$h{\rightarrow}0$, Eq.(44) can be reduced to Eq.(22) which is the result for the reflecting boundary condition. The long time behavior of the remaining probability can be obtained also by following the similar procedure as before and the result becomes

$$P(\tau) = 1 - [1 - h\sqrt{\beta}x_o(h\sqrt{\beta}x_o+1)^{-1} + h\sqrt{\beta}x_o \exp(2\beta Q)$$
$$\times (h\sqrt{\beta}x_o+1)^{-2}]$$
$$\times \exp[\tau h^2 \exp(2\beta Q)/(h\sqrt{\beta}x_o+1)^2]$$
$$\times \mathrm{erfc}[\tau^{1/2}h\exp(\beta Q)/(h\sqrt{\beta}x_o+1)]$$
$$+ \sqrt{\beta}x_o \exp(\beta Q)(h\sqrt{\beta}x_o+1)^{-1}(\pi\tau)^{-1/2} \qquad (49)$$

which reduces to the second expression in Eq.(26) in the limit of $h{\rightarrow}0$.

The remaining probability in three-dimensional case with spherical symmetry for the radiation boundary condition can be obtained in the long time limit and we found that Eq.(41) is recovered in the limit of $h{\rightarrow}0$. Details of this calculation will be reported elsewhere.

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Concentration Dependence of the ν₁ Isotropic Raman Band of Nitromethane in Chloroform-d, Pyridine-d₅, 1,3,5-Trifluorobenzene, and Hexafluorobenzene

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Concentration dependences of the isotropic Raman band width and the peak position for the ν_1 (C–H stretching) mode of nitromethane in chloroform-d, pyridine-d₅, 1,3,5-trifluorobenzene, and hexafluorobenzene have been investigated. For all solutions, the experimental concentration dependences have been well described by the concentration fluctuation model of Knapp and Fischer when appropriate values for the effective numbers (N) of nearest neighbors were used. For the CH_3NO_2/C_6F_6 solution, an abnormally small value (2) of N indicates strong intermolecular interaction.

Introduction

Vibrational relaxation in liquid has attracted much attention recently.[1-11] Such an information is usually obtained through the analysis of infrared or Raman band shapes. For a real time investigation of the process, picosecond laser technique using two lasers, one for vibrational excitation and the other for probing, has been utilized also.[5,6] In the vibrational band shape analysis, Raman scattering is more advantageous than the infrared absorption spectroscopy. This is due to the fact that the two mechanisms contributing to the vibrational band shape, namely, the vibrational and the reorientational relaxations[12] can be separated experimentally in the Raman spectroscopy through polarization analysis. Hence, the vibrational relaxation is most frequently investigated by analyzing the isotropic Raman band shape. Temperature,[7,8] pressure,[7,8] and concentration[1,8,9] dependences of the isotropic Raman band width provide useful information on the fundamental nature of the process. Several mechanisms such as the phase relaxation,[11] the resonant energy transfer,[13] and the energy relaxation[4] have been proposed, of which the first two are generally considered to be the most important.

In solution, there is another mechanism contributing to the vibrational band broadening of the solute molecules. This mechanism, first proposed by Bondarev and Mardaeva,[14] is due to the fluctuation of the solute concentration in a microscopic environment. This concentration fluctuation model for band broadening has been further developed theoretically by Knapp and Fischer,[15] and its validity examined experimentally for various binary liquid systems.[9,10,16]

In the present work, the concentration dependences of the isotropic Raman band width of the ν_1 (C–H stretching) mode of nitromethane in $CDCl_3$, pyridine-d₅, 1,3,5-trifluorobenzene, and hexafluorobenzene are investigated. The major objective of the study is to investigate the further details of the concentration fluctuation mechanism, such as the effect of the

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size and the number of molecules in the microscopic environment, and their interaction with the solute vibrational mode.

Experimental

Details of the apparatus and experimental techniques to determine the Raman band widths have been described previously.[17] Briefly, Raman spectra were recorded with a JASCO Raman spectrophotometer (Model R300) using 514.5 nm line of an argon ion laser (Spectra-Physics model 164-09). The DC detection system in the original instrument was replaced by a photon counting system (EG & G PAR Model 1105/1120) to improve S/N ratio. Spectra were recorded at room temperature using capillary sample cell. The spectral slit width of the spectrometer was 2.3 cm^{-1}. The slit effect on the observed Raman band widths was corrected using the formula proposed by Tanabe.[18]

$$\delta_t = \delta_a [1 - (s/\delta_a)^2] \tag{1}$$

where δ_t and δ_a are true and apparent band width (full width at half maximum, FWHM), respectively, and s is the spectral slit width determined using the fluorescence lines from the laser. Since the depolarization ratio for the ν_1 band was very small (<0.02), the isotropic Raman band was obtained without using a polarization analyzer.[19]

All reagents were purchased from Aldrich Chemical Company and were used without further purification.

Results and Discussion

The isotropic Raman band widths for the totally symmetric ν_1 (C–H stretching) mode of nitromethane in CDCl$_3$, pyridine-d$_5$, 1,3,5-trifluorobenzene, and hexafluorobenzene solutions have been measured at various solute concentrations. The results for each solutions are shown in Figures 1-4, respectively. Also shown in the figures are the concentration dependences of the peak position of the ν_1 mode in each solutions. The error bars in the figures indicate the two standard deviations (95% confidence level). The measured isotropic Raman band width (FWHM) and the peak position of the ν_1 mode of neat CH$_3$NO$_2$ are 16.4 cm^{-1} and 2966.5 cm^{-1}, respectively. Notice that upon infinite dilution of CH$_3$NO$_2$ in each solvents, both the band width and the peak position have changed substantially.

A peak shift of a solute vibrational mode upon dilution is due to the change in the interaction of that particular mode with the surrounding molecules. The accompanying change in the band width was explained by Bondarev and Mardaeva[14] in terms of the concentration fluctuation in the microscopic environment surrounding a solute molecule. That is, different molecules see different concentrations such that they contribute to the spectrum at different frequencies. Assuming a static Gaussian distribution of concentration fluctuation, the following expression was derived for the additional band width in the mixture.

$$\nu_{1/2} = 2 (2\ln 2)^{1/2} \Delta \Omega [c (1-c)/N]^{1/2} \tag{2}$$

where c is the solute concentration in mole fraction, N is the number of neighboring molecules which interact with the reference mode, and $\Delta\Omega$ is the total peak shift between the neat liquid and the solution at infinite dilution. However, since the residual band shape is Lorentzian while the concentration distribution was assumed Gaussian, the overall band shape in solution would have the appearance of a Voigt profile, making the above expression invalid. Also, further experimental investigations by Fujiyama et al.[20] and by Döge et al.[21] revealed that the concentration dependences of vibrational band widths were affected not only by $\Delta\Omega$ but also by $\Delta\Gamma$ (the total change in band width between the neat liquid and the solution at infinite dilution).

Knapp and Fischer[15] elaborated theoretically the concept proposed by Bondarev and Mardaeva. In their model, the continuous Gaussian distribution of the concentration in a microscopic volume was replaced by a discrete binomial distribution. Also, not only the static but also the dynamic aspect of the concentration fluctuation which would arise due to the diffusion process were taken into account. The importance of the dynamic contribution in the CDCl$_3$/CCl$_4$ binary system was emphasized recently by Asthana et al.[16] This dynamic contribution becomes conspicuous only when the values for $\Delta\Omega$ and $\Delta\Gamma$ are very small. The dynamic contribution can be ignored for the systems investigated in the present paper, because the value for $\Delta\Omega$ and $\Delta\Gamma$ are fairly large ($|\Delta\Omega| = 4\sim13$cm^{-1}, $|\Delta\Gamma| = 1.5\sim3.5$ cm^{-1}). In our previous work[9] on the concentration dependences in the CH$_3$CN/CCl$_4$ and the CD$_3$CN/CCl$_4$, an approximate Voigt profile expression for a vibrational band shape in solution was utilized. Such an expression was found adequate for the investigation of the vibrational band broadening mechanisms. In the present work, a more rigorous formalism developed by Knapp and Fischer will be adopted. Its validity and usefulness will be investigated by comparing with the above experimental results.

The microscopic environment surrounding the reference molecule is distinguished by the composition of the N effective nearest neighbors. Hence, there are total of N + 1 different environmental states depending on the number n of the solvent molecules among the effective neighbors. In the static limit, the overall spectral function can be thought as the weighted sum of the Lorentzian spectral functions for each environmental states. The following expressions have been proposed by Knapp and Fischer.

$$I(\omega) = \sum_{n=0}^{N} C_n I_n(\omega) \tag{3}$$

$$I_n(\omega) = \frac{1}{\pi [i(\omega - \omega_0 - n\Delta\Omega/N) + (\gamma_0 + n\Delta\Gamma/N)]} \tag{4}$$

where ω_0 and γ_0 are the frequency and the band width (half width at half maximum) of the reference mode, respectively. The weighting factor C_n is the probability to find n solvent molecules among N effective neighbors, represented by the discrete binomial distribution.

$$C_n = {}_N C_n (1-c)^n c^{N-n} \tag{5}$$

Using this formalism, the overall peak shape, and hence the width and the position of an isotropic Raman band can be calculated from the information on $\Delta\Omega$, $\Delta\Gamma$, and N.

For the binary solution systems studied in the present work, the widths and the positions of the ν_1 mode of CH$_3$NO$_2$ have been calculated using the above formalism. The parameters used in the calculation for each systems are listed in Table 1. The values for $\Delta\Omega$ and $\Delta\Gamma$ were estimated from the ex-
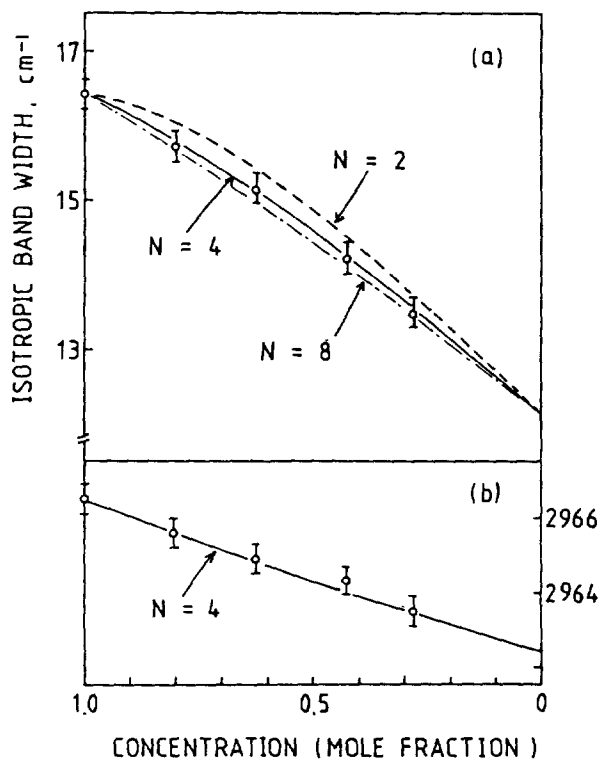
Figure 1. Concentration dependences of the width(a) and position(b) of the isotropic v_1 band of CH_3NO_2 in $CDCl_3$. Circles denote the experimental data. Curves are the results of the concentration fluctuation calculation with the N values indicated, respectively. The calculated peak positions are almost the same for different N values.

Figure 2. Concentration dependences of the width(a) and position(b) of the isotropic v_1 band of CH_3NO_2 in pyridine-d_5. See Figure 1 for explanation.

Figure 3. Concentration dependences of the width(a) and position(b) of the isotropic v_1 band of CH_3NO_2 in 1,3,5-trifluorobenzene. See Figure 1 for explanation.

perimental data. The calculation for each systems was carried out with various values for N. The results of the calculation for each systems are shown in Figures 1-4. It is to be noted from the figures that for all the systems investigated the experimental data can be reproduced adequately by calculation using appropriate values for N. For all the systems investigated, different values of N have been found to influence the calculated peak positions only slightly. Within the experimental errors for the band widths, a few different values for N could reproduce the experimental data for solutions in $CDCl_3$, pyridine-d_5, and 1,3,5-$C_6H_3F_3$. However, for C_6F_6 solution the effect of different N on the band width was rather dramatic. Hence, for this system the calculation could be made to agree with the experimental data only with $N = 2$.

The ranges of N values for each systems which can reproduce the experimental data are listed in Table 1. For CH_3NO_2 in $CDCl_3$, pyridine-d_5, and 1,3,5-$C_6H_3F_3$, the numbers of the nearest neighbors which interact effectively with the v_1 mode are somewhere around 5. This result is in general agreement with the previous reports[9,10,15] on other binary systems such as v_1 of CH_3I in $CDCl_3$, v_2 of CH_3I in CH_3CN, v_2 of CH_3CN and CD_3CN in CCl_4, *etc.*.

The effective number of interacting neighbors for the v_1 mode of CH_3NO_2 in C_6F_6 is smaller than that for any other system investigated thus far. In the last column of Table 1, van der Waals diameters[22] for the solvent molecules are listed for comparison. The van der Waals diameter of hexafluorobenzene is slightly larger than those for other solvent molecules. However, the difference in molecular size is not large enough to justify the substantial difference in the effec-
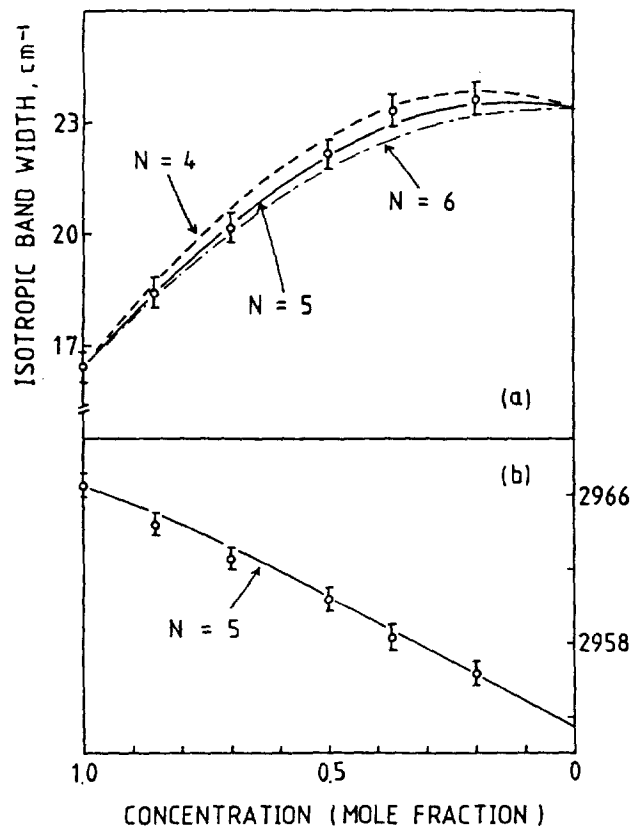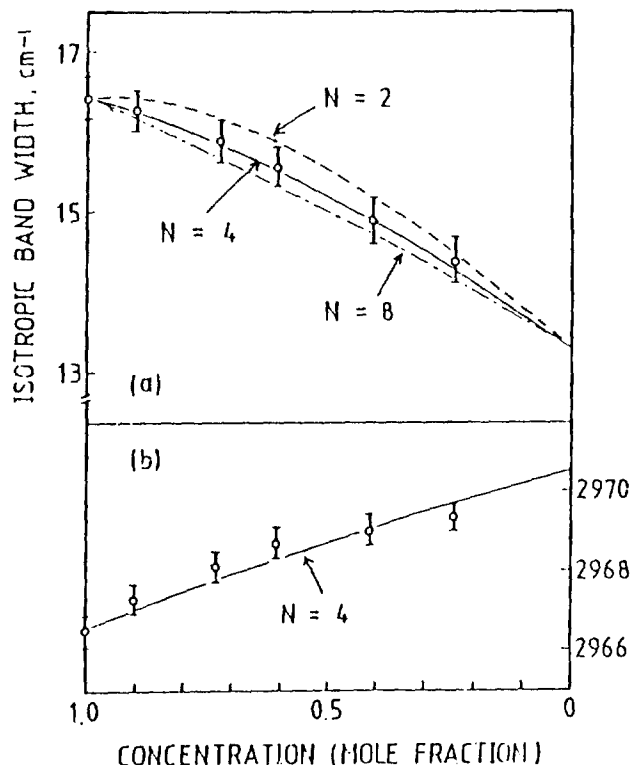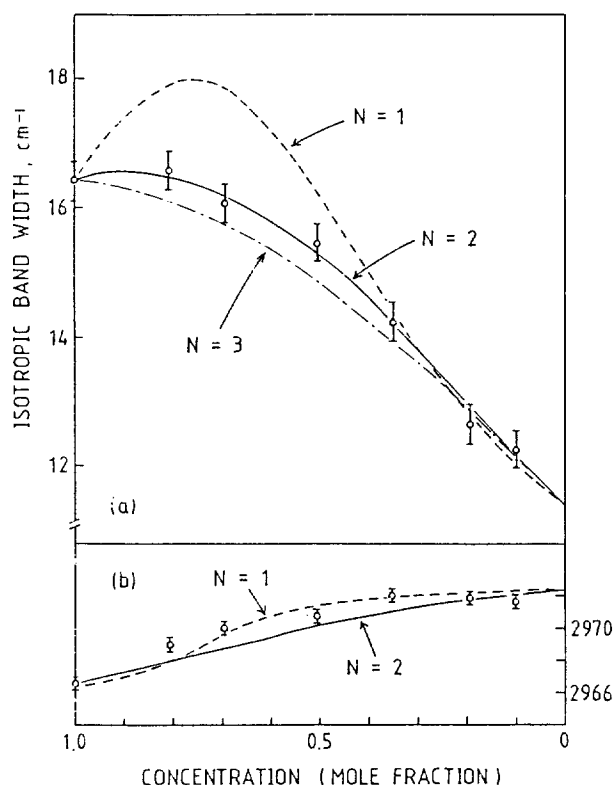
Figure 4. Concentration dependences of the width(a) and position(b) of the isotropic v_1 band of CH_3NO_2 in C_6F_6. The calculated position curves for $N \geqslant 3$ are very similar to the one obtained with $N = 2$.

tive numbers of interacting neighbors among the systems.

In binary solutions including hexafluorobenzene, strong intermolecular interaction has been observed frequently. From the depolarized Rayleigh scattering experiments on the carbon disulfide/hexafluorobenzene binary solution system, Brown et al.[23] observed a tendency for parallel orientation of neighboring molecular axes whereas no such ordering was found for the carbon disulfide/benzene system. Strong interaction in binary solutions of hexafluorobenzene in benzene, toluene, and mesitylene has been indicated in thermodynamic[24] and spectroscopic data.[25-28] For example, Hwang et al.[25,26] observed an unusually weak viscosity dependence of the reorientational motion of hexafluorobenzene in benzene and mesitylene. This was interpreted as due to the existence of a very strong interaction between the solute and the solvent molecules, or the formation of transient complex between the molecules. It is to be noted, however, that the transiency of such a complex which would be the same order of magnitude as the reorientation time ($1\sim10$ psec) is still much longer than the vibrational period (~0.1 psec). Hence, the effect of a very strong interaction can be manifested in the isotropic Raman

Table 1. Parameters Used for the Concentration Fluctuation Calculation ($\Delta\Omega$, $\Delta\Gamma$), Effective Nearest Neighbors (N), and van der Waals Diameters (d_w)

Solvents	$\Delta\Omega$, cm⁻¹	$\Delta\Gamma$, cm⁻¹	N	d_w, Å
$CDCl_3$	−4.1	−2.130	$3\sim8$	5.13
pyridine-d_5	−13.1	3.495	$4\sim6$	5.24
$1,3,5$-$C_6H_3F_3$	4.0	−1.555	$3\sim8$	5.64
C_6F_6	5.8	−2.505	2	5.91

band. The situation for the CH_3NO_2/C_6F_6 binary system may be similar. Namely, a very effective interaction between these molecules may limit the number of the neighboring molecules which can interact with the reference mode. The nature of the interaction in this system is not clear, however. For the C_6F_6/C_6H_6 system, this was attributed to the quadrupole-quadrupole interaction.[29]

To summarize, the concentration dependences of the v_1 (C–H stretching) mode of CH_3NO_2 in various solvents could be explained adequately by the concentration fluctuation model. The peak position of the band hardly showed any dependence on the effective number of neighboring molecules. The band width was found to be more sensitive to this value. Due to the limited accuracy of the experimental data this value could not be determined unequivocally. Based on the results for solutions in $CDCl_3$, pyridine-d_5, and $1,3,5$-$C_6H_3F_3$, it seemed that the size of the solvent molecule did not greatly affect the number of effective nearest neighbors. The concentration dependence of CH_3NO_2/C_6F_6 could be explained with an N value which was substantially smaller than those for the above systems. This was explained as due to the presence of strong intermolecular interaction in the CH_3NO_2/C_6F_6 system. Hence, the present method may be useful for the investigation of intermolecular interaction in binary liquid systems.

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MO Studies on the Gas–Phase Reaction of Dypnone Oxide with Chloride Ion[†]

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The MNDO calculations were performed in order to investigate the gas–phase reaction mechanism of 2–propene–1–al oxide, as a model compound of dypnone oxide(1,3–diphenyl–2–butene–1–one oxide) with the chloride ion. Optimized geometries and heats of formation for two probable concerted pathways, CHO and H migration, were determined and their activation energies were obtained. MO results show that although the formyl migration is thermodynamically more favorable than the hydride migration, the latter kinetically predominates over the formyl migration, which is contrary to the established migrating preferences. It is concluded that the hydride migratory propensity is catalyzed by the chloride ion by reducing the capability of the carbonyl π bond to participate in the migration.

Introduction

The acid–catalyzed ring–opening reactions of various epoxide derivatives have been a subject of numerous experimental and theoretical investigations.[1] The migratory propensity of the carbonyl group was first established by House in a series of mechanistic papers[2] and this intramolecular carbonyl group migration was reported with epoxy ketones, and so on.
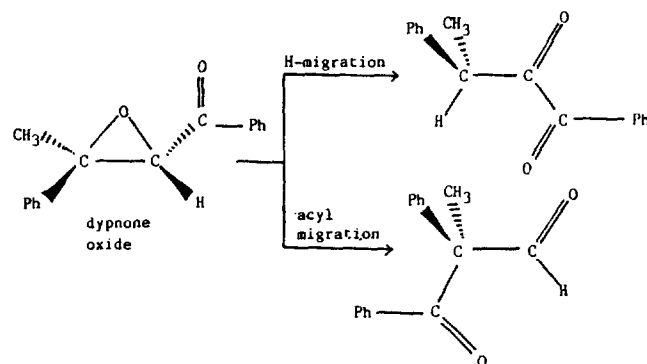
Scheme 1

Recently experimental studies on the Lewis acid catalyzed reaction of 1,3–diphenyl–2–butene–1–one oxides(dypnone oxides) were reported by Bach, *et al.*.[3] They suggested that the reaction mechanism involving the intramolecular migration as in scheme 1. The major findings were that while protic acids and mild Lewis acids readily induced the carbonyl group migration, nucleophilic Lewis acids led to the hydride migration.

The theoretical investigations of the chemical reaction mechanism must be attained from the determination of the transition state(TS) structure. Recently various MO theoretical methods to determine the TS structure have been developed and successfully applied to various organic reaction systems. Our efforts in this work will be directed toward establishing the migrating nature of the substituents in the ring–opening reaction of the epoxide by MO theoretical studies.

Calculation

In order to reduce the complexity of the molecular structure of the substrate, we chose the simplest reaction of 2–propene–1–al oxide with the chloride ion as a model reaction. The calculations were carried out by the MNDO method.[4] Ground state geometries of the reactants were optimized starting from the standard geometries. Transition states were