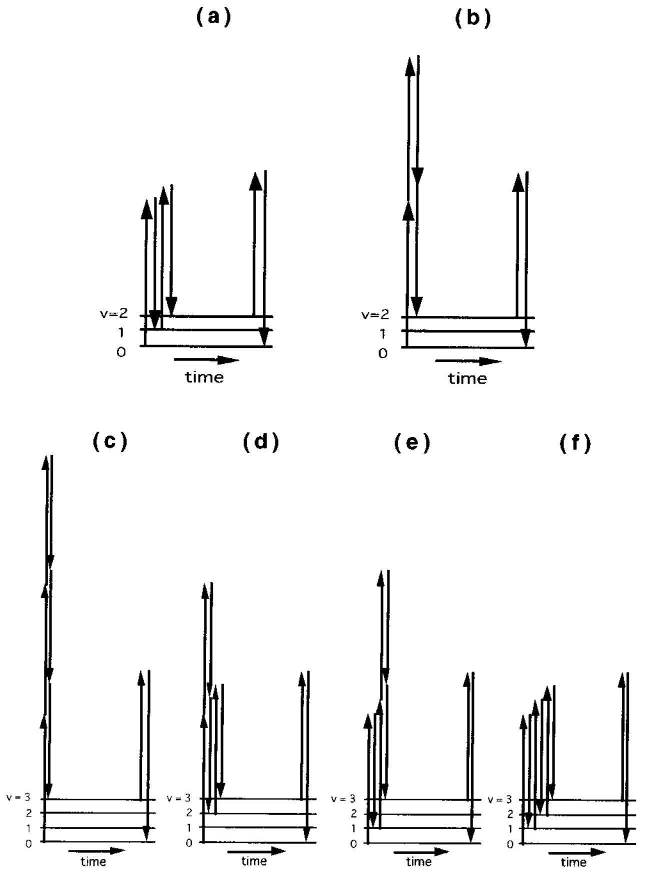

**Figure 4.** Possible quantum pathways for the overtone dephasing signals. a and b are for the $v = 2$ signal, and c−f are for the $v = 3$ signal.

that the two pathways yield the same time dependence. Figure 5 shows laser power dependencies of the signal intensities. Each signal has right dependencies on both the femtosecond and picosecond laser powers; namely, the $v = 2$ signal depends on the femtosecond pulse in the third order and on the picosecond pulse in the second order, and the $v = 3$ signal depends on the femtosecond pulse in the fourth order and on the picosecond pulse in the third order.

Identification of the signal should be done very carefully, since the intensities of the higher-order signals are extraordinarily small compared to that of the fundamental, and sometimes the higher-order signals may be interfered by lower-order stray light. The identification procedure for the higher-order signals has been discussed in detail.[16−19,23] We have checked the wavelength at the peak intensity, the laser power dependence, the concentration dependence, and so on, to identify the signals.

We have confirmed with special care that the signals come from the true higher-order nonlinearity, but not from sequential cascading third-order signals, since the cascading signals have the same laser power dependence as the true higher-order signals and the overall phase-matching condition is also the same as that of the true signal.[31,32] In this experiment we are using a boxcars configuration for the three input beams, and there might be a possibility that cascading signals are observed instead of the true higher-order signal. We can neglect this possibility by the following observations. First, we have done the temporally two-dimensional overtone dephasing experiment using three femtosecond and one picosecond pulses, and we can safely avoid the contribution of cascading signals in these multipulse experiments.[21] The same time profile of the signal was observed as that of the temporally one-dimensional overtone signal,[21] which shows that the present overtone signal comes from the true fifth-order nonlinearity. We have also found that the signal intensity depends on the concentration in a way expected for the true higher-order signal. Sometimes the cascading signal was reported in the frequency domain experiment.[31,32] The major difference between the frequency domain and the present experiments might come from the difference in the interaction length of the pulse with the material; by the tight focusing condition of the pulses, the interaction region of the pulses with material can be designed to be much smaller than that of the frequency domain experiment, in which the true higher-order signal predominantly contributes and the cascading effect can be eliminated.

In $CHCl_3$ ($CDCl_3$) the second highest fundamental frequency is the $\nu_4$(e) mode at 1216 cm$^{-1}$ (908 cm$^{-1}$).[30] Therefore, the C−H and C−D stretching modes are well-separated from other vibrational modes in frequency, and we can safely say that the observed signals come from the overtone signals of the C−H or C−D stretching mode and not from any combination bands or overtone bands of the other vibrational modes.

Since the spectral width of the femtosecond pulse is broad enough (~200 cm$^{-1}$), the $v = 2$ and 3 states can be coherently excited by this method even though the mode is anharmonic. The transition frequency of $v = 3$ of $CHCl_3$ in liquid is reported to be 8700 cm$^{-1}$.[30] To investigate the effect of the anharmonicity on the time profile of the signal, we have set the wavelength of the Stokes pulse so that $3(\omega_L - \omega_S)$ is equal to 8700 cm$^{-1}$ ($\lambda_{\text{Stokes}} = 722$ nm). In this case the quantum pathway c in Figure 4 predominantly contributes to the signal. The obtained $v = 3$ signal has the same decay time constant as that observed previously within experimental error.

### 4.2. Comparison with Theoretical Prediction.

In this section we compare the experimental results with predictions by the stochastic theory. We first summarize the experimental results. (1) All of the dephasing signals can be fitted well by a single-exponential function. (2) The ratio of the time constant of the $v = 1$ and 2 signals, $\tau_{v=1}/\tau_{v=2}$, is similar for the $CHCl_3$ and $CDCl_3$ cases, namely, around 2.3, but the ratio of the $v = 1$ and 3 signals, $\tau_{v=1}/\tau_{v=3}$, differs with the system.

As was shown in the previous paper, the stochastic theory cannot explain the fundamental and overtone dephasing simultaneously if we use an exponential function for the time correlation function of the fluctuation of the transition frequency. The fundamental signal of $CDCl_3$ is fitted in terms of eqs 16 and 18, and the obtained parameters are as follows: $D = 1.34$ ps$^{-1}$ and $\tau = 0.28$ ps. This set of parameters is in the rapid modulation limit ($D\tau \ll 1$), which gives a nearly single-exponential decay for the fundamental and overtones. Consequently, the decay time constants of the overtones show a $v^2$-dependence. However, the experimental results show the subquadratic dependence on the quantum number.

The time correlation function of the fluctuation, $\langle\Delta\omega(t)\,\Delta\omega(0)\rangle$, is sometimes expressed as a sum of two components,

$$\langle\Delta\omega(t)\,\Delta\omega(0)\rangle = \langle\Delta\omega(t)\,\Delta\omega(0)\rangle_{\text{fast}} + \langle\Delta\omega(t)\,\Delta\omega(0)\rangle_{\text{slow}} \tag{19}$$

to include both the homogeneous and inhomogeneous effects to the vibrational broadening. Here, the first component is in the rapid modulation limit ($D\tau \ll 1$) and the second component is near or in the slow modulation limit ($D\tau \geq 1$). However, we have already shown that this two-component model also cannot explain the fundamental and overtone ($v = 2$) signals of the *sym*-methyl stretching of $CD_3I$ in a binary mixture with

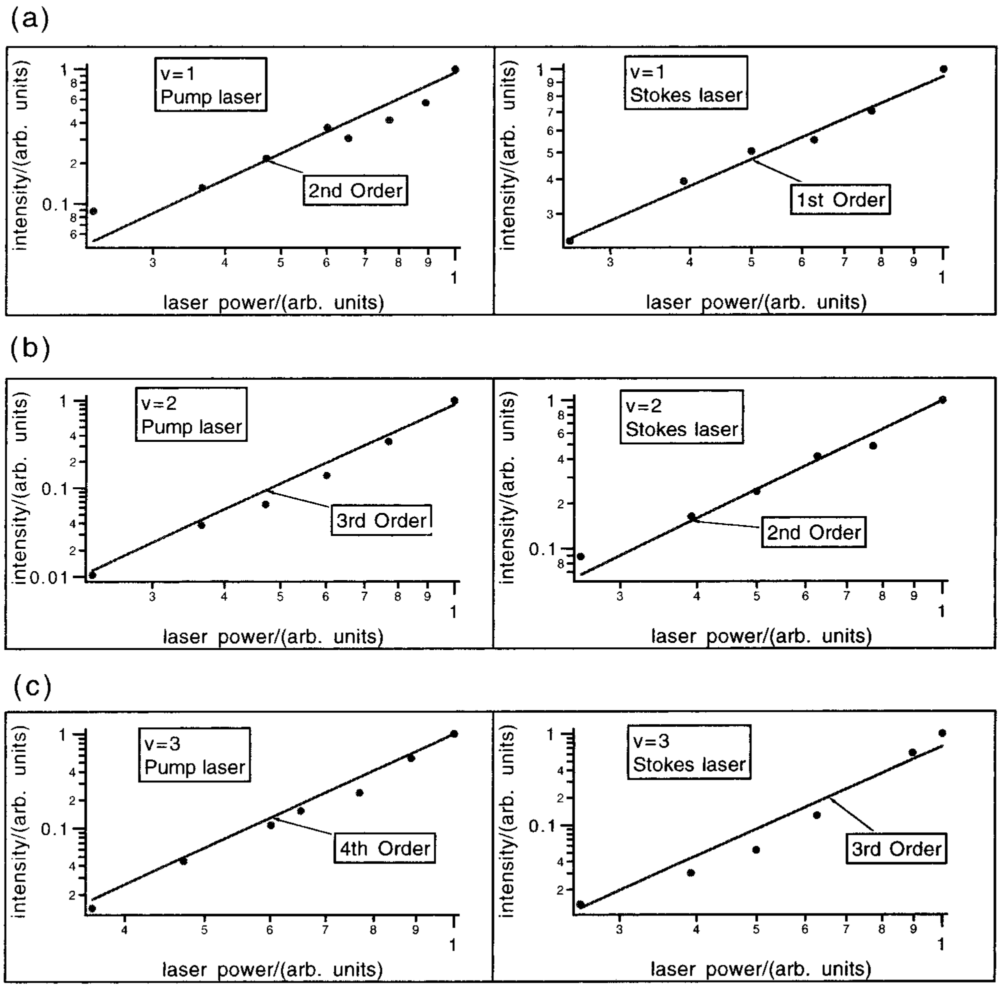

**Figure 5.** Laser power dependencies on the dephasing signals.

$CHCl_3$,[20] which is a well-known partially inhomogeneously broadened system due to the local concentration fluctuation.[12]

So far we have used an exponential form for the time correlation function $\langle \Delta\omega(t)\, \Delta\omega(0)\rangle$. This is based on the assumption that the force–force autocorrelation function (eq 15) can be expressed by an exponential form. The force–force autocorrelation function is connected to a time-dependent memory friction, $\zeta(t)$, by the fluctuation–dissipation theorem,

$$\langle F(t)\, F(0)\rangle = k_B T \langle \zeta(t)\, \zeta(0)\rangle \qquad (20)$$

where $k_B$ and $T$ are the Boltzmann constant and temperature. However, recent computer simulation and analytical theory on liquid dynamics have clearly shown an existence of the ultrafast component in this autocorrelation function.[24,33] The ultrafast component can be well-represented by a Gaussian function, which is caused by an inertial-type motion of liquid molecules. Bern and co-workers performed MD simulations to investigate the relationship between the frequency-dependent friction and vibrational dephasing.[33] From their simulation, it can be seen that the typical time correlation function of $\zeta(t)$ shows a Gaussian decay character in the early stage, which is followed by a nearly exponential decay in the case of a diatomic molecule.

We have performed a model calculation of the time profile of the signal with a time correlation function of the fluctuation, which is expressed as

$$\langle F(0)\, F(t)\rangle = D_g^{\,2} \exp(-(t/\tau_g)^2) + D_e^{\,2} \exp(-t/\tau_e) \qquad (21)$$

Here the parameters are determined in a rather arbitrary way. We first assume that $\tau_g$, a time constant of the Gaussian component, is in the range from 10 to 100 fs since this time scale is related to the inertial motion of the liquid molecule. Then, with fixed $\tau_g$, other parameters, $D_g$, $D_e$, and $\tau_e$ are estimated so that the calculated signal for $v = 1$ reproduces the experimental results. Finally, the overtone signal decay is calculated by eq 15 and the obtained parameters. However, the inclusion of the Gaussian component does not improve the theoretical prediction for the overtone signals. This is because the fast Gaussian component gives a signal in the rapid modulation limit. Regardless of the functional form, if the time correlation function decays fast enough, that component is detected as a “rapidly modulating” component. This can be readily understood from eq 7. If $\langle \Delta\omega_{n0}(t)\, \Delta\omega_{n0}(0)\rangle$ decays fast enough and is nearly zero after a representative time of $t_r$

$$\langle \Delta\omega_{n0}(t)\, \Delta\omega_{n0}(0)\rangle \approx 0 \qquad t \gg t_r \qquad (22)$$

then

$$\int_0^t dt'\,(t-t')\langle \Delta\omega_{n0}(t')\, \Delta\omega_{n0}(0)\rangle \approx n^2(C_1 t - C_2) \qquad t \gg t_r \qquad (23)$$

where $C_1$ and $C_2$ are constants. Therefore, the time profile of the signal can be well-represented by a single exponential, and the decay time constants of the overtones are proportional to $v$.[2]

**4.3. Possible Causes for the Deviation from the Prediction.** In this section we discuss possible causes for the deviation from the theoretical predictions.

*4.3.1. Effect of $T_1$.* So far, we have only considered the pure vibrational dephasing, $T_2$*, and ignored the effect of the population relaxation, $T_1$. Normally, $T_1$ of a polyatomic molecule is much longer than $T_2$ and can only play a minor role in the vibrational dephasing process.[34-36] $T_1$ of the C−H stretching of $CHCl_3$ was reported to be 24 ps by a IR pump−probe study[37] and 23 ps by incoherent anti-Stokes scattering after strong infrared excitation.[38] The vibrational population relaxation time of the $v$ state, $T_{1,v}$, can be estimated from the Landau−Teller equation,

$$T_{1,v} = \frac{1}{v} T_{1,v=1} \tag{24}$$

Then, $T_{1,v=2}$ and $T_{1,v=3}$ are estimated to be 11.5 and 7.7 ps for the C−H stretching of $CHCl_3$, respectively, and it is guaranteed that the effect of $T_1$ is not important in the present case.

However, recently Fayer and co-workers measured $T_1$ of the $v = 2$ state of the CO stretching of some carbonyl compounds from a beating signal in the infrared photon echo.[39] In the infrared photon echo experiment, if the vibrational mode is weakly anharmonic, the second excitation pulse yields coherence not only between the $v = 1$ and 0 states but also between the $v = 2$ and 1 states. Consequently, the different quantum pathways produce radiation fields with different frequencies, which interfere with each other, giving a beat in the signal. Measuring this quantum beat, one can estimate $T_1$ of the $v = 2$ state as well as the $v = 1$ state. The ratio of $T_{1,v=1}/T_{1,v=2}$ was obtained for the CO stretching of tungsten hexacarbonyl, rhodium dicarbonylacetylacetonate, and a mutant of myoglobin−CO (H64V−CO), and the values are 11, 5, and 2.5, respectively. The ratio was found to be largely system-dependent and larger than the prediction by the Landau−Teller relation. They explained the large $T_{1,v=1}/T_{1,v=2}$ values by invoking an opening of a new relaxation pathway for relaxation from the $v = 2$ state to the $v = 0$ state. This result suggests that in the present cases $T_1$ of the overtones might be much shorter than the prediction by the Landau−Teller equation and affect the vibrational dephasing of the overtones. However, in order to have an effect on the dephasing, $T_1$ of the overtones should be on the order of sub-picosecond at least. This value is 2 orders of magnitude smaller than that of $T_1$ of the $v = 1$ state and is physically rather unrealistic. Therefore, we conclude that the effect of $T_1$ on the overtone dephasing is negligible.

*4.3.2. Rotation−Vibration Coupling.* Schweizer and Chandler[40] and Myers and Markel[8] showed that the effective potential for the vibration−rotation centrifugal coupling is the rotational kinetic energy,

$$V_{\text{vib-rot.}} = J^2/2I \tag{25}$$

where $J$ is the angular momentum, $I = \mu r$ is the moment of inertia, and $\mu$ is the reduced mass. Myers and Markel[8] and Gayathri and Bagchi[24] pointed out that the rotation−vibration coupling may give a different quantum number dependence on the line shape to that expected from the stochastic theory. However, for the system studied here, as Schweizer and Chandler showed,[40] the contribution of vibration−rotation coupling is negligible.

*4.3.3. Resonant Transfer.* We discuss a possible contribution of intermolecular resonant transfer to the dephasing of the higher vibrational state. 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 $v = 2$ excited molecule to a ground-state molecule ($v = 0$) requires a substantial rotational or translational contribution to compensate for 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. 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, it is interesting to see an isotropic dilution effect on the overtone dephasing.

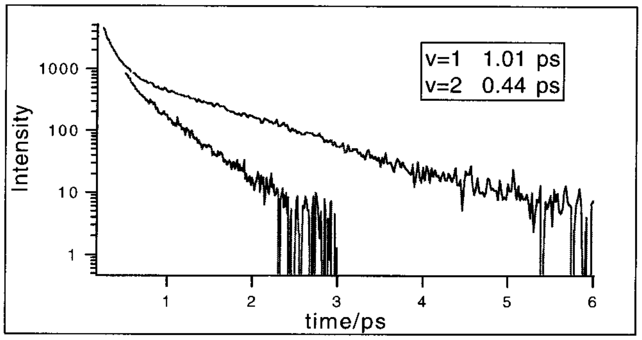

**Figure 6.** Time profiles of the overtone ($v = 2$) and fundamental bands of the C−D stretching of $CDCl_3$ in a 1:1 binary mixture with $CHCl_3$.

Figure 6 shows the dephasing signals of the fundamental and the first overtone ($v = 2$) of the C−D stretching of $CDCl_3$ in a equimolar mixture with $CHCl_3$. Both decay time constants are similar to those in the pure solvent, and we did not see any noticeable change in either the fundamental or overtone dephasing. It is concluded that resonant transfer does not play an important role in this case.

*4.3.4. Polyatomic Nature of Molecule.* Considering that the line widths of vibrational progression of $I_2$ can be explained well by the stochastic theory and in the case of the polyatomic molecules the ratios of $\Delta\nu(v{=}2)/\Delta\nu(v{=}1)$ often lie between 2 and 3, it is suggested that the deviation from the theoretical prediction may come from polyatomic natures of the molecule. In this subsection we propose possible mechanisms for the vibrational dephasing characteristic to poliatomic molecules.

The first candidate is the off-diagonal anharmonic coupling. Equation 17, which is valid for a diatomic molecule with an anharmonic coupling, shows a quadratic dependence of the amplitude of the fluctuation on the vibrational quantum number. This theoretical model for the diatomic molecule was extended to the polyatomic molecule case;[28,40] however, it does not include the effect of the off-diagonal anharmonicity in the vibrational Hamiltonian. The C−H stretching of $CHCl_3$ couples with other intramolecular lower frequency normal modes anharmonically, and the off-diagonal anharmonic coupling may give a different quantum number dependence on the time correlation function of the fluctuation from that predicted by the stochastic theory.

The next point we discuss is a coupling of the high-frequency mode with combination bands or other overtone bands. Recently, Berg and co-workers performed a Raman echo experiment on the *sym*-methyl stretch of ethanol-1,1-$d_2$ in the low-temperature glass (12 K), and they found that even at low temperatures the dephasing remains homogeneous.[13] They proposed solvent-assisted intramolecular vibrational redistribution (IVR) for the dephasing mechanism. For a medium-sized molecule such as ethanol, the number of the overtone and

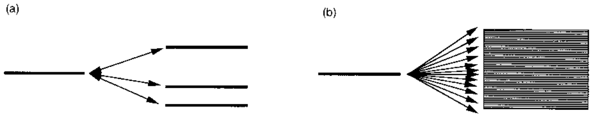

**Figure 7.** Schematic picture for the vibrational interaction. (a) medium sized molecule case where combination or overtone bands which can interact with a high-frequency mode are rather limited. (b) Large seized molecule case where many vibrational bands can interact with a high-frequency band.

combination bands which can couple to a high-frequency mode is rather limited. In this case population transfer from the high-frequency mode to states within $k_BT$ can be a reversible process and does not contribute to $T_1$ (Figure 7a). This mechanism should be distinguished from irreversible population transfer which can often be observed in a large molecule (Figure 7b). If this solvent-assisted IVR is a dominant mechanism in our system, the experimental results may be explained by assuming that in the higher vibrational excited state the density of state gets larger but the coupling with combination and overtone modes gets much smaller. This is one proposal for the explanation to the deviation from theoretical prediction, and further experimental and theoretical studies are needed to clarify this point.

## 5. Summary

Vibrational dephasing of the overtone bands ($v = 2$ and 3) of chloroform and its deuterated analogue has been studied by higher-order nonlinear spectroscopy in the time domain. The overtone vibrational dephasing signals as well as the fundamental ones are represented well by a single-exponential function. These dephasing signals are not explained by the stochastic theory; even a Gaussian component is included in the time correlation function of the fluctuation of the transition frequency. Effects of resonant transfer and population relaxation are found not to be important for the deviation from the theoretical prediction. It is suggested that the polyatomic natures of the molecules may be responsible for this deviation. A deeper understanding of overtone dephasing is important for further development of the two-dimensional Raman spectroscopy and vibrational echo experiments.

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