nitrogen for 20 min. The ampule was then placed in a dry ice–acetone bath under nitrogen and 0.01 ml of boron trifluoride etherate was added to the solution. After 20 hours the polymerization mixture was poured into a large volume of water. The precipitated polymer was collected and reprecipitated from acetone into water. Theus obtained polymer was then dried in a vacuum oven at 40°C. **2₆**: 1.12 g (72% yield): $\eta_{inh} = 0.20$ dl/g (c 0.5 g/dl in chloroform at 20°C).

Preparation of H–T Alternating Copolymer 3₆. A representative procedure was as follows: In a pyrex glass ampule were placed 1.40 g (20 mmol) of methyl vinyl ketone, 3.83 g (67 mmol) of methyl vinyl ether, 0.046 g of AIBN, and 1.3 ml of benzene. The ampule was then placed in a dry ice–acetone bath and evacuated. The ampule was sealed under vacuum and placed in an oil bath kept at 65°C. After 15 hours the ampule was opened and excess methyl vinyl ether and benzene solvent was removed by rotary evaporator. The resulting viscous polymer was dissolved in acetone and then poured into a large volume of water. The precipitated polymer was collected and reprecipitated two times from acetone into water. Thus obtained polymer was then dried in a vacuum oven at 40°C. **3₆**: 1.84 g (72% yield); $\eta_{inh} = 0.40$ dl/g (c 0.5 g/dl in chloroform at 20°C). The ^{1}H NMR spectrum of **3₆** indicated that the composition of the polymer was approximately 1.0:1.0.

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Study of Vibrational Dephasing of Simple Molecules in Liquids

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A theory in which the Enskog hard sphere collisional dynamics complements the hydrodynamic theory is applied to the fast modulation dephasing dynamics in liquids which leads to homogeneous line broadening in the isotropic Raman spectra. The dephasing times of several molecules in pure liquids and in trace solutions in the solvent CCl₄ are calculated and these are compared with experimental values. The temperature dependence of the dephasing time of liquid acetonitrile and the isothermal density dependence of the dephasing time of liquid methyl iodide are also investigated.

Introduction

The dephasing of molecular vibrations in liquids has been studied for many years experimentally and theoretically as a probe of molecular interactions and dynamics in liquids[1]. The dephasing phenomena can be experimentally investigated by the isotropic Raman line shape and the picosecond coherent anti-Stokes Raman spectroscopy in the frequency and time domains, respectively. Several theoretical and experimental studies[1-11] have shown that the isotropic Raman line shape provides a direct and useful probe of only the vibrational pure dephasing among various physical mechanisms. The isotropic Raman line shapes are recently known to be significantly inhomogeneously broadened even in nonpolar or non–hydrogen bonded liquids[12]. In such cases, picosecond coherent Raman experiments can be used to study the homogeneous vibrational dephasing dynamics in inhomogeneously broadened vibrational line shapes[13].

The physical processes in weak coupling regime which give rise to the vibrational pure dephasing can be divided into fast and slow modulation processes according to their time scales. The fast modulation process gives rise to the homogeneous broadening in isotropic Raman spectra and the slow modulation process causes the inhomogeneous line broadening.

A number of theoretical models have been proposed to explain dephasing phenomena. Among several models for the vibrational dephasing in the fast modulation process, the isolated binary collision model proposed by Fischer and

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Laubereau[14] and Oxtoby's hydrodynamic model[15] are taken to be the representative quantitative theories. Recently, Schweizer and Chandler[16] have proposed a theory which has unified the fast and slow modulation processes by treating them with the Enskog hard sphere collisional dynamics and the mean field theory, respectively. The isolated binary collision model emphasizes the role of the binary collinear collision in the short range repulsive exponential potential. On the other hand only collective effects are considered in the hydrodynamic model by regarding a vibrating molecule as a macroscopic body embedded in a viscoelastic continuum. All these theories are based on two opposite effects in molecular interactions, i.e. collisional and collective effects.

We believe that the dephasing dynamics in fast modulation processes can be best described when molecular interactions in liquids include appropriately both the collisional and collective effects. Sung and Stell[17] have recently proposed a theory for the translational diffusion of a solute particle of arbitrary size and mass in solution, in which they generalize the Enskog theory of trace solution so as to incorporate the dynamic correlation that gives rise to the correct hydrodynamic law as well as the microscopic collisional effect in the two opposite limits.

In order to incorporate the collisional and collective effects of molecular interactions in the dephasing dynamics of fast modulation processes, we have applied the theory of Sung and Stell to the dephasing dynamics by considering atoms in the vibrating molecule as solute particles dissolved in a solvent composed of structureless spherical particles. Their theory has never been applied to the vibrational dephasing dynamics before. After reviewing necessary theoretical background in which the theory of Sung and Stell is appropriately adapted, we calculate the dephasing times of serveral molecules in pure liquids and in trace solutions in the solvent CCl_4. These results are compared with experimental values and with other theories. Finally, the temperature dependence of the dephasing time of liquid acetonitrile and the isothermal density dependence of the dephasing time of liquid methyl iodide are also investigated.

Theoretical Background

We consider a fundamental vibrational transition between well-separated two vibrational levels and assume that the vibrational relaxation occurs through the weak coupling of a quantum vibrational system to a classical heat bath of rotational, and translational degrees of freedom. Neglecting the energy relaxation and the resonance transfer, the normalized vibrational correlation function is given by[15]

$$<Q(t)Q(0)> = Re \ e^{-i\omega_0 t} <\exp\{-i \int_0^t dt' \ \omega(t')\}> \quad (1)$$

where ω_0 is the transition frequency of the vibrational mode of interest in the isolated molecule and

$$\hbar \omega(t) = V_{11}(t) - V_{00}(t) \quad (2)$$

In the above equation, $\omega(t)$ is the instantaneous frequency shift induced by the solvent and V_{ii} is the diagonal matrix element of the coupling Hamiltonian V(t) of the vibrational mode to the heat bath. The cumulant expansion of Eq.(1) can be truncated at the second order in the weak coupling limit[16]

$$<Q(t)Q(0)> = Re \ e^{-i(\omega_0 + <\omega>)t} \exp[- \int_0^t dt'(t - t')$$

$$\times <\Delta\omega(t') \Delta\omega(0)>] \quad (3)$$

where

$$\Delta \omega(t) = \omega(t) - <\omega> \quad (4)$$

and $<\omega>$ is the average frequency shift.

According to the stochastic line shape theory, in the fast modulation limit where the environmental fluctuation rate is faster than the dephasing rate, the following approximation is valid:

$$\exp[- \int_0^t dt'(t - t') <\Delta\omega(t')\Delta\omega(0)>]$$

$$\approx \exp[-t \int_0^\infty dt' <\Delta\omega(t')\Delta\omega(0)>] \quad (5)$$

Then Eq.(3) can be rewritten as

$$<Q(t)Q(0)> = Re \ e^{-i(\omega_0 + <\omega>)t} e^{-t/\tau_{ph}} \quad (6)$$

where τ_{ph}^{-1} is the dephasing rate defined by

$$\tau_{ph}^{-1} = \int_0^\infty dt <\Delta\omega(t)\Delta\omega(0)> \quad (7)$$

In this case, the isotropic Raman line shape given by the Fourier transform of Eq.(6) is a homogeneously broadened Lorentzian at the frequency $\omega_0 + <\omega>$ with a half-width τ_{ph}^{-1}.

The coupling Hamiltonian V(t) which modulate the vibrational frequency in an adiabatic manner is assumed to be a rapidly varying stochastic interaction potential $V_i(t)$. V(t) may also include the vibration-rotation coupling term[19] due to the dependence of moments of inertia on the vibrational coordinates. This coupling term is neglected for simplicity, although it can significantly contribute to the dephasing of small molecules[20,21]. The vibrational Hamiltonian of a single normal mode Q is taken to be of the anharmonic oscillator form with potential[15]

$$V_i = \frac{\omega_0}{2} Q^2 + KQ^3 \quad (8)$$

where K is the anharmonic cubic force constant. The cubic anharmonicity has a very crucial contribution in dephasing[15,22].

If we relate the interaction potential $V_i(t)$ to the stochastic random forces on atoms in the vibrating molecule following Oxtoby's method[15], the instantaneous frequency shift is given by

$$\omega(t) = - \sum_i (\frac{3(-K)l_{ik}}{\omega_0^3 m_i^{1/2}} + \frac{l_{ik}^2}{2\omega_0 L m_i}) F_i(t) \quad (9)$$

where $F_i(t)$ is the stochastic random force, acting on the i-th atom of the vibrating molecule, projected in the direction of the normal mode of interest. l_{ik} is the matrix element[27] which relates the k-th normal coordinate of interest to the i-th atomic displacement, m_i is the mass of the i-th atom in the vibrating molecule, and L is a characteristic potential range parameter. If we neglect the cross correlation of the forces on different atoms, the dephasing rate is given, from Eqs.(7) and (9), by

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$$\tau_{ph}^{-1} = \sum_i \left[\frac{3(-K)l_{ik}}{\omega_0^3 m_i^{1/2}} + \frac{l_{ik}^2}{2\omega_0 L m_i} \right]^2 \int_0^\infty dt < \Delta F_i(t) \Delta F_i(0) > \tag{10}$$

where

$$\Delta F_i(t) = F_i(t) - <F_i> . \tag{11}$$

Regarding each of the atoms in the vibrating molecule as a solute particle dissolved in the sea of solvent particles, the integral of the force autocorrelation function can be related to the friction constant by the fluctuation–dissipation theorem[23]

$$\int_0^\infty dt < \vec{F}(t) \cdot \vec{F}(0) > = 3k_B T \zeta \tag{12}$$

where $\vec{F}(t)$ is the fluctuating random force exerted on a solute sphere in the solvent, and ζ is the friction constant of the solute sphere. If we assume that an atom in the vibrating molecule is exposed only half spherical side to the solvent, the integral in Eq.(10) is given by

$$\int_0^\infty dt < \Delta F_i(t) \Delta F_i(0) > = \frac{1}{2} k_B T \zeta_i \tag{13}$$

where ζ_i is the friction constant of the i-th atom in the vibrating molecule when it is completely exposed to the solvent. Then Eq.(10) becomes

$$\tau_{ph}^{-1} = \frac{1}{2} k_B T \sum_i \left[\frac{3(-K)l_{ik}}{\omega_0^3 m_i^{1/2}} + \frac{l_{ik}^2}{2\omega_0 L m_i} \right]^2 \zeta_i \tag{14}$$

Now we can evaluate the dephasing time τ_{ph} by determining the friction constant ζ_i of the i-th atom in the vibrating molecule against forces exerted by the surrounding solvent. Oxtoby[15] has obtained ζ_i from the hydrodynamic theory under the slip boundary condition by regarding the solvent as a continuous medium. In this case ζ_i is given by

$$\zeta_i = 4\pi \eta_s (\sigma_i / 2) \tag{15}$$

where η_s and σ_i are the solvent shear viscosity and the diameter of the i-th atom in the vibrating molecule, respectively.

On the other hand, Schweizer and Chandler[16] have evaluated ζ_i from the Enskog theory for dense gases. For the i-th atom in the vibrating molecule dissolved in solvent molecules of diameter σ_s and mass M, the friction constant is given by

$$\zeta_i = \frac{8}{3} n_s \bar{\sigma}_i^2 (2\pi \mu_i k_B T)^{1/2} g(\bar{\sigma}_i) \tag{16}$$

where

$$\bar{\sigma}_i = (\sigma_i + \sigma_s)/2, \quad \mu_i = m_i M / (m_i + M) \tag{17}$$

n_s is the solvent number density which can be obtained directly from the solvent density ρ and $g(\bar{\sigma}_i)$ is the contact value of the radial distribution function, which may be obtained by the Mansoori–Carnahan–Starling–Leland approximation[24] in trace solution,

$$g(\bar{\sigma}_i) = [1 - y + y/(1+S_i)][1 - y + 2y/(1+S_i)]/(1-y)^3 \tag{18}$$

with

$$y = \frac{\pi}{6} n_s \sigma_s^3, \quad S_i = \sigma_s / \sigma_i \tag{19}$$

The hydrodynamic theory in which the solvent is regard-ed as a continuous medium is inadequate because atoms in the vibrating molecule are so smaller than solvent molecules that the important collisional effect is neglected. The Enskog theory which includes only the instantaneous collisional effect in low density fluids neglects the collective effect due to repeated collisions in dense liquids.

The translational diffusion theory recently proposed by Sung and Stell[17] explains well both the collisional and collective effects of solvent molecules to the solute of arbitrary size and mass by combining the hydrodynamic theory and the Enskog theory. So we have evaluated the friction constant from the theory of Sung and Stell in order to incorporate both the collisional and collective effects of molecular interactions in the dephasing dynamics.

Regarding the i-th atom in the vibrating molecule as a hard sphere of diameter σ_i dissolved in a solvent composed of structureless spherical particles of diameter σ_s, the friction constant ζ_i is directly given from the theory of Sung and Stell as

$$\zeta_i^{-1} = \zeta_i^{*E\ -1} + \zeta_i^{*H\ -1} \tag{20}$$

where ζ_i^{*E} and ζ_i^{*H} are the Enskog and hydrodynamic friction constants, respectively, modified by the effective solvent diameter σ_s^* and the effective solvent–solute reduced mass μ_i^*:

$$\zeta_i^{*E} = \frac{8}{3} n_s \bar{\sigma}_i^{*2} (2\pi \mu_i^* k_B T)^{1/2} g(\bar{\sigma}_i^*) \tag{21}$$

$$\zeta_i^{*H} = 4\pi n_s \bar{\sigma}_i^* \tag{22}$$

where $\bar{\sigma}_i^* = (\sigma_i + \sigma_s^*)/2$, which is the effective solute–solvent core radius, and $g(\bar{\sigma}_i^*)$ is the contact value of the radial distribution function given by the modified Mansoori–Carnahan–Starling–Leland approximation[17]·

$$g(\bar{\sigma}_i^*) = [\{(1-y^*)^2 + 4y^*(1-\frac{1}{2}y^*)\} + S_i^*\{1+y^* - (1-y^*)^2 - 4y^*$$
$$\times (1-\frac{1}{2}y^*)\}]\{1 - y^* + y^*/(1+S_i^*)\}\{1 - y^* + 2y^*/(1+S_i^*)\}$$
$$/[(1+y^*)(1-y^*)^3] \tag{23}$$

with

$$y^* = \pi n_s \sigma_s^{*3}/6, \quad S_i^* = \sigma_s^*/\sigma_i \tag{24}$$

The procedure for determining the effective solvent diameter σ_s^* and the effective solute–solvent reduced mass μ_i^* is given in Appendix.

Results and Discussion

Dephasing times for the symmetric stretching modes of several simple molecules in pure liquids and in trace solutions in solvent CCl_4 are calculated by evaluating ζ_i in Eq.(14) with the hydrodynamic theory (τ_{ph}^H), the Enskog theory (τ_{ph}^E), and the theory of Sung and Stell (τ_{ph}^{SS}), respectively.

The values for the parameters needed are given in Table 1. The matrix elements l_{ik} for the symmetric stretching modes are simply determined by the normal mode analysis[27]. The characteristic potential range parameter L is determined as in Ref. 14. The anharmonic force constant K is evaluated by the methods given in Ref. 15. The diameters of atoms in vibrating molecules are taken to be the van der Waals diameters[28]. Reported solvent molecular diameters are slightly different in the literature depending on the methods of evalua-

Table 1. Parameter Values for Calculating the Dephasing Times

	$\omega_o(cm^{-1})$	T(K)	$\eta_s(cp)$	$\rho_s(g/cm^3)$	$\sigma_s(A)$	$L(10^{-9}cm)$	$-K$ $(10^{47}g^{1/2}cm^{-1}\ s^{-2})$
N_2	2326	77	0.158[e]	0.808[a]	3.84[*]	2.20	74.8
O_2	1552	90	0.190[e]	1.14[a]	3.60[*]	2.06	30.1
CS_2	656	298	0.354[b]	1.263[a]	4.64[*]	2.65	1.47
CH_3I	525	298	0.465[b]	2.265[c]	4.70[*]	2.69	1.72
$CHCl_3$	3020	303.2	0.510[b]	1.480[b]	5.11[*]	2.92	236
CH_3CCl_3	2939	298	0.832[c]	1.329[c]	5.54[*]	3.16	131
CH_3I	2948	298	0.465[b]	2.265[c]	4.70[*]	2.69	131
CH_3CN	2943	298	0.345[d]	0.777[d]	4.13[*]	2.36	131
CH_3CH_2OH	2929	298	1.180[e]	0.785[c]	4.58[*]	2.62	130
CH_3OH	2836	298	0.553[c]	0.787[b]	3.75[f]	2.14	124
CCl_4		298	0.903[b]	1.585[b]	5.44[*]	3.11	

[a] Ref. 1. [b] Ref. 31. [c] Ref. 12. [d] A. Diamond, A. Fanelli, and S. Petrucci, *Inorg. Chem.* **12**, 611 (1973), Table 1. [e] K. Tanabe, and J. Hiraishi, *Mol. Phys.* **39**, 1507 (1980). [f] K. Tanabe, *Chem. Phys.* **38**, 125 (1979). [*] These are taken from the values which are used to calculate collision times in Ref. 14.

Table 2. Calculated and Experimental Dephasing Times of Several Molecules in pure Liquids

	$\omega_o(cm^{-1})$	$\tau_{ph}^E(ps)$	$\tau_{ph}^H(ps)$	$\tau_{ph}^{SS}(ps)$	$\tau_{ph}^{Ex}(ps)$
CH_3CCl_3	2939	8.0	0.52	3.2	2.6 (2.5)[a]
CH_3I	2948	5.8	0.54	2.5	2.4 (2.1)[a]
CH_3CN	2943	7.4	1.01	4.0	5.4 (1.6)[a]
CH_3CH_2OH	2929	5.3	0.32	2.3	2.5 (0.59)[a]
CH_3OH	2836	5.0	0.53	2.7	2.4 (0.55)[a]
N_2	2326	111	121	103	150[d], 159[b,c]
O_2	1552	45	57	44	85[b,c]
CS_2	656	20	21	18	21[e]
CH_3I	525	1.9	1.2	1.5	2.3[f,g]
$CHCl_3$	3020	2.6	0.27	1.0	1.2[b,i]

[a] Ref. 12. Numbers in parentheses are obtained from the isotropic Raman data. [b] M. Scotto, *J. Chem. Phys.* **49**, 5362 (1968). [c] W. R. L. Clements and B. P. Stoicheff, *Appl. Phys. Lett.* **12**, 246 (1968). [d] A. Laubereau. *Chem. Phys. Lett.* **27**, 600 (1974). [e] R. B. Wright, M Schwartz, and C. H. Wang, *J. Chem. Phys.* **58**, 5125 (1973). [f] Ref. 10. [g] Ref. 26. [h] J. Schroeder. V. H. Schiemann, and J. Jonas. *Mol. Phys.* **34**, 1501 (1977). [i] A. Moradi-Araghi and M. Schwartz, *J. Chem. Phys.* **71**, 166 (1979).

tion. Since these values are not much different, we have taken the values which are used to calculate collision times in Ref. 14.

The calculated dephasing times for the symmetric stretching modes of several molecules in pure liquids are given and compared with experimental values (τ_{ph}^{Ex}) in Table II. In the case of CH_3- symmetric stretching modes, the experimental values are obtained from selective picosecond vibrational dephasing experiments[12]. Experimental data from the isotropic Raman line shapes are also included in the parentheses just for reference. In other cases the experimental values are obtained only from the isotropic Raman line shapes due to the lack of picosecond experimental data. Since the isotropic Raman line shapes are known to be significantly inhomogeneously broadened[12], only selective picosecond experiments give the quantitative comparison with the theory. The experimental data from the isotropic Raman line shapes may be used only for crude comparisons.

Table 3. Calculated and Experimental Dephasing Times of Several Molecules in Trace Solutions in Solvent CCl_4

	$\omega_o(cm^{-1})$	$\tau_{ph}^E(ps)$	$\tau_{ph}^H(ps)$	$\tau_{ph}^{SS}(ps)$	$\tau_{ph}^{Ex}(ps)$
CH_3CCl_3	2939	8.2	0.47	3.3	2.7[a]
CH_3CN	2943	8.3	0.48	3.4	2.7[a,b]
CH_3OH	2836	7.5	0.43	3.0	1.1[c]
$CHCl_3$	3020	2.9	0.16	1.2	1.3[c]
N_2	2326	29.7	6.3	14.5	10.6[d]

[a] Ref. 30. [b] J. Yarwood, R. Arndt, and G. Döge, *Chem. Phys.* **25**, 387 (1977). [c] A. Moradi-Araghi and M. Schwartz, *J. Chem. Phys.* **71**, 166 (1979). (The value is obtained by extrapolating to infinite dilution.) [d] Y. Le Duff, *J. Chem. Phys.* **59**, 1984 (1973).

For all CH_3- symmetric stretching modes, the dephasing times predicted by using the theory of Sung and Stell agree excellently with experimental values. The hydrodynamic theory predicts much smaller values and the Enskog theory predicts larger values than experimental values. These results show that the dephasing times of CH_3- symmetric stretching modes can be best predicted when both the collective and collisional effects are incorporated.

In other cases listed in Table II, the dephasing times predicted by three theories are not much different. The reason for this result is not immediately obvious. However, for N_2 and O_2 smaller values compared with experimental values may be due to the neglect of the vibration-rotation coupling. Brueck[20] has shown that for small molecules like N_2 and O_2 the vibration-rotation coupling contributes to the motional narrowing of the line width even in the liquid state as in the gas phase. The computer simulation[29] has also shown that the vibration-rotation coupling increases the dephasing time for liquid nitrogen by 5%-10%. There is another interesting point to notice. For N_2 and O_2, $\tau_{ph}^H > \tau_{ph}^E$ which is opposite to the trend for CH_3- symmetric stretching modes. The reason for this is not clear at the moment and further investigations would be necessary to clarify this point.

In Table III we have tabulated the dephasing times of several molecules in trace solution in the solvent CCl_4. Here, all experimental values are obtained only from the isotropic Raman line widths. The dephasing times which can be ob-
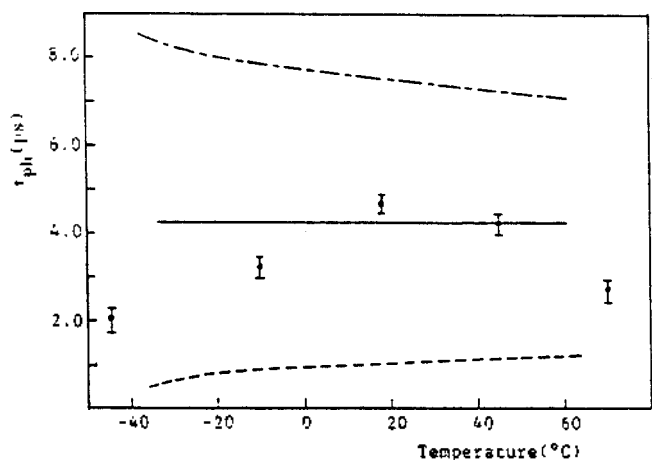
Figure 1. Temperature dependence of the dephasing time of CH_3CN. Experimental values from Ref. 25 ($\frac{\top}{\bot}$ $\frac{\top}{\bot}$), the Enskog theory (———), the hydrodynamic theory (- - - - -), and the theory of Sung and Stell (————).

Figure 2. Isothermal density dependence of the dephasing time of CH_3I at 30°C. Experimental values from Ref. 26 (———), the Enskog theory (— — — —), the hydrodynamic theory (- - - - -), and the theory of Sung and Stell (————), ρ_o is the isothermal density at the pressure of 1 bar.

tained from picosecond probing technique might be a little bit larger than the listed values, since the isotropic Raman line shapes might be inhomogeneously broadened as in pure liquids[30]. Results in Table 3 again show that the theory of Sung and Stell gives the best prediction for the dephasing times compared with other theories.

The case of $CHCl_3$ is interesting to notice. The viscosity of $CHCl_3$ in pure liquid is much smaller than that of the solvent CCl_4 as we can see from Table 1. The hydrodynamic theory in which the dephasing time is inversely proportional to the viscosity, therefore, predicts much shorter dephasing time in CCl_4 solution than that in pure liquid. However, the experimental dephasing time in CCl_4 solution is slightly longer than that in pure liquid. The values of the dephasing times predicted by the Enskog theory and by the theory of Sung and Stell show increasing tendency as we go from the pure liquid to the trace solution in CCl_4 as in experimental results. This fact shows that the collisional effect which is neglected in the hydrodynamic theory plays an important role in the dephasing dynamics and when the collisional effect is complemented with the collective effect more satisfactory results can be obtained. Previously, the isolated binary collision model, corrected for the anharmonicity, was compared with experimental results along with the hydrodynamic model[15]. The agreements of the results by the isolated binary collision model with experimental values are very poor, even worse than those by the hydrodynamic theoretical predictions, although in the isolated binary collision model the collective effects are introduced through the viscosity-dependent collision frequency. In this respect, the treatment of the collective effect as in the theory of Sung and Stell is more appropriate.

The temperature dependence of the dephasing time of acetonitrile in pure liquid is presented in Figure 1. There, the dephasing time predicted by the Enskog theory decreases and that predicted by the hydrodynamic theory increases with temperature, whereas the dephasing time predicted by the theory of Sung and Stell is almost independent of temperature. All these facts do not agree with the result of selective picosecond vibrational dephasing experiments[25]. The temperature independence of dephasing time predicted by the theory of Sung and Stell may be due to the fact that the different
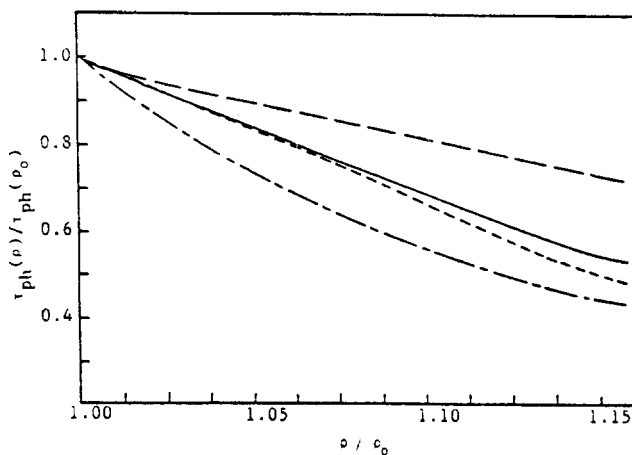
degrees of temperature-dependent contribution of the collisional and collective effects are not taken into consideration. At high temperature, the collisional effect is more important than the collective effect because of the increased environmental fluctuations, and at low temperature, the situation is reversed. The poor agreement between the theoretical predictions and the experimental results for N_2 and O_2 may also be explained in part by the same effect. If the hydrodynamic theory and the Enskog theory are combined in such a way that the former contributes more to the dephasing dynamics at low temperature while the latter does more at high temperature, the same temperature dependence as the experimental results may be expected.

The isothermal density dependence of the dephasing time of methyl iodide is presented in Figure 2. All three cases show rapid density dependence compared with the experimental result obtained from the isotropic Raman line width. Since both the hydrodynamic and Enskog theories are strongly dependent on the density, the theory of Sung and Stell also predicts rapid density dependence. But the agreement with the experimental result is still poor although it is much improved compared with other theories. The reason for this may be due to the fact that we have neglected the slow modulation process which causes the inhomogeneous line broadening. Another explanation may be provided by the fact that again the different degrees of density-dependent contribution of the collisional and collective effects are not considered.

Recently, Schweizer and Chandler[16] have proposed a theory for the effects of repulsive and slowly varying attractive forces on vibrational dephasing. There, they have unified the repulsive forces which give rise to homogeneous broadening and the attractive forces which lead to inhomogeneous broadening by treating repulsive forces and attractive forces with the Enskog hard sphere collisional dynamics and the mean field theory, respectively. The density dependence of the isotropic Raman line width of methyl iodide is well explained by the theory of Schweizer and Chandler. Since the isotropic Raman line shape can be both homogeneously and inhomogeneously broadened, the quantitative prediction of the isotropic Raman line shape is possible only when both the fast

and slow modulation processes are included. But the selective picosecond vibrational dephasing experiment makes it possible to investigate the fast modulation dephasing dynamics.

In conclusion, the fast modulation dephasing dynamics which leads to homogeneous line broadening in the isotropic Raman spectra can be quantitatively described when the collisional and collective effects of fluctuating environment are appropriately incorporated by using the theory in which the Enskog hard sphere collisional dynamics complements the hydrodynamic theory.

Appendix

The effective solvent diameter σ_s^* is the value which satisfies the following equation according to Ref. 17

$$g(\sigma_s^*) = 1 + 4y \, g(\sigma_s) \tag{A1}$$

where $g(\sigma_s)$ is the radial distribution function at $r = \sigma$, which is given by the Mansoori-Carnahan-Starling-Leland approximation in trace solution as

$$g(\sigma_s) = (1 - \frac{1}{2}y)/(1-y)^3 \tag{A2}$$

Eq.(A1) can be rewritten with the help of Eqs.(23) and (A2) as

$$(1+y\gamma^3+y^2\gamma^4-y^3S_i\gamma^7-y^3\gamma^9+y^3S_i\gamma^{10})(1+S_i\gamma-yS_i\gamma^4)$$

$$\times (1+S_i\gamma+y\gamma^3-yS_i\gamma^4) - (1+y\gamma^3)(1+S_i\gamma)^2(1-y\gamma^3)^3$$

$$\times \{1+4y(1-\frac{1}{2}y)/(1-y)^3\} = 0 \tag{A3}$$

where σ_s^* has been replaced by $y\sigma_s$. The numerical solution of Eq.(A3) about γ at given y and S_i gives σ_s^*.

The effective solute-solvent reduced mass μ_i^* is obtained from Eq.(4.7) in Ref. 17 as

$$\mu_i^* = \mu_i[(\sigma_i+\sigma_s)/(\sigma_i+\gamma_B\sigma_s)]^4 \tag{A4}$$

where γ_B is obtained from the numerical solution of Eq.(A3) at $y \to 0$.

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