

Concentration Dependences of the Isotropic Raman Line Widths of Acetonitrile and Acetonitrile-d₃ in Carbon Tetrachloride

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Received September 10, 1985

Concentration dependences of the isotropic Raman line widths for the ν_1 (C-H and C-D) and the ν_2 (C≡N) modes for CH₃CN and CD₃CN in CCl₄ solutions have been investigated. For the ν_1 modes, the dephasing seems to be a good description for the isotropic line broadening in CCl₄ solution even though the concentration fluctuation can reproduce the experimental results also. For the ν_2 modes, the concentration fluctuation was the dominant mechanism for the concentration-dependent line broadening.

Introduction

Raman spectroscopy is a useful technique for the study of vibrational and rotational relaxations for molecules in liquid phase.¹⁻⁴ Widths of the isotropic and anisotropic Raman components of totally symmetric vibrational modes provide information on the vibrational and rotational relaxation time, respectively. Separating the contributions from these line broadening mechanisms through polarization measurements is one of the advantages of Raman technique over the infrared absorption spectroscopy, even though the combination of two techniques can be even more helpful.⁷

Several mechanisms have been proposed to explain the vibrational relaxation of molecules in the liquid phase. Most important of these are the phase relaxation⁸ and the resonant energy transfer.⁹ Recently, Knapp and Fischer¹⁰ proposed the concentration fluctuation model to explain the concentration dependence of the vibrational relaxation line width in solution. This was an advanced form of the original concept proposed by Bondarev and Mardaeva.¹¹ The isotropic Raman line widths in CH₃I/CDCl₃¹⁰, C₆H₅CN/C₆H₆¹², CDCl₃/CCl₄¹³, etc. were found to contain contributions from the concentration fluctuation, necessitating consideration of this mechanism in the investigation of the vibrational line broadening in solution.

In the present work, the concentration dependences of the isotropic Raman line widths of the ν_1 (C-H and C-D stretching) and ν_2 (C≡N stretching) modes of CH₃CN and CD₃CN in CCl₄ will be investigated. Various models for the vibrational line broadening will be compared in this connection.

Experimental

Raman spectra were obtained with a Raman spectrophotometer (JASCO model R-300) equipped with a photon counting system (EG & G PAR model 1105/1120). 514.5 nm line of an argon ion laser (Spectra-Physics model 164-09) was used as the exciting source. Samples were introduced to the capillary sample cell at room temperature (25 ± 1°C). The spectral slit width of the spectrometer was adjusted in the range 1.5~2.5 cm⁻¹ depending on the signal intensity. The slit effect on line width was corrected using the formula proposed by Tanabe.¹⁴

$$\delta_t = \delta_a [1 - (s/\delta_a)^2] \quad (1)$$

where δ_t and δ_a are true and apparent line width (FWHM), respectively, and s is the spectral slit width determined using the fluorescence lines from the laser. Since the depolarization

ratios for both the ν_1 and ν_2 Raman lines were very small (<0.02), the isotropic spectra were approximated by the parallel component spectra.¹⁵

$$I_{iso} \approx I_{11} \quad (2)$$

Since the low frequency region of the ν_2 Raman line in CH₃CN was contaminated by some secondary structure^{1,2} or hot bands of the type $\nu_2 + \nu_8 - \nu_8$ ¹⁶, the line width of the mode was measured from the high frequency portion. Solution densities were determined using a Weld pycnometer. Spectroscopic grade CH₃CN and CCl₄ from Merck and CD₃CN from Aldrich were used without further purification.

Results and Discussion

Vibrational relaxation in liquid acetonitrile has been extensively investigated using Raman¹⁻⁵ and infrared¹⁷ spectroscopic methods. In particular, Schroeder *et al.*³ measured the Raman line shapes of the $\nu_1(a_1)$ C-H and C-D fundamentals in liquid acetonitrile and acetonitrile-d₃ as a function of pressure and temperature. The isotropic Raman line width which is the contribution from the vibrational relaxation was found, both for the C-H and C-D modes, to be almost constant upon isotopic dilution. Hence, the resonant energy transfer was ignored as a mechanism for the vibrational relaxation of the ν_1 mode. The pressure and temperature dependence of the isotropic Raman line width of this mode was found to be in qualitative agreement with the dephasing mechanism developed in the form of the isolated binary collision (IBC) model by Fischer and Laubereau.⁸ In this work, the isotropic Raman line widths for the ν_1 C-H and C-D fundamentals of CH₃CN and CD₃CN, respectively, were measured as functions of their concentrations in CCl₄ solutions. The results are shown in Figures 1 and 2. The error bars indicate the standard errors in the 95% confidence limit. Also shown in the figures are the changes in the peak frequencies of each modes upon dilution. Notice that both the line widths and peak frequencies of each modes decrease upon dilution in CCl₄. To evaluate the isotropic line widths predicted from the dephasing model, the modification by Tanabe⁵ of the original IBC model was utilized. Briefly, the overall isotropic line width was estimated as a sum of the contributions from the solute-solute and the solute-solvent interaction.

$$\delta_{RH} = (\delta_{RH})_{\text{solute-solute}} + (\delta_{RH})_{\text{solute-solvent}} \quad (3)$$

The dephasing line widths from each components were calculated using the following equation.

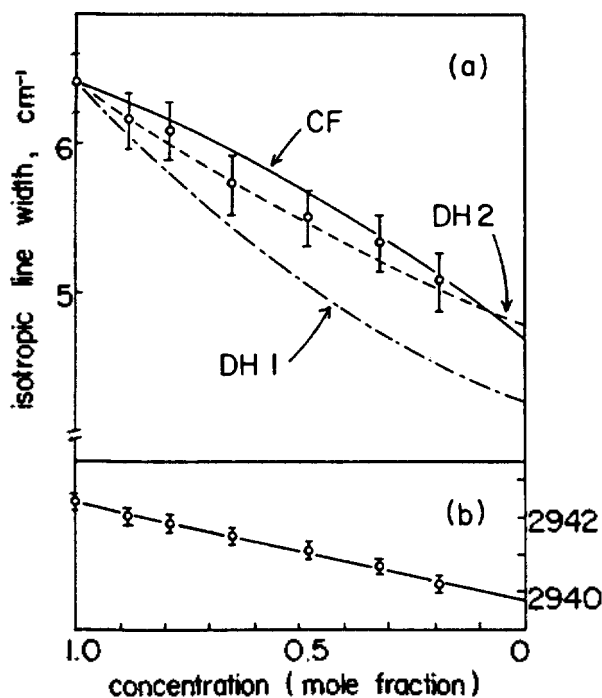


Figure 1. Concentration dependence of the width(a) and position(b) of the isotropic ν_1 line of CH_3CN . Circles denote the experimental data. Solid line curves marked CF are the result of the concentration fluctuation calculation. Curves marked DH 1 and DH 2 are widths from the dephasing model with the CCl_4 hard sphere diameter of 5.10 Å, and 5.20 Å, respectively.

$$(\delta_{\text{FH}})_{ij} = \frac{4\mu_{ij}\gamma^4 k_B T \Gamma_{ij}}{\pi c M^2 \omega^2 L_{ij}^2} \quad (4)$$

Here, μ_{ij} is the reduced mass of the colliding molecular pair, $\gamma = m_A/(m_A + m_B)$ is the factor denoting the relative magnitude of vibrational coordinates of atoms, Γ_{ij} is the collision frequency, M is the reduced mass of the vibrating oscillator with angular frequency ω , and L_{ij} is the factor expressing intermolecular potential in the exponential form. k_B , c and T are the Boltzman constant, speed of light and the sample temperature, respectively. In general, the calculations based on the above equations are not in quantitative agreement with the measured values due to the anharmonicity effect.¹⁸ Instead of including the anharmonicity correction in the above equations, Tanabe⁵ proposed to use an experimental scaling factor. In the present evaluation, the calculated dephasing widths at each concentrations were simply normalized using the experimental line width for the neat liquid as the reference. Hard sphere diameters¹⁹ of CH_3CN , CD_3CN and CCl_4 were taken to be 4.13 Å, 4.13 Å and 5.10 Å, respectively. In a binary solution, the concentration in the vicinity of a reference molecule can be different from the prepared bulk concentration. Knapp and Fischer¹⁰ derived an expression for the contribution of such concentration fluctuation to the isotropic line width based on the assumption of binomial distribution of the nearest neighbor molecules. When the diffusion of the liquid particles which is slower than the vibrational relaxation is ignored, the isotropic line shape is given by the real part of the following expression.

$$I(\omega) = \frac{1}{\pi} \frac{F(-i\Delta\tau)}{\Delta\Lambda \sqrt{2c(1-c)/N} (-i\Delta\tau)} \quad (5)$$

where

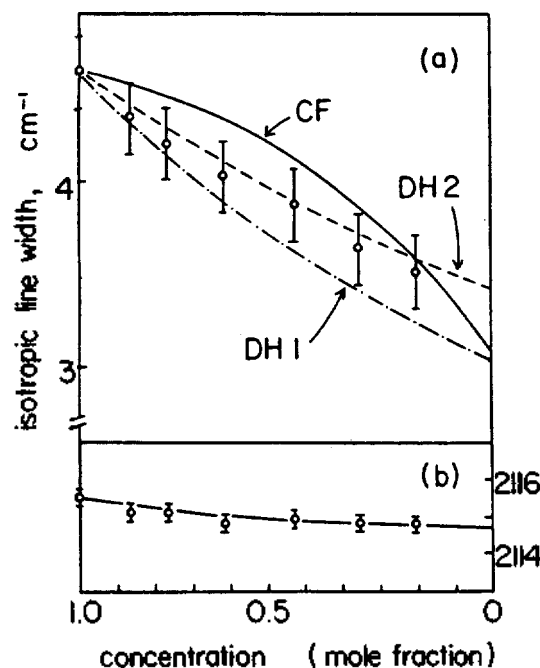


Figure 2. Same as in Figure 1 except that this is for the ν_1 line of CD_3CN .

Table 1. Parameters (cm^{-1}) used for the Concentration Fluctuation Calculation

Molecules	Vibrational modes	ω_0	$\Delta\omega$	γ_0	$\Delta\gamma$
CH_3CN	ν_1	2942.4	-2.2	3.20	-0.85
	ν_2	2254.8	2.6	1.87	0.39
CD_3CN	ν_1	2115.5	-1.0	2.30	-0.75
	ν_2	2261.2	2.8	2.01	0.84

$$F(x) = \sqrt{\pi} z e^{x^2} \text{erfc}(z),$$

erfc(z) standing for the complementary error function. Expansion forms for the complementary error function can be found in the literatures.^{20,21} In Eqn.(5), c and N are the solute concentration in mole fraction and the number of the nearest neighbor molecules, respectively and the expressions for $\Delta\Lambda$ and $\Delta\tau$ are given below.

$$\Delta\Lambda = \Delta\omega + i\Delta\gamma \quad (6)$$

where $\Delta\omega$ and $\Delta\gamma$ are the changes in the frequency and line width (HWHM) upon infinite dilution, respectively.

$$\Delta\tau = \frac{c\Delta\Lambda + \omega_0 - \omega + i\gamma_0}{\Delta\Lambda \sqrt{2c(1-c)/N}} \quad (7)$$

where ω_0 and γ_0 are the frequency and line width for the neat liquid, respectively. For the solutions of methyl iodide in various solvents, Knapp and Fischer found that the five nearest neighbors (N) exerted effective interaction.

The theoretical isotropic line widths for the ν_1 mode using the dephasing model and the concentration fluctuation model are shown in Figures 1 and 2. Concentration dependences of the peak frequencies as calculated from the concentration fluctuation model are also shown. Values for the parameters (ω_0 , $\Delta\omega$, γ_0 , $\Delta\gamma$) used for this type of calculation are listed in Table

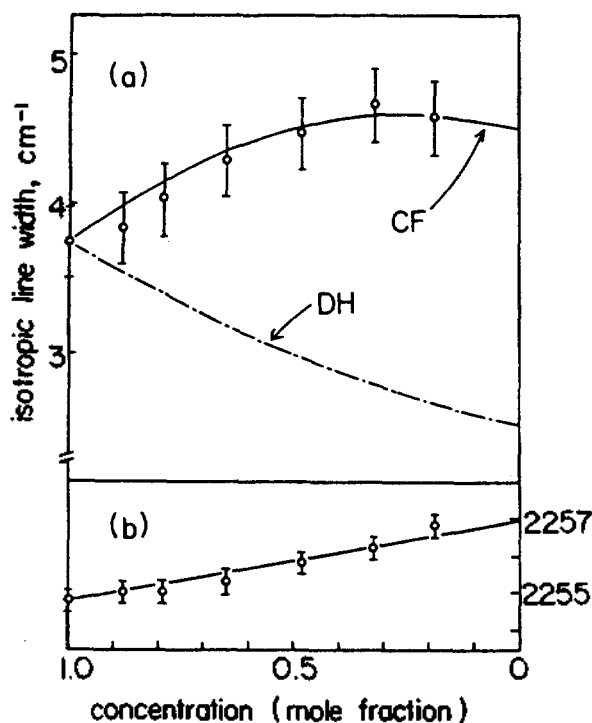


Figure 3. Concentration dependence of the width(a) and position(b) of the isotropic ν_1 line of CH_3CN . Circles denote the experimental data. Curves marked CF and DH are the results calculated with the concentration fluctuation and the dephasing models, respectively.

1. It may seem in the figures that the concentration fluctuation is a better description of two models for the concentration dependence of the isotropic ν_1 line width. However, the calculated dephasing line width is rather sensitive to the hard sphere diameters of the solute and solvent molecules. Literature values^{19,22,23} for the hard sphere diameter of a molecule show a discrepancy in the range of $\sim 0.3 \text{ \AA}$. When 5.20 \AA was used as the hard sphere diameter of CCl_4 , the dephasing calculation was in excellent agreement with the experimental data as shown in Figures 1 and 2. Hence, it is likely that the dephasing is the dominant line broadening mechanism for the ν_1 mode in the CCl_4 solution as in neat liquid.

Vibrational relaxation for the ν_2 mode of acetonitrile has not received as much attention as its ν_1 counterpart. Whittenburg and Wang² observed the increase in the isotropic line width of the ν_2 mode as CH_3CN was diluted with CCl_4 . This phenomenon, which is contrary to what is expected from the dephasing theory and the resonant energy transfer, was explained as due to the importance of pair correlation in CH_3CN . However, the pair correlation has been usually ignored to explain an isotropic Raman line width. The concentration dependences of the positions and widths of the ν_2 modes for CH_3CN and CD_3CN in CCl_4 solutions are shown in Figures 3 and 4, respectively. Here again, the error bars indicate the standard errors in the 95% confidence limit. Results of the theoretical calculations using the dephasing and the concentration fluctuation models are also shown in the figures. It is clear from the figures that the concentration fluctuation model is in good agreement with the experimental concentration dependences, while the dephasing model shows marked devia-

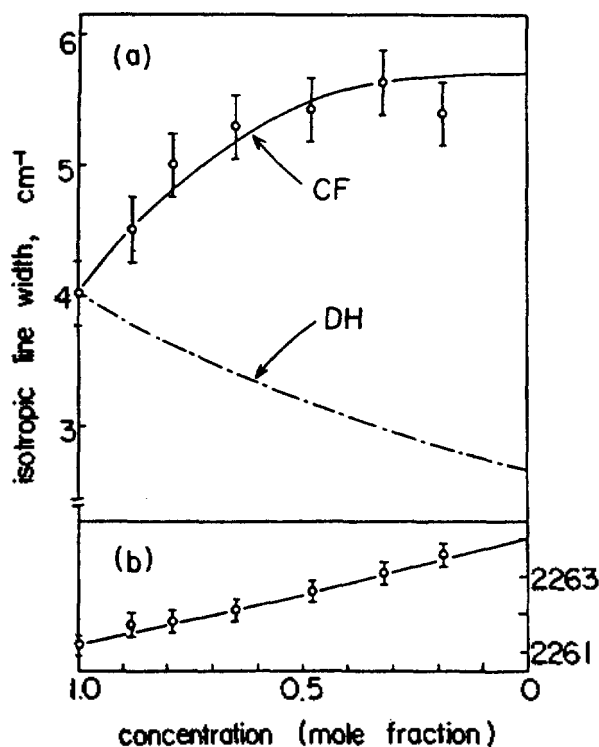
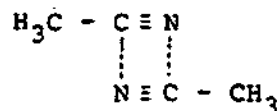


Figure 4. Same as in Figure 3 except that this is for the ν_1 line of CD_3CN .

tion from the experimental data. Even though the concentration fluctuation is a good description for the concentration dependences of the ν_2 line widths, it does not mean that the dephasing process is not an important relaxation mechanism for this mode in neat liquid. That is, it is still possible that the dephasing mechanism is the major relaxation process in neat liquid while the additional increase in line width upon dilution is due to the concentration fluctuation. Further experimental investigations such as the determination of the pressure and temperature dependence are needed to elucidate the nature of the vibrational relaxation process for the ν_2 mode.

It is interesting at this point to discuss the possibility of acetonitrile dimer formation based on the present results. Freedman and Nixon²⁴ suggested that the sideband structures for the ν_2 and ν_4 modes in the infrared spectrum were due to the dimer formation.



However, the fact that the concentration dependence of the isotropic ν_2 line width is adequately described by the concentration fluctuation is a strong argument against such a possibility. Thus, the present results support the assignment of the ν_2 sideband as hot bands of the type $\nu_2 + \nu_8 - \nu_8$ as suggested by Fini and Mirone.¹⁴

To summarize, the dephasing and the concentration fluctuation models could explain adequately the concentration dependences of the isotropic ν_1 line widths. However, based on the previous experimental investigations in neat liquid, it is likely that the isotropic ν_1 line width in solution is mainly due to the dephasing vibrational relaxation. Contrary to the

ν_1 case, the concentration fluctuation has been found to be a dominant line broadening mechanism for the ν_1 mode of acetonitrile in CCl₄ solution.

Acknowledgement. This work was supported by a grant from Korean Science and Engineering Foundation.

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Attempts on the Preparation of Lithium Trialkoxyborohydrides. Stability and Stereoselective Reduction of Cyclic Ketones

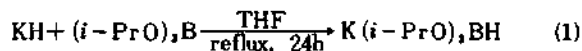
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The reaction of potassium trialkoxyborohydrides of varying steric requirements with lithium chloride in tetrahydrofuran(THF) was examined in detail to establish the generality of this synthesis of the corresponding lithium trialkoxyborohydrides. The metal ion exchange reaction between potassium triisopropoxyborohydride and lithium chloride in THF proceeded instantly at room temperature and the corresponding lithium salt was very stable toward disproportionation. However, for R = *s*-Bu, *t*-Bu and 2-methylcyclohexyl, with increasing steric requirement, the lithium derivatives were unstable and thus dissociated into (RO)BH₂ and (RO)₂B⁻. The stereoselectivity of lithium triisopropoxyborohydride(LIPBH) in the reduction of representative cyclic ketones was examined and compared with that of the potassium derivative.

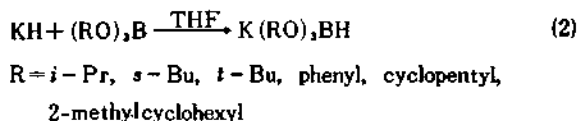
Introduction

On effort to develop the new selective reducing agents possessing unique reducing characteristics, the method for preparation of potassium triisopropoxyborohydride(KIPBH) from triisopropoxyborane and potassium hydride was recently developed (eq 1).¹ This reagent is very stable toward disproportionation at room temperature when stored over an excess amount of potassium hydride.



The systematic study on the reaction of KIPBH with representative organic compounds under standardized conditions revealed that the reagent is a very mild reducing agent which can reduce only aldehydes, ketones and disulfides, and shows an excellent degree of stereoselectivity in the reduc-

tion of cyclic ketones.² Accordingly, development of a general procedure for the syntheses of potassium trialkoxyborohydrides in tetrahydrofuran(THF) has been of considerable interest. Recently, a general synthesis of potassium trialkoxyborohydrides by treating the corresponding trialkoxyboranes with excess potassium hydride in THF was reported (eq 2).³



However, there has been no reports on the synthesis of stable lithium trialkoxyborohydrides. So far it has been known that the metal ion of borohydrides plays an important role in the reduction of organic compounds.⁴ Thus, it is expected that