

Computer simulation study of the subquadratic quantum number dependence of vibrational overtone dephasing: Comparison with the mode-coupling theory predictions

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Experimental studies have demonstrated that the vibrational dephasing of overtones do not always follow the quadratic quantum number (n) dependence predicted by the Kubo–Oxtoby theory of vibrational line shapes. While the reason for this failure of the theory is not quite clear yet, a recent theory suggested that the pronounced Gaussian time dependence of the frequency-modulation time-correlation function (tcf) could be a possible reason [Gayathri *et al.*, *J. Chem. Phys.*, **107**, 10381 (1997)]. The theoretical study was based on a mode coupling theory calculation of the force–force time-correlation function that is required in the calculation of the frequency-modulation tcf. In order to test this and other predictions of the above study, detailed computer simulations of two neat liquids have been carried out. The systems studied are N–N stretch in liquid N₂ and the C–I stretch in CH₃I. It is found that although the frequency-modulation time-correlation function is largely Gaussian in both the cases, the overtone dephasing remains largely quadratic in n for N₂. For methyl iodide, on the other hand, a pronounced sub-quadratic n dependence has been observed. Both the theory and the computer simulations suggest that this nonquadratic dependence can be expected when not only the decay of the frequency time-correlation function is Gaussian but the time scale of decay of the frequency-modulation tcf is comparable to that of the normal coordinate. The latter can happen when the following conditions are satisfied. First, the frequency of the normal mode should not be too large. Second, the mean-square fluctuation of the frequency-modulation and the anharmonicity coefficient of vibration should be large. It is found that both for N₂ and CH₃I, the resonant energy transfer between different molecules is significant. The effect of rotational–vibrational coupling, on the other hand, is found to be negligible for the systems studied. © 1999 American Institute of Physics. [S0021-9606(99)52601-9]

I. INTRODUCTION

A great advantage of studying vibrational relaxation (VR) is that it allows us to probe directly the dynamics of a chemical bond, its properties, and motions.^{1–8} In the past, the study of vibrational phase relaxation has been carried out using mostly Raman and infrared (IR) line shape analyses. While these studies provide valuable information about the interaction of a chemical bond with the surrounding solvent, many questions remained unanswered because the frequency domain measurements often tend to mask the details of the dynamics. Recently, several nonlinear optical techniques have been developed which also probe the vibrational motion directly in the time domain, thanks to the developments in the ultrashort laser spectroscopy. One can now ask and hope to answer some of the outstanding issues in this field.

In this article we are concerned with one such ill-understood problem of vibrational dephasing in liquids. It is long known that the overtone dephasing rates do not always exhibit the *quadratic* quantum number (n) dependence predicted by the classical Kubo–Oxtoby theory.² Instead, one sometimes finds a weaker dependence which is closer to be-

ing linear for large quantum numbers. The best known example is the overtone dephasing of the C–I stretch of methyl iodide in hexane.⁶ More recently, seventh order nonlinear studies by Tominaga and Yoshihara clearly demonstrated this sub-quadratic dependence for the C–H stretch of CHCl₃ both in neat liquid and in a mixture of CHCl₃ and CDCl₃.⁸ A similar sub-quadratic n dependence has also been observed for dephasing of the hot bands of C≡N[−] in normal and deuterated water.⁹ While the sub-quadratic quantum number dependence has actually been known for a long time, it is only recently that systematic studies of this aspect have been undertaken.

In a recent article,¹⁰ we used the mode coupling theory to calculate the time-dependent friction on the atoms of the vibrating diatom. The mode coupling theory is known to provide accurate description of the time dependence of friction—both in the short and in the long times.^{11,12} The results of this theory were somewhat surprising. A clear sub-quadratic quantum number dependence was found for the C–I stretch of methyl iodide. Moreover, the theory showed that this sub-quadratic dependence was primarily due to the Gaussian nature of the decay of the normal coordinate (Q) time correlation function (tcf), $\langle Q(0)Q(t) \rangle$, the latter of course originates from a strongly Gaussian decay of the frequency (ω) modulation tcf, $\langle \Delta\omega(t)\Delta\omega(0) \rangle$. Note that the

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Kubo–Oxtoby theory² usually assumes an exponential decay of the frequency time-correlation function. This latter assumption always leads to the quadratic quantum number dependence.

The theory further suggested that sub-quadratic n dependence can emerge only if the vibrational phase relaxation and the frequency-modulation time-correlation function both decay on the same time scale. This could happen when the following conditions are satisfied. First, the harmonic frequency (ω_0) of the mode in question should not be too large. The mean-square fluctuation of the frequency-modulation ($\Delta\omega_0^2$) should be large. Lastly, the anharmonicity (K_{111}) should be significant.

In order to test the theoretical predictions, we have carried out extensive molecular-dynamic MD simulations of vibrational dephasing and the results are reported here. These simulations also have several advantages over direct experimental observations. They allow one to probe and answer questions which are not directly accessible to experiment. By simply varying the parameters of the simulation, one can study the effect of various contributions to the overall line shape. Such level of detail is impossible to obtain in experiments on real liquids. There are also several other reasons for undertaking such a simulation study. They are listed below.

1. In the theoretical investigation of vibrational dephasing, the mode coupling theory was used to calculate the time-dependent friction, $\langle F(t)F(0) \rangle$, on the atoms of the vibrating diatom. This was done to obtain the friction on the bond in terms of the friction on the atoms involved in the diatom. This is an approximation. The friction on the bond can be straightforwardly obtained using simulations.

2. Other dephasing mechanisms, such as resonance energy transfer (RT) and vibrational–rotational (VR) contributions, which can be substantial, are usually neglected in the theoretical studies. These are difficult to model theoretically but can be included in a simulation.

3. Mode-coupling theory (MCT) is a microscopic theory for determining the time-dependent friction. However, in order to apply this theory, both the solute and solvent molecules are assumed to be Lennard-Jones *spheres*. For example, in the case of CH₃I, friction was obtained using MCT for CH₃ in CH₃I Lennard-Jones spheres and Iodine in CH₃I Lennard-Jones spheres. Such approximations can be avoided in simulations where real shape of the molecules can be included.

However, a direct simulation of vibrating molecules is extremely difficult. It is possible but would have two major problems as pointed out by Oxtoby *et al.*:^{3,4} For very high-frequency vibrations of 1000–3000 cm⁻¹, the vibrational motion is much faster than the other degrees of freedom such as the translational and rotational motions. The quantum-mechanical nature of such high-frequency vibrational motion would have to be neglected, and rapid vibrational motion would require a much shorter time step of integration, leading to poor statistics. The latter problem may, however, be avoided with the use of recently developed reversible reference system propagator algorithm (RESPA) or numerical analytical propagator algorithm (NAPA) which are specifically used for simulating high-frequency vibrations but with

reasonably large time steps.¹³ However, this still involves extensive computation. To avoid this problem, a quantum-mechanical perturbation theory, for the vibrational motion, has been used often to express the dephasing rate in terms of auto- and cross-correlation functions of bond-force terms and its derivatives. Since these are estimated at the equilibrium bond length, they may be obtained from simulations of classical, nonvibrating molecules. This feature allows the calculation to be carried out and also gives rise to a tremendous computational saving. Such a calculation, via MD simulations was first carried out by Oxtoby, Levesque, and Weiss to study dephasing in nitrogen near its boiling point (B.P.).

Thus, the prediction of the Kubo–Oxtoby based theory on sub-quadratic quantum number dependence can be easily verified using rigid-molecule simulations, if one chooses two systems with widely different behavior. Therefore, simulation studies on two systems—N₂ and CH₃I—were carried out. While CH₃I was an obvious choice for the study, N₂ was studied because of the following reasons.

1. To benchmark the results against earlier simulations of the liquid N₂ system near its boiling point by Oxtoby, Levesque, and Weiss.^{3,4} Also, they had studied the dephasing of only the fundamental.

2. Vibrational frequency of N–N (2326 cm⁻¹) is much larger than that of C–I (525 cm⁻¹).

3. The fundamental vibrational dephasing of N–N in N₂ is much slower (≈ 150 ps near boiling point)¹⁴ in comparison to that of C–I in CH₃I (2.3 ps).⁷

4. The overtone dephasing of N–N is believed to follow a quadratic dependence because of an exponential relaxation of the normal-coordinate tcl^{2-4} while CH₃I is known to give rise to a sub-quadratic behavior.

The results of the simulations for liquid N₂ near B.P. are as follows. It is found that the frequency-modulation time correlation is indeed largely a Gaussian function of time. The dephasing in nitrogen, however, shows largely *quadratic* n dependence for smaller quantum numbers, eventually becoming linear for large quantum numbers. The quadratic n dependence is because of the clear separation of time scales of the frequency-modulation and the normal-coordinate correlation functions.

The results of the simulations for methyl iodide are as follows. Many of the predictions of the mode coupling based theory for CH₃I are found to be correct. It is found, as from MCT, that the frequency-modulation time correlation is indeed largely a Gaussian function of time. Also, the overtone dephasing rates show subquadratic n dependence even for small quantum numbers (like, $n=2$ and $n=3$). The reasons that contribute to such a behavior are the following. The frequency of the C–I normal mode (525 cm⁻¹) is not too large, the anharmonicity coefficient of vibration is quite large and, CH₃I being a highly dense liquid, the mean-square fluctuation of the frequency modulation also tends to be large. It is also found that the resonant energy transfer between different molecules is quite significant in CH₃I. The effect of rotational–vibrational coupling, on the other hand, is found to be negligible.

The organization of the rest of the paper is as follows. In the next section, we briefly discuss the theoretical formalism

of the Kubo–Oxtoby theory and a little of the mode coupling theory to explain the origin of the Gaussian time dependence of the force–force time-correlation function. In Sec. III, we discuss the systems and simulation details. In Sec. IV, we discuss simulation results and overtone vibrational dephasing behavior in N_2 . Section V concludes briefly.

II. THEORETICAL DISCUSSION: INCLUSION OF RESONANCE ENERGY TRANSFER AND VIBRATIONAL–ROTATIONAL CONTRIBUTIONS

The broadened isotropic Raman line shape for the n th overtone $[I_{n0}(\omega)]$ is the Fourier transform of the vibrational normal coordinate $[Q(t)]$ time-correlation function for the n th overtone given by²

$$I_{n0}(\omega) = \int_0^\infty \exp(i\omega t) \langle Q(t)Q(0) \rangle_{n0} dt. \quad (1)$$

The experimental observables are either the line shape function, $I(\omega)_{n0}$, or the normal coordinate time-correlation function, $\langle Q(0)Q(t) \rangle_{n0}$, as in the time domain experiments of Tominaga and Yoshihara.⁸ The normal coordinate time correlation is related to frequency-modulation time-correlation function by

$$\langle Q(t)Q(0) \rangle_{n0} = \text{Re} \exp(i\omega_{n0}t) \left\langle \exp \left[\int_0^t dt' \Delta \omega_{n0}(t') \right] \right\rangle, \quad (2)$$

where ω_{n0} is the frequency for the 0 to n transition of the isolated molecule and $\hbar \Delta \omega_{n0}(t) = V_{nn}(t) - V_{00}(t) + \sum_j V_{ij}(t)$ is the fluctuation in energy between vibrational levels n and 0 where n and 0 represent vibrational quantum numbers. V_{nn} is the Hamiltonian matrix element of the coupling of the vibrational mode to the solvent bath while $\sum_j V_{ij}(t)$ represents the contribution from the resonant energy transfer between two molecules i and j . $\Delta \omega(t)_{n0}$ is, therefore, the instantaneous shift in the vibrational frequency due to interactions with the solvent molecules. One usually performs a cumulant expansion of Eq. (2).¹⁵ This leads to an expression of the normal coordinate time-correlation function in terms of the frequency-modulation time-correlation function.²

The potential-energy part of the Hamiltonian for the normal mode (Q) was assumed to be of the following anharmonic form:

$$H_{\text{vib}} = \frac{1}{2} \mu \omega_0^2 Q^2 + \frac{1}{6} f Q^3, \quad (3)$$

where μ is the reduced mass, ω_0 is the vibrational frequency, and f is the anharmonic force constant. Note that Q in the above equation is not in the mass-weighted form as used in the theoretical work.

If V is the oscillator–medium interaction potential, then using perturbation theory, one finds the following expression for the fluctuation in overtone frequency gap, $\Delta \omega_{n0}(t)$:^{2,3}

$$\begin{aligned} \hbar \Delta \omega_{n0}(t) = & (Q_{nn} - Q_{00}) \left(\frac{\partial V}{\partial Q} \right)_{Q=0}(t) \\ & + \frac{1}{2} ((Q_{nn}^2 - (Q_{00}^2)) \left(\frac{\partial^2 V}{\partial^2 Q} \right)_{Q=0}(t) \\ & + Q_{n0}^2 \sum_{j \neq i} \left(\frac{\partial^2 V}{\partial Q_i \partial Q_j} \right)_{Q=0}(t) + \dots \end{aligned} \quad (4)$$

In the estimation of $\Delta \omega_{n0}(t)$, only the first three terms were considered neglecting the higher order terms. The third term accounts for the resonance-energy transfer contribution. This was omitted in the theoretical modeling. A useful method of experimentally studying resonant transfer is by eliminating its contribution via isotopic dilution.¹⁶ As pointed out earlier, the first term is not zero for an anharmonic potential and actually makes the maximum contribution to dephasing. When anharmonicity is included, then one finds, using perturbation theory, the following expressions for the matrix elements of Eq. (4):

$$\begin{aligned} Q_{nn} - Q_{00} &= \frac{n\hbar(-f)}{2\mu^2\omega_0^3}, \quad (Q_{nn}^2 - (Q_{00}^2)) \approx \frac{n\hbar}{\mu\omega_0}, \\ \text{and } Q_{n0}^2 &\approx \delta_{n1} \frac{\hbar}{2\mu\omega_0}, \end{aligned} \quad (5)$$

where only the lowest order term was retained in each case. In the above, μ is the reduced mass, ω_0 is the vibrational frequency and δ_{n1} is the Kronecker delta. So, Eq. (4) can be written, for the i th molecule, as

$$\begin{aligned} \hbar \Delta \omega_{n0}^i(t) = & \frac{n\hbar(-f)}{2\mu^2\omega_0^3} F_{1Q}^i + \frac{n\hbar}{2\mu\omega_0} F_{2Q}^i \\ & + \delta_{n1} \frac{\hbar}{2\mu\omega_0} {}^{1/2} \sum_{i \neq j} F_{3}^{ij}, \end{aligned} \quad (6)$$

where the meaning of the force terms and the equations can be obtained by comparing Eq. (6) with Eq. (4). Unless stated explicitly, the superscript i is not used in the frequency and the force terms in the subsequent discussions.

While the atom–atom (AA) contributions are given by Eq. (6), the vibration–rotation (VR) contribution to the broadening of the line shape is given by^{5,6}

$$\begin{aligned} \langle \Delta \omega(t) \Delta \omega(0) \rangle_{n0,VR} = & (\Delta R_{n0} / \hbar I_m r_e)^2 (\langle J^2(t) J^2(0) \rangle \\ & - \langle J^2 \rangle^2), \end{aligned} \quad (7)$$

where J is the angular momentum, I_m is the moment of inertia value at the equilibrium bond length, r_e , and μ is the reduced mass. $\Delta R_{n0} = (Q_{nn} - Q_{00}) - 3(Q_{nn}^2 - Q_{00}^2)/2r_e$ where $(Q_{nn} - Q_{00})$ and $(Q_{nn}^2 - Q_{00}^2)$ are the quantum-mechanical expectation values of the bond length displacement and its square corresponding to the n th level given by Eq. (5).

We next neglect the cross correlation between the vibrational–rotational term (VR) and the atom–atom (AA) force terms, which allows the total frequency time-correlation function to be written as the sum of the respective pure correlation terms as follows:

$$\langle \Delta \omega(t) \Delta \omega(0) \rangle = \langle \Delta \omega(t) \Delta \omega(0) \rangle_{n0,AA} + \langle \Delta \omega(t) \Delta \omega(0) \rangle_{n0,VR}. \quad (8)$$

An important ingredient of Oxtoby's work² was the decomposition of the force on the normal coordinate, $-(\partial V/\partial Q)$, in terms of the force on the atoms involved. Assuming that the forces on the different atoms of the diatomic to be uncorrelated, that the resonance energy transfer and vibrational-rotation contributions to be negligible and that the area of contact of each atom with the solvent to be a half-sphere, Oxtoby derived the following expression for the frequency time-correlation function as follows:²

$$\langle \Delta \omega_{n0}(t) \Delta \omega_{n0}(0) \rangle = \frac{n^2}{2} \sum_i \left[\frac{3(-K_{111})l_{ik}}{\omega_0^3 m_i^{1/2}} + \frac{l_{ik}^2}{2\omega_0 L m_i} \right]^2 \times \langle \mathbf{F}_i(\mathbf{t}) \mathbf{F}_i(\mathbf{0}) \rangle, \quad (9)$$

where L is the characteristic potential range, m_i is the mass of the atom, ω_0 is the vibrational frequency, K_{111} ($=f/6\mu^{3/2}$, where μ is the diatomic reduced mass) is the anharmonic force constant, l_{ik} is the characteristic length, and $\langle \mathbf{F}_i(\mathbf{t}) \mathbf{F}_i(\mathbf{0}) \rangle$ represents the force-force correlation function on the atom i moving along the direction of vibration. Please note that the above equation does not include neither resonant energy transfer or the vibrational-rotational contribution to dephasing. It is quite difficult to model them theoretically but can be (and has been) in a simulation.^{1,3,4}

The presence of n^2 in the above equation is the reason why the vibrational overtone dephasing rate is usually assumed to exhibit the quadratic n dependence. However, the observable is *not* the frequency-modulation time-correlation function, $\langle \Delta \omega_{n0}(0) \Delta \omega_{n0}(t) \rangle$, as is usually assumed, but either $I_{n0}(\omega)$ or $\langle Q(t)Q(0) \rangle_{n0}$. The average relaxation time is, therefore, *not* defined by integrating over the frequency time-correlation function. Rather, it is defined by directly integrating over the $\langle Q(t)Q(0) \rangle_{n0}$ correlation function as in the following form:

$$\tau_{vm} = \int_0^\infty dt \langle Q(t)Q(0) \rangle_{n0}. \quad (10)$$

The overtone linewidth is inversely proportional to the dephasing time τ_{vm} ^{2,10} which in turn is related to $\langle Q(t)Q(0) \rangle_{n0}$ as in the above equation. When $\langle Q(t)Q(0) \rangle_{n0}$ is biphasic, the sub-quadratic dependence can arise out of a combination of the Gaussian and exponential relaxation behaviors as explained below. When the decay of $\langle Q(t)Q(0) \rangle_{n0}$ is fully exponential as in the following form:

$$\langle Q(t)Q(0) \rangle_{n0} = \exp(-n^2 t/\tau), \quad (11)$$

then the relaxation time obtained using Eq. (10) gives a quadratic dependence of the dephasing rate on n . On the other hand, when the decay of $\langle Q(t)Q(0) \rangle_{n0}$ is fully Gaussian as in the following expression:

$$\langle Q(t)Q(0) \rangle_{n0} = \exp(-n^2 t^2/\tau^2), \quad (12)$$

the relaxation time obtained using Eq. (10) gives a *linear* dependence of the dephasing rate on n . From our earlier work,¹⁰ microscopic calculations show that $\langle Q(t)Q(0) \rangle_{n0}$ is indeed partly Gaussian and partly exponential and so gives

rise to a sub-quadratic dependence. Note that there could be several other sources for the sub-quadratic quantum number dependence; we shall address this issue later.

In order to understand the time dependence of the normal coordinate time-correlation function, $\langle Q(t)Q(0) \rangle_{n0}$, one requires an accurate calculation of the force-force time-correlation function on the normal coordinate in the liquid. In an earlier work,¹⁰ such a calculation was carried out by using the mode-coupling theory (MCT).^{11,12} The mode-coupling theory analysis showed that the pronounced Gaussian decay of the force-force time-correlation function can indeed make the decay of the normal coordinate time-correlation function for the overtone dephasing (involving quantum number 0 and n) also partly Gaussian. This Gaussian nature of the normal coordinate time-correlation function increases with the quantum number n because the rate of decay increases with n and shorter and shorter time scales are probed. For the C-I stretch of methyl iodide, the above factors led to a pronounced sub-quadratic dependence of the dephasing rate on n .

A physical picture that emerged from the theoretical study was that the Gaussian decay mechanism of the sub-quadratic quantum number dependence can be effective *only if the time scales of decay of the frequency-modulation time-correlation function and the normal coordinate time-correlation function are comparable*. As already mentioned, this is possible when the harmonic frequency of the bond is not too large, the anharmonicity is significant and the mean-square fluctuation is large.

Dephasing mechanisms can be homogeneous (due to rapid modulation effects) or inhomogeneous (due to slow modulation effects). Using the frequency-modulation tcf, one can also verify whether the dephasing mechanism is homogeneous or inhomogeneous. This can be done as follows. Let τ_{cn} be the average frequency correlation decay time for the n th overtone defined as

$$\tau_{cn} = \int_0^\infty \langle \Delta \omega_{n0}(t) \Delta \omega_{n0}(0) \rangle / \langle \Delta \omega_{n0}(0) \Delta \omega_{n0}(0) \rangle. \quad (13)$$

If the frequency fluctuations are weak enough and τ_c short enough such that

$$\langle \Delta \omega_{n0}^2(0) \rangle^{1/2} \tau_{cn} \ll 1, \quad (14)$$

then the Raman spectrum can be said to be homogeneously broadened or in the motional narrowing limit. On the other hand, if

$$\langle \Delta \omega_{n0}^2(0) \rangle^{1/2} \tau_{cn} \gg 1, \quad (15)$$

the spectrum is inhomogeneously broadened.

If a Raman spectrum is homogeneously broadened, $\langle \Delta \omega_{n0}(t) \Delta \omega_{n0}(0) \rangle$ can be calculated by averaging over all molecules.^{1,3} On the other hand, if the spectrum is inhomogeneously broadened, selective averaging of $\langle \Delta \omega_{n0}(t) \Delta \omega_{n0}(0) \rangle$ would be carried out over those molecules for which $\omega_0 + \omega_i(0)$ lies close to a given frequency ω .^{1,3} In the case of liquid N₂, Eq. (14) is valid, so that the added complications of inhomogeneous broadening need not be considered.

In the homogeneous limit, the average dephasing time for the n th overtone is usually defined using the frequency-modulation tcf (τ_{vm}^ω) as

$$[\tau_{vm}^\omega]^{-1} = \int_0^\infty dt \langle \Delta\omega_{n0}(t) \Delta\omega_{n0}(0) \rangle. \quad (16)$$

However, as argued earlier, the dephasing time is given by integrating the normal-coordinate tcf $\langle Q(t)Q(0) \rangle$ and not $\langle \Delta\omega_{n0}(t) \Delta\omega_{n0}(0) \rangle$.

III. SYSTEMS AND SIMULATION DETAILS

A microcanonical (N,V,E) molecular-dynamics simulation of a system of 256 rigid N_2 diatomic molecules was carried out using the leap-frog algorithm.^{17,18} As mentioned earlier, a quantum-mechanical perturbation theory for the vibrational motion (Q) has been used here and thereby expressed the dephasing rate in terms of auto- and cross-correlation functions of F_{1Q} , F_{2Q} , and F_{3Q} . Since these are estimated at $Q=0$ [Eq. (4)], they may be obtained from simulations of rigid molecules.

For the intermolecular potential-energy (V_{ij}) between two molecules i and j , the following site-site Lennard-Jones type was employed:

$$V_{ij} = \sum_{a,b}^{1,2} V(r_{iajb}), \quad (17)$$

where $V(r_{iajb})$ is the Lennard-Jones atom-atom potential with

$$V_{iajb} = 4\epsilon_{iajb} \left[\left(\frac{\sigma_{iajb}}{r_{iajb}} \right)^{12} - \left(\frac{\sigma_{iajb}}{r_{iajb}} \right)^6 \right], \quad (18)$$

where r_{iajb} (or r_{iajb}) is the distance between a th atom on molecule i and b th atom on molecule j , ϵ_{iajb} is the Lennard-Jones well-depth potential and σ_{iajb} is the Lennard-Jones diameter. For dissimilar a and b atoms, ϵ_{iajb} and σ_{iajb} are estimated from those of the similar spheres through the combining rule $\epsilon_{iajb} = \sqrt{\epsilon_{aa}\epsilon_{bb}}$ and $\sigma_{iajb} = (\sigma_{aa} + \sigma_{bb})/2$.¹⁹

For the above potential form, the quantities F_{1Q}^i , F_{2Q}^i , and F_{3Q}^i are to be calculated for the i th molecule in order to obtain the atom-atom contribution to the frequency-modulation value as described in Eq. (6). The steps involved are described in the Appendix.

In the NVE simulations, the system of 256 rigid diatomic was enclosed in a cubic box and periodic boundary conditions were used. The thermodynamic state of the system corresponds to a density of $\rho^* = \rho\sigma^3$ and a temperature of $T^* = k_B T/\epsilon$ where k_B is the Boltzmann constant. For liquid N_2 near boiling point, the thermodynamic state of the system corresponds to a density of $\rho^* = 0.62965$ and a temperature of $T^* = 2.03$ for $\epsilon/k_B = 37.3$ K and $\sigma = 3.31$ Å. This state point is also the one chosen by Oxtoby *et al.* for their simulation study. As N_2 is a homonuclear diatomic, the atom-atom interaction potential between the a th atom of i th and j th atom of the N_2 molecule is given as follows:

$$V_{iajb} = 4\epsilon \left[\left(\frac{\sigma}{r_{iajb}} \right)^{12} - \left(\frac{\sigma}{r_{iajb}} \right)^6 \right], \quad (19)$$

where r_{iajb} (or r_{iajb}) is the distance between a th atom on molecule i and b th atom on molecule j .

While N_2 is a homonuclear diatomic, CH_3I is treated as a heteronuclear diatom with a bond between CH_3 pseudoatom and I atom. The Lennard-Jones (LJ) parameters for the CH_3 system were taken as $\epsilon/k_B = 146.6$ K and $\sigma = 3.85$ Å and, for the I system as $\epsilon/k_B = 400$ K and $\sigma = 4$ Å.⁶ The scaling parameters used in the simulation for CH_3I are the LJ parameters of CH_3I , $\epsilon/k_B = 467$ K and $\sigma = 4.6$ Å.¹⁹ The reduced atomic density $\rho\sigma^3$ (or ρ^*) for CH_3I is 0.918 at a temperature of 303 K.^{5,19} The intermolecular potential is given by Eq. (17).

Starting from an initial face-centered-cubic (fcc) lattice configuration, the system was allowed to equilibrate for 60 000 time steps. The unit of time, τ , is $\sqrt{(m\sigma^2/\epsilon)}$ with m the mass of the molecule. τ is calculated to be equal to 3.147 ps for the N_2 system and 2.782 ps for the CH_3I system. The integration step was 0.0004 τ . This sampling time interval was chosen after a few preliminary test runs. A cutoff of 3.2σ was used in evaluating the forces.

IV. RESULTS AND DISCUSSION

The pair-correlation functions for the nuclei of the diatom, [which are, g_{Na} and g_{Nb} in the case of N_2 , $g_{CH_3}(r)$ and g_I in the case of CH_3I], together with the pair correlation for their respective molecular centers [$g_{N_2}(r)$ and $g_{CH_3I}(r)$], are shown in Fig. 1. In both N_2 and CH_3I , all the pair-correlation functions are effectively unity at distances beyond ≈ 3.0 , indicating a virtually uniform distribution. This is probably sufficient to justify the cutoff we have imposed at 3.2σ in evaluating the forces. The pair-correlation functions are strongly correlated till, approximately, $r^* = 2.25$, in both the cases. This probably implies that the nuclei pair-correlation functions are less sensitive to correlations of orientation around and beyond these separations. In the case of CH_3I , a distinct ‘‘shoulder’’ region appears in the region $1.0 < r^* < 1.4$. This shoulder might be due to orientations where two nearest-neighbor diatoms lie perpendicular to each other in a T configuration resulting in higher density distributions around the molecule.^{20,21} This feature is not observed in the pair distribution function of N_2 . This could be due to the less density of N_2 than CH_3I . However, formation of T configuration for liquid N_2 in restricted systems like N_2 on graphite surface²⁰ and in confined systems like N_2 in carbon nanotubes have been reported earlier.²¹

The dynamic friction or the force time-correlation function, $C_F(t)$, is defined by the following:

$$C_F(t) = \frac{\langle \mathbf{F}(t) \cdot \mathbf{F}(0) \rangle}{\langle \mathbf{F}(0) \cdot \mathbf{F}(0) \rangle}, \quad (20)$$

where \mathbf{F} is the force on the molecular center-of-mass, respectively. One of the typical characteristics of dense liquids is that $C_F(t)$ exhibits a minimum which is often negative. This is due to the rebound of the molecule in question against the cage formed by its nearest neighbors,²² a phenomenon referred to as the cage effect. Since CH_3I is a highly dense liquid and N_2 is also rather dense near its boiling point, the force time-correlation functions of both the liquids should

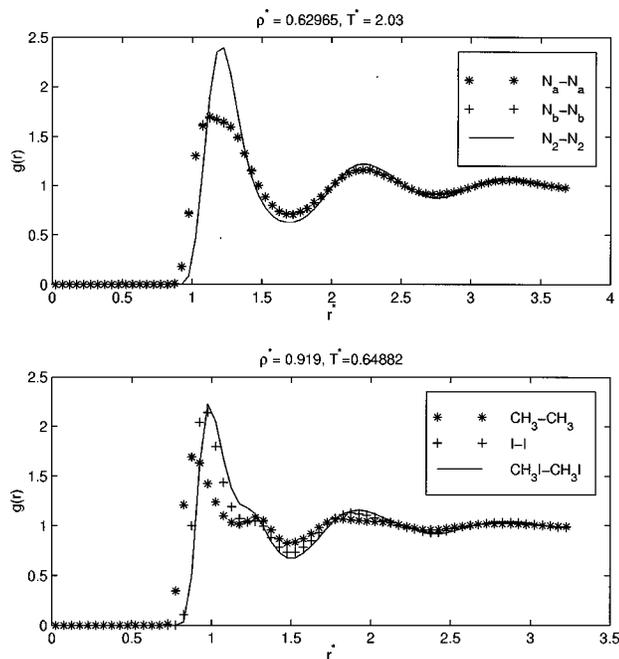


FIG. 1. (a) The simulated pair-correlation functions for the nuclei N_a and N_b of N_2 , g_{N_a} and g_{N_b} , and for its molecular center, g_{N_2} . (b) The simulated pair-correlation functions for the nuclei CH_3 and Iodine of CH_3I , g_{CH_3} and g_I , and for its molecular center, g_{CH_3I} . The distribution functions show distinct “shoulder” regions that could arise from formation of T configurations in the liquid state.

reflect the rebound effect, although the effect should be larger for CH_3I . The force time-correlation functions shown in Figs. 2(a) and 2(b) for N_2 and CH_3I , respectively, clearly show the cage effect in both the systems.

A criterion of rebound may be given by the following equation:²³

$$r_F = \frac{\langle F^2 \rangle^{1/2} \tau_F(0)}{(3mk_B T)^{1/2}}, \quad (21)$$

where $\langle F^2 \rangle$ is the mean-squared force acting on a molecule in the liquid, $\tau_F(0)$ is the first time which $C_F(t)$ passes through zero, m is the mass of a molecule, k_B is the Boltzmann constant, and T is the absolute temperature. The larger the r_F , more significant is the degree of rebound. r_F is calculated to be equal to 0.97 and 0.84 for N_2 and CH_3I , respectively.

The simulated force-correlation profiles [$\langle F(t)F(0) \rangle$ vs t plots] of the nuclei for the two systems [shown in Figs. 2(a) and 2(b)] show characteristics rather similar to those obtained from MCT for CH_3I .^{10,12} In both the cases, the friction on the atom shows a *strong bimodal response*—a Gaussian behavior in the initial time followed by a slowly relaxing decay. In addition, the time scales of the decays are also in good agreement with those obtained from theory for CH_3I .

A. Vibrational dephasing in nitrogen

As mentioned earlier, the frequency-modulation value [$\Delta\omega(t)$] can be directly obtained from simulations using Eq. (6). The required parameters are shown in Table I. The average of the frequency-modulation value $\langle \Delta\omega \rangle$ gives the Raman line shift. This shift is found to be equal to 1.9 ± 0.1

cm^{-1} for the first overtone. The experimentally reported value of the shift is $-1.7 cm^{-1}$.¹⁴ The prediction of the wrong sign for the gas-to-solution frequency shift could be due to the neglect of changes in bond polarizability upon vibrational excitation.^{4,24} The frequency-modulation tcf for the first overtone [$\langle \Delta\omega_{10}(t)\Delta\omega_{10}(0) \rangle$] obtained with the inclusion of all the four dephasing mechanisms is as shown in Fig. 3(a). The decay behavior is found to be strongly Gaussian. On the other hand, $\langle Q(t)Q(0) \rangle_{10}$ is predominantly exponential [Fig. 3(b)]. This is primarily because the mean-square fluctuation value is not very large. This leads to a wide separation of time scales between the frequency-modulation and the normal-coordinate correlation functions.

The root-mean-square value of the frequency modulation $\langle \Delta\omega_{10}(0)\Delta\omega_{10}(0) \rangle^{1/2}$ was calculated to be equal to $1.4 cm^{-1}$ and the frequency-modulation correlation time τ_{c1} to be $0.127 ps$ which are quite close to the values reported in Refs. 3 and 4. Since $\langle \Delta\omega_{10}(0)^2 \rangle^{1/2} \tau_{c1} = 0.037 \ll 1$, the system is in the homogeneous limit.

As Eq. (16) is valid in the homogeneous limit, the dephasing time for the first overtone τ_{v1}^o is calculated to be $95 \pm 5 ps$. However, use of Eq. (10) gives a longer dephasing time of around $110 \pm 10 ps$. The experimental value reported is $150 \pm 15 ps$.¹² The obtained dephasing times for the first overtone is compared with the earlier theoretical, simulation, and experimental observations in Table II.

Overtone studies show that the Gaussian component in $\langle Q(t)Q(0) \rangle_{n0}$ becomes increasingly prominent in the initial time scale as n increases [Fig. 3(b)]. For N_2 near B.P., this becomes significant, though not dominant, only with higher energy levels (around $n > 7$). Therefore, only limited sub-quadratic dependence was observed at higher quantum levels as shown in Fig. 5.

The contributions to the dephasing from the four different mechanisms F_{1Q} , F_{2Q} , F_{3Q} , and VR were calculated separately. The results are shown in Table III. The results show the importance of anharmonicity (or F_{1Q}) in the vibrational dephasing of N–N. This is because of the large anharmonicity value associated with the N–N vibration.

The treatment of N–N vibration as harmonic (i.e., consideration of only F_{2Q} term) gives a dephasing time longer by a factor of 30. Oxtoby *et al.* have reported a similar observation.³ The isolated binary collision model²⁵ for dephasing of harmonic oscillators in liquids developed by Fischer and Laubereau predicts a factor of 20 for N_2 .³ The calculation with only the resonant-transfer (RT) contribution (F_{3Q}) was found to give a dephasing time much slower (Table III) than that due to the harmonic term. The vibration-rotation contribution, on the other hand, was found to be substantial. Brueck,²⁶ using a generalized rotational diffusion model, had shown that the VR coupling can contribute significantly to the isotropic linewidth in liquid nitrogen.

By selective inclusion of the individual contributions of the various mechanisms, their cross-correlation effects were also studied. These results are also shown in Table III. The additional dephasing mechanism might increase or decrease the dephasing time because the sign of its contribution is determined by the cross-correlation terms. As mentioned ear-

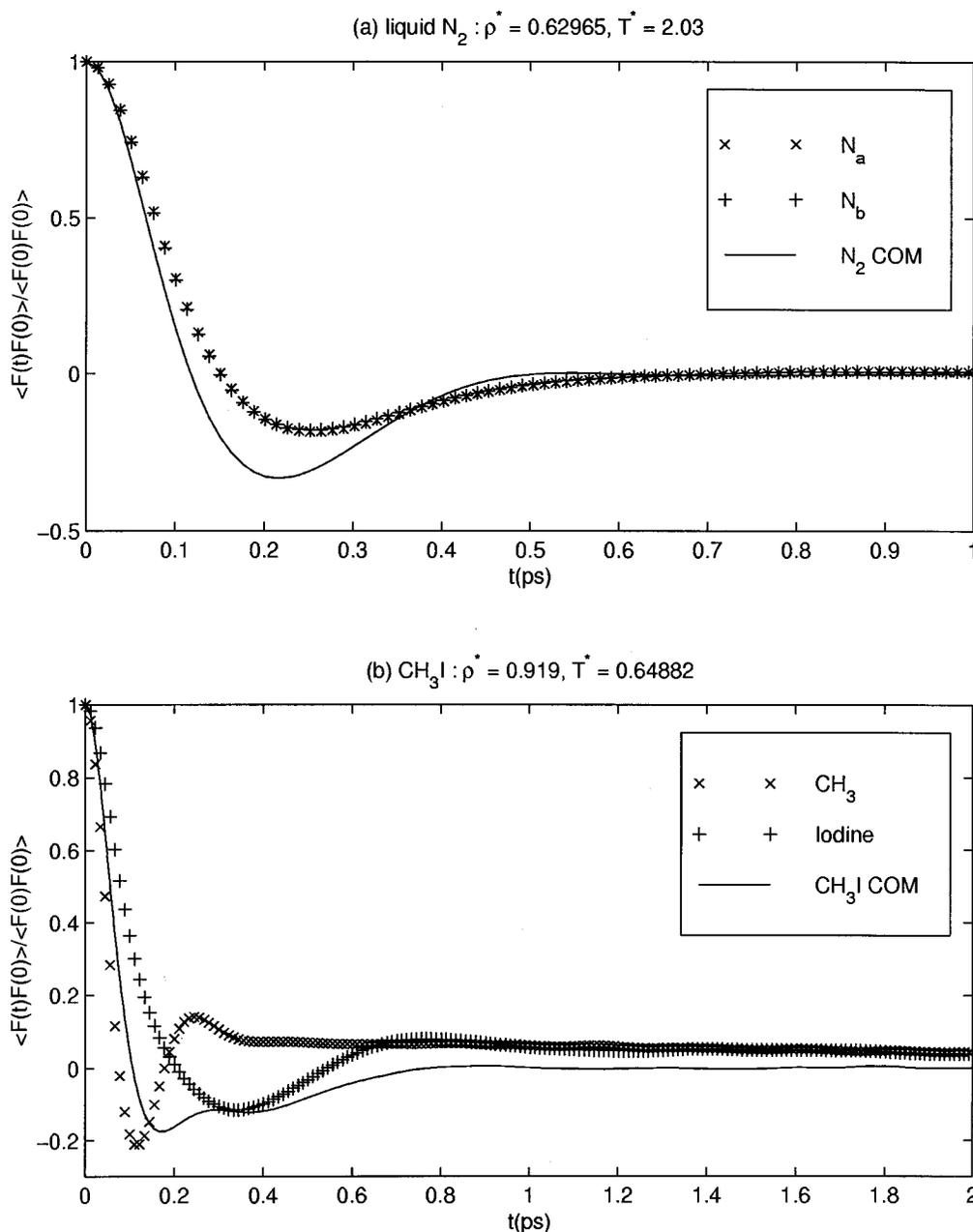


FIG. 2. (a) MD simulated normalized force correlation functions for the nuclei N_a and N_b of N_2 and for its molecular center of mass (COM), clearly exhibiting a fastly relaxing component in the initial time scale. The decay shows a minimum indicating cage effects. (b) MD simulated normalized force correlation functions of the pseudoatoms CH_3 and Iodine of CH_3I and for the center-of-mass of CH_3I . The decay profiles clearly show a Gaussian component in the initial time scale followed by a slower damped oscillatory behavior and exhibit cage effects.

lier, the inclusion of anharmonicity decreases the dephasing time.

Similarly, the vibrational-rotational contribution is also found to decrease the dephasing time by 5%–10%. When the

TABLE I. Values of the parameters for the N–N stretching in liquid- N_2 and the CH_3 –I stretching in liquid- CH_3I .

System	ω_0 cm^{-1}	$-f$ $10^{14} g/cm s^2$	r_e $10^{-8} cm$
N_2	2326	17.8	1.09
CH_3I	525	1.08	2.14

vibrational-rotation contribution was included, τ_v was found to decrease from 126 ± 4 ps to 110 ± 5 ps. Note that Oxtoby *et al.*⁴ found τ_v to increase when VR was included. This, they had reported, was due to the frequency-modulation correlation decay becoming more rapid with the inclusion of vibrational-rotation contributions. No such decrease in the frequency-modulation correlation time was observed.

As mentioned earlier, the RT contribution was found to be negligible as its inclusion did not change the dephasing time. This is against the observation of a considerable increase in the overall dephasing time with the inclusion of the RT term reported by Oxtoby *et al.*³

Note here that the contributions from the resonant en-

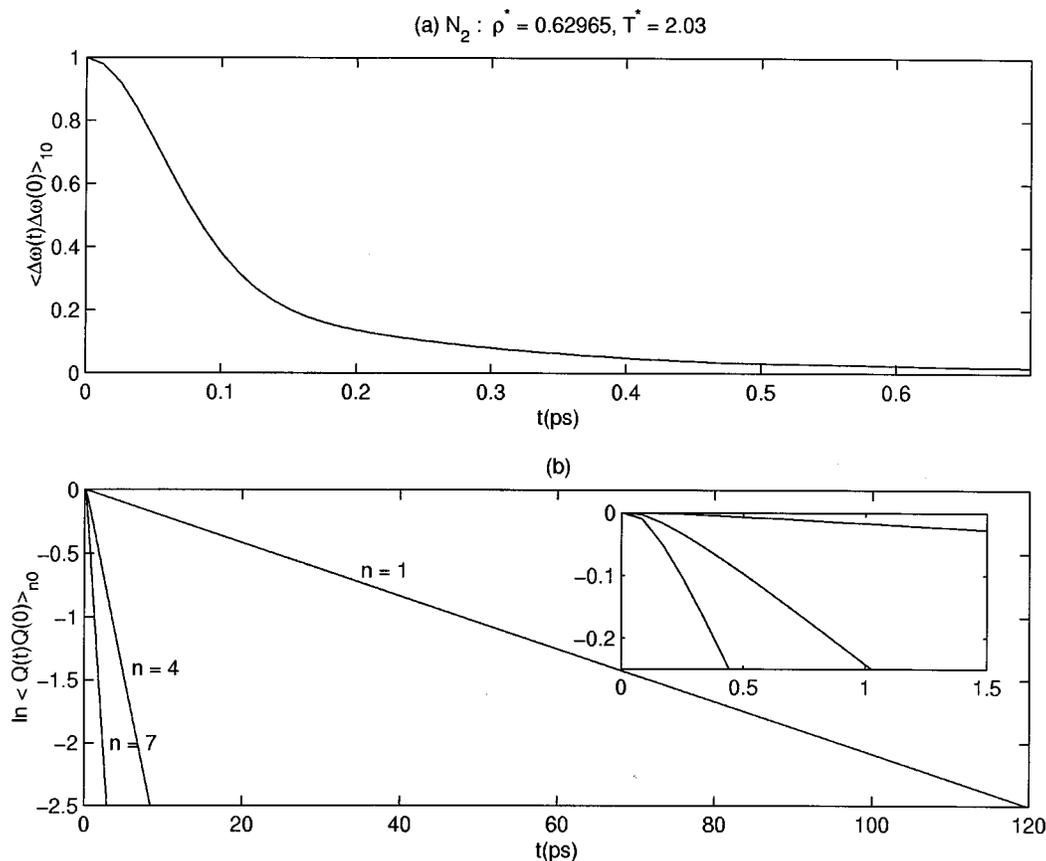


FIG. 3. (a) MD simulated normalized frequency-modulation time-correlation function for the first quantum level in N_2 . The plot shows a clear Gaussian component in the initial time scale followed by a slower decay. (b) Plot of $\ln \langle Q(t)Q(0) \rangle_{n0}$ vs t for N_2 for quantum levels $n=1, 4,$ and 7 . The results clearly show largely exponential behavior in the initial time scale even for higher quantum numbers, $n=4$ and $n=7$. The relaxation time scale is widely separated from that of $\langle \Delta\omega_{10}(t)\Delta\omega_{10}(0) \rangle$ relaxation leading to a largely quadratic quantum number dependence of the dephasing rate. The inset shows the increasing Gaussian component present in the short time scale as n increases.

ergy transfer and vibrational-rotation being relatively small in comparison to that due to anharmonicity, the determination of the extent of their role in the dephasing mechanism is quite likely to be sensitive to the simulation errors.

B. Vibrational dephasing in methyl iodide

The frequency modulation values $[\Delta\omega_{n0}(t)]$ was directly estimated using Eq. (4). The required parameters are shown in Table I. From the time and ensemble averaging of $\Delta\omega_{10}(t)$, the Raman line shift $\langle\omega_{10}\rangle$ is calculated to be around 9.7 cm^{-1} for CH_3I . Also, $\langle\Delta\omega_{10}(0)\Delta\omega_{10}(0)\rangle^{1/2}$ is calculated to be equal to 8.8 cm^{-1} and $\tau_{c1}=0.09 \text{ ps}$. This leads to $\langle\Delta\omega_{10}(0)^2\rangle^{1/2} \tau_{c1}$ value of 0.167 . This value is probably not sufficiently small to fully justify the treatment of a system as in the motional narrowing limit. Nevertheless,

considering that this has been obtained for a highly dense liquid like CH_3I , it seemed quite reasonable to proceed with the homogeneity assumption.

The frequency-modulation tcf for the first overtone $[\langle\Delta\omega_{10}(t)\Delta\omega_{10}(0)\rangle]$ obtained with the inclusion of all the four dephasing mechanisms is as shown in Fig. 4(a). The decay behavior is found to be strongly Gaussian. $\langle Q(t)Q(0) \rangle_{10}$ is also found to be substantially Gaussian in the initial time scale. The dephasing time for the one level of C-I stretching mode of CH_3I was then calculated to be $3.2 \pm 0.4 \text{ ps}$, using $\langle\Delta\omega_{10}(t)\Delta\omega_{10}(0)\rangle$ [Eq. (16)] and a longer dephasing time of around $3.42 \pm 0.3 \text{ ps}$ using $\langle Q(t)Q(0) \rangle_{10}$ [Eq. (10)]. A comparison of this result with the earlier theoretical and experimental observations is shown in Table II. The overtone dephasing in the case of CH_3I is much faster

TABLE II. Comparison of the dephasing times obtained using simulations from this study with that of earlier simulations (Ref. 3), the mode-coupling theory (Ref. 10), hydrodynamic theory (Ref. 2) and experiment (Refs. 7 and 12) for the first overtone of the N-N stretching in liquid- N_2 and the CH_3 -I stretching in liquid- CH_3I .

System	ρ^*	T^*	τ_{v1} (sim.) ps	τ_{v1} [sim., (Ref. 3)] ps	τ_{v1} (MCT) ps	τ_{v1} (HT) ps	τ_{v1} (expt) ps
N_2	0.629 65	2.03	110 ± 10	125 ± 10 (Ref. 3)		121 (Ref. 2)	150 ± 15 (Ref. 12)
$\text{CH}_3\text{-I}$	0.918	0.65	3.42 ± 0.3		2.6 ± 10	1.2 (Ref. 2)	2.3

TABLE III. Contributions to dephasing from the four mechanisms (F_{1Q} , F_{2Q} , F_{3Q} , and VR) obtained from simulations for the first overtone of the N–N stretching in liquid- N_2 ; both auto and cross correlations are given.

Terms	$\langle \Delta \omega^2(0) \rangle_{10}^{1/2}$ (ps $^{-1}$)	τ_{c1} (ps)	τ_{v1}^{ω} (ps)
F_{1Q}	0.211	0.13	172
F_{2Q}	0.050	0.123	3215
F_{3Q}	0.077	0.189	14 840
VR	0.099	0.312	321
$F_{1Q}+F_{2Q}$	0.259	0.129	115
$F_{1Q}+F_{2Q}+F_{3Q}$	0.280	0.129	98
$F_{1Q}+F_{2Q}+F_{3Q}+VR$	0.293	0.127	92

than in the case of N_2 primarily because the mean-square fluctuation value $\langle \Delta \omega_{10}(0)^2 \rangle$ is quite large due to the not very high vibrational frequency ($\omega_0 = 525 \text{ cm}^{-1}$).

Note that there is a considerable overlap of time scales between the frequency-modulation and the normal-coordinate time-correlation functions. This is in contrast to the widely separated time scales observed in the case of N_2 . The overall dephasing behavior for the CH_3 –I stretching

was, therefore, found to exhibit substantial sub-quadratic quantum number dependence even for lower quantum levels as shown in Fig. 5. These observations are similar to the experimental observations that have been reported for the C–I stretching of CH_3I in hexane⁶ and C–D stretching of CD_3I in neat liquid.⁸

As described earlier in the theoretical analysis, the sub-quadratic n dependence clearly arises from the Gaussian component of $\langle Q(t)Q(0) \rangle_{10}$ [shown in Fig. 4(b)] in the initial time scale which increases with increase in the quantum number n , which strongly reflects the presence of the Gaussian component, as in the frequency modulation tcf. This is responsible for the nearly linear n dependence in the higher levels in the case of CH_3I because of dominant Gaussian behavior.

The contributions to the dephasing from the four different mechanisms F_{1Q} , F_{2Q} , F_{3Q} , and VR were calculated separately. The results are shown in Table IV. The results show the importance of anharmonicity (or F_{1Q}) in the vibrational dephasing of CH_3 –I. However, unlike in N_2 , the harmonic term (F_{2Q}) contribution is also substantial.

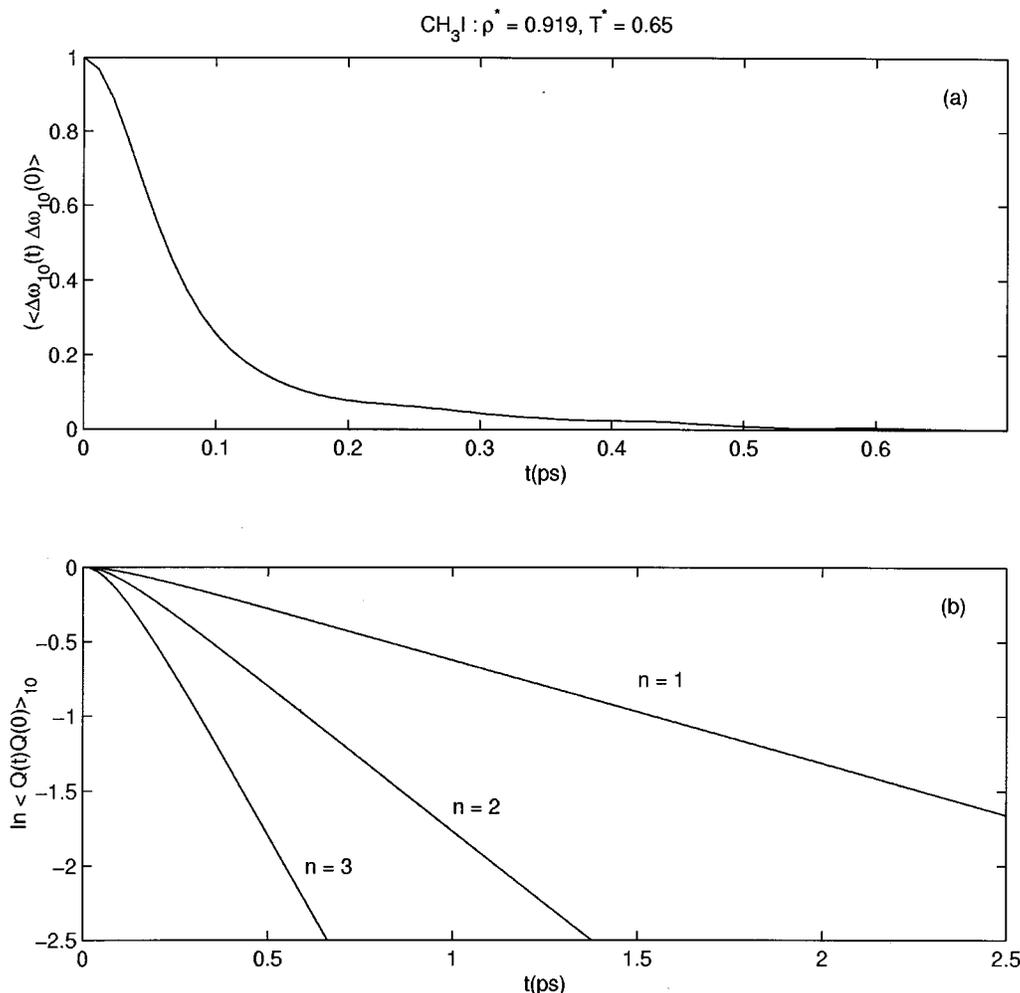


FIG. 4. (a) MD simulated frequency-modulation time-correlation function for CH_3I . The plot shows a clear Gaussian component in the initial time scale followed by a slower decay. (b) Plot of $\ln \langle Q(t)Q(0) \rangle$ vs t for CH_3I for the first three quantum levels. The results show strong Gaussian behavior in the initial time scale leading to a sub-quadratic quantum number dependence. The relaxation time scale is comparable with that of $\langle \Delta \omega_{10}(0) \Delta \omega_{10}(0) \rangle$.

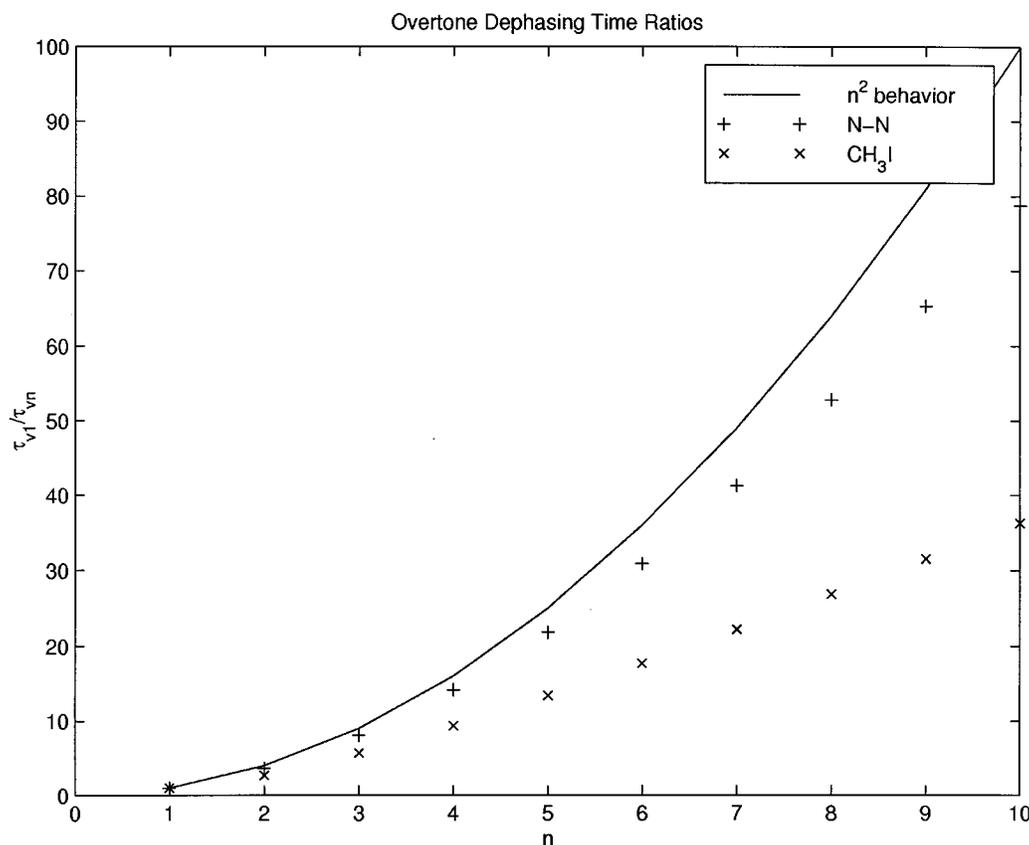


FIG. 5. Plots of ratios of vibrational dephasing times (τ_{v1}/τ_{vn}) is plotted as a function of the quantum number n for N–N stretching in N_2 and CH_3 –I stretching in neat- CH_3I . The results show close to a quadratic n dependence for N_2 and a highly sub-quadratic dependence for CH_3I .

In the case of CH_3I , the resonance energy transfer (RT) contribution was found to be quite substantial. RT leads to a decrease in the overall dephasing time from 4.7 to 3.42 ps. The RT contributions calculated from three different simulation runs were found to be about 25%–35% of the total contribution. It is probably so for any highly dense liquid, such as CH_3I , as the molecules are very close and the atom–atom interactions are strong in such a case. Isotopic dilution studies in other systems have shown that the effect of resonant transfer on the linewidth may be about 10%–20% but is often much less.¹⁶

Vibration–rotation contribution in CH_3I , on the other hand, was found to be very small and negligible as the molecular rotational motions tend to be highly constrained in a

dense liquid. The dephasing time related to VR contribution was found to be very slow (Table IV).

V. CONCLUSION

Molecular-dynamics simulations were carried out to determine the origin of the subquadratic quantum number dependence of the vibrational dephasing rate. As mentioned earlier, such subquadratic quantum number dependence has been known for a long time and has again been observed recently by Tominaga and Yoshihara.⁸ Additional motivations to carry the simulation work were to test the theoretical predictions based on the mode-coupling theory and also to supplement and substantiate the theoretical work. It is found, as in the theoretical work,¹⁰ that the time dependence of the friction on the molecule is strongly biphasic, with an initial ultrafast Gaussian component which dominates the decay of the force–force time correlation function.

The sub-quadratic dependence arises primarily from the nonexponential decay of $\langle Q(t)Q(0) \rangle$ in the initial time scale in the case of CH_3I . This is in contrast to the largely quadratic dependence observed in liquid N_2 because of the almost exponential decay of its $\langle Q(t)Q(0) \rangle$ correlation function. N_2 and CH_3I , therefore, represent widely different quantum number dependence of the overtone dephasing in liquids. For the C–I stretch in CH_3I , the quantum number dependence is sub-quadratic even for lower quantum numbers, that is for $n=2$ and 3. In the case of N_2 near B.P., on

TABLE IV. Contributions to dephasing from the four mechanisms (F_{1Q} , F_{2Q} , F_{3Q} , and VR) obtained from simulations for the first overtone of the CH_3 –I stretching in liquid- CH_3I ; both auto and cross correlations are given.

Terms	$\langle \Delta \omega^2(0) \rangle_{10}^{1/2}$ (ps ⁻¹)	τ_{c1} (ps)	τ_{v1}^w (ps)
F_{1Q}	0.713	0.119	18.68
F_{2Q}	0.815	0.099	17.14
F_{3Q}	0.925	0.109	10.7
VR	0.011	0.130	60 000.0
$F_{1Q}+F_{2Q}$	1.492	0.094	4.76
$F_{1Q}+F_{2Q}+F_{3Q}$	1.826	0.093	3.26
$F_{1Q}+F_{2Q}+F_{3Q}+VR$	1.842	0.091	3.25

the other hand, only a limited sub-quadratic behavior is observed and that too for higher quantum levels.

The biphasic force–force time correlation function in combination with other relevant factors such as resonance transfer mechanism and vibrational–rotational contribution can lead to a sub-quadratic dependence of the overtone vibrational dephasing rate. In the case of CH₃I, while the resonant energy transfer contributions are found to be significant, vibration–rotation contributions are found to be negligible. Dephasing due to resonant energy transfer was found to be not highly significant in liquid N₂. Vibration–rotation contribution, however, was found to be quite substantial for N₂ near the boiling point. Detailed density and temperature-dependent studies on N₂ have shown that vibration–rotation coupling becomes very important at higher temperatures and lower densities.

It must be stressed here that N₂ and CH₃I were modeled as two neutral Lennard-Jones spheres separated by a bond. In real situations, these spheres carry partial charges because both N₂ and CH₃I are dipolar. The dipolar interactions among molecules can significantly contribute to the mean-square force at the initial time, particularly in the case of CH₃I as N₂ is a weakly interacting dipolar system. This can also give rise to a fast Gaussian decay at the short times. Both these effects will tend to lower the value of the dephasing time. This might partly explain the discrepancy of about 1 ps between the observed and the simulated times in the case of CH₃I.

Oxtoby *et al.* have carried out a simulation study of vibrational dephasing in liquid nitrogen near B.P. using a multiparameter potential which includes short-range valence, dispersion, and quadrupole interactions.⁴ However, they did not find any significant change in the dephasing time as N₂ is a weakly interacting dipolar liquid. For methyl iodide, however, these dipolar forces are expected to be significant. As emphasized earlier, our aim here is to study the possible origin of sub-quadratic quantum number dependence of vibrational dephasing. The dipolar forces are not expected to change the scenario proposed here.

The simulations carried out here assume a rigid bond model to obtain the forces on the normal coordinate. As discussed by Berne and co-workers,¹³ the time-correlation functions of the forces for the rigid bond can be different from those for a real, flexible bond. This could be significant for a high overtone state, in particular for the C–I stretch in methyl iodide. For the latter, one could use the new simulation techniques like RESPA or NAPA¹³ to incorporate the effects of the vibrations on the structure and dynamics of the surrounding solvent molecules. For N₂, however, the situation could be different because of the very high frequency of vibration. This point deserves further study.

The simulation study considered the frequency modulation as the only mechanism which could lead to deviations from Kubo–Oxtoby theory. As mentioned earlier, there are several other mechanisms such as the off-diagonal anharmonic coupling between different modes in a polyatomic molecule which need to be considered^{1,2} in order to obtain a full understanding of the sub-quadratic quantum number dependence of vibrational dephasing.

APPENDIX

The quantities F_{1Q}^i , F_{2Q}^i , and F_{3Q}^i are to be calculated in order to obtain the frequency-modulation value as described in Eq. (6). These are obtained as follows. Let Q_i and Q_j denote the same normal coordinate of two different molecules i and j , respectively. Then

$$\frac{\partial V_{ij}}{\partial Q_i} = \sum_{iajb} \frac{dV_{ij}}{dr_{iajb}} \frac{\partial r_{iajb}}{\partial Q_i}, \quad (\text{A1})$$

and similarly

$$\frac{\partial V_{ij}}{\partial Q_j} = \sum_{iajb} \frac{dV_{ij}}{dr_{iajb}} \frac{\partial r_{iajb}}{\partial Q_j}. \quad (\text{A2})$$

The use of the above relations and further differentiation of the terms give^{3,27}

$$F_{1Q}^i = - \sum_{j \neq i} \sum_{a,b=1}^2 \gamma_a \frac{dV(r_{iajb})}{dr_{iajb}} \frac{\mathbf{r}_{iajb} \cdot \mathbf{u}_{ia}}{r_{iajb}}, \quad (\text{A3})$$

$$F_{2Q}^i = \sum_{j \neq i} \sum_{a,b=1}^2 \gamma_a^2 \left(\left[\frac{d^2 V(r_{iajb})}{d^2 r_{iajb}} - \frac{1}{r_{iajb}} \frac{dV(r_{iajb})}{dr_{iajb}} \right] \times \frac{(\mathbf{r}_{iajb} \cdot \mathbf{u}_{ia})^2}{r_{iajb}^2} + \frac{1}{r_{iajb}} \frac{dV(r_{iajb})}{dr_{iajb}} \right). \quad (\text{A4})$$

$$F_{3Q}^{ij} = - \sum_{j \neq i} \sum_{a,b=1}^2 \gamma_a \gamma_b \left(\left[\frac{d^2 V(r_{iajb})}{d^2 r_{iajb}} - \frac{1}{r_{iajb}} \frac{dV(r_{iajb})}{dr_{iajb}} \right] \times \frac{(\mathbf{r}_{iajb} \cdot \mathbf{u}_{ia})(\mathbf{r}_{iajb} \cdot \mathbf{u}_{jb})}{r_{iajb}^2} + \frac{1}{r_{iajb}} \frac{dV(r_{iajb})}{dr_{iajb}} (\mathbf{u}_{ia} \cdot \mathbf{u}_{jb}) \right). \quad (\text{A5})$$

where $\gamma_{a(=1 \text{ or } 2)} = [m_{a(=1 \text{ or } 2)}/m_1 + m_2]$ with m_1 and m_2 being the masses of 1 and 2 atoms, respectively, of molecule i . Similarly, $\gamma_{b(=1 \text{ or } 2)} = [m_{b(=1 \text{ or } 2)}/m_1 + m_2]$ for the b th atom of molecule j . $\mathbf{r}_{iajb} = \mathbf{r}_{jb} - \mathbf{r}_{ia}$ and \mathbf{u}_{ia} is the vector oriented from the center-of-mass of molecule i to the a th atom.

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