

ionomer are shifted to lower frequencies (1116.9cm<sup>-1</sup>, 1080.2cm<sup>-1</sup>) in the ionomer blend.

We consider the possible local structure for multiplet in order to account for the observed two bands of asymmetric stretching carboxylate anion and the frequency shifts in the ionomer blend. We postulate that Figure 7 shows the possible structure for the ionomer blend. One carboxylate anion is connected with the two ionic pairs (octahedral structure). That is, one oxygen ion of the carboxylate ion constitutes an ionic multiplet with sulfonate ion (octahedral structure) and the other oxygen forms another ionic multiplet. By considering the possible local structure for the multiplet, it is concluded that the frequency shift is caused by the inductive effect of sulfonate ion, and that the multiplet structure is a reasonable one. But, as to the ionic aggregation, more works have to be done to justify our postulation.

### Conclusion

From this work, the following items are concluded. (1) Ionic interaction leads to considerable frequency shifts between the spectrum of the blend and the sum of the spectra of the pure ionomers. In view of these results, the barium cation binds the carboxylate anion and sulfonate anion intermolecularly and compatibilize the blend. (2) By considering the possible local structure of the blend, it is concluded that the frequency shift is caused by the inductive effect of the sulfonate ion, and that the local structure also well explains the spectral splittings. **Acknowledgements.** We acknowledge the Korea Research Center for Theoretical Physics and Chemistry for a partial support of this work. One of the authors, (J.I. Sohn) is indebted to the Korea Science and Engineering Foundation for the research grant awarded to him.

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## Study of Diffusion-controlled Processes. Solution of the Smoluchowski Equation with a Step Potential

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The Smoluchowski equation with a step potential is solved in one-dimensional case and three-dimensional case with spherical symmetry. Exact analytic expressions for the solution and the remaining probability are obtained in one-dimensional case for the reflecting boundary condition and the long time behavior of the remaining probability is compared with the earlier work. In three-dimensional case, only the long time behavior is evaluated. More general case with the radiation boundary condition is also investigated and the results are shown to approach correct limits of the reflecting boundary condition.

### Introduction

Recently, study of diffusion-controlled processes has been

very active in order to investigate various chemical phenomena occurring in solution<sup>1,2</sup>. The quantity of interest in these processes is the coordinate and time dependent probability distribution function which satisfies the diffusion equation.

The type of the diffusion equation most widely used at present is the Smoluchowski equation which incorporates the contribution of an external force field.<sup>3</sup>

The solution of the Smoluchowski equation subject to relevant boundary condition yields rich information on chemical reactions in solution. However, exact solutions of the Smoluchowski equation are known only for a limited number of cases<sup>4,5</sup> and it is the purpose of this work to obtain analytic solutions for a simple model potential in one-dimensional case and three-dimensional case with spherical symmetry. The kind of process treated here with these solutions is the desorption process which may be regarded as a chemical reaction at the surface. We assume that all the molecules are adsorbed on a surface in monolayer. The surfactant molecule initially adsorbed on the surface can escape, or desorb, from the surface because of the random forces from incessant collisions with the thermally agitated surroundings. To escape from the surface into the bulk liquid the surfactant molecule must escape from the potential well which reflects the effect of the external force field caused by the surroundings.

The form of the potential considered in this work is the step potential. The well depth and the well width of the potential may be related to the physical properties of the surfactant molecules as well as the nature of the surroundings.

Some time ago, Bilkadi, *et al.*<sup>6</sup> treated the same potential in one-dimensional case only and obtained the solution with the help of the Green function for a finite strip. However, their general solution is of the formal expression which is not amenable to an explicit evaluation. Only after introducing the long time approximation, they were able to get an explicit expression in this limit. By using the method of variation of parameters, we obtain exact analytic expressions for the solution and the remaining probability in one-dimensional case and the long time behavior of the remaining probability is compared with theirs. Our general solution can be evaluated explicitly and the general time-dependence can be investigated easily. In addition to the one-dimensional case we also consider here the three-dimensional case with spherical symmetry and the long time behavior of the remaining probability is investigated. In both cases the reflecting boundary condition is adopted and more general cases with the radiation boundary condition is discussed at the end.

### One-dimensional Case

The probability distribution function  $f(\vec{r}, t)$  is governed by the well-known Smoluchowski equation given by

$$\partial f(\vec{r}, t) / \partial t = D \vec{\nabla} \cdot (\vec{\nabla} f + \beta f \vec{\nabla} W) \quad (1)$$

where  $D$  is the diffusion constant,  $\beta$  is the Boltzmann factor, and  $W$  is the interaction potential. In one-dimensional case the above equation is simplified as

$$\partial f(x, t) / \partial t = D (\partial^2 f / \partial x^2 + \beta \partial (f \partial W / \partial x) / \partial x) \quad (2)$$

If we introduce the following variable transformations

$$\begin{aligned} \tau &= \beta D t \\ y &= \sqrt{\beta} x \\ U &= \beta W \end{aligned} \quad (3)$$

Eq.(2) can be rewritten as

$$\partial f / \partial \tau = f'' + U' f' + U'' f \quad (4)$$

where primes denote differentiations with respect to  $y$ . Further simplification can be made by introducing a reduced distribution function  $\rho(y, \tau)$  defined by

$$\rho = f \exp(U) \quad (5)$$

and Eq.(4) is reduced to

$$\partial \rho / \partial \tau = \rho'' - U' \rho' \quad (6)$$

Taking the Laplace transformation gives

$$z \bar{\rho} - \rho(0) = \bar{\rho}'' - U' \bar{\rho}' \quad (7)$$

where

$$\bar{\rho} \equiv \int_0^\infty d\tau \rho \exp(-z\tau)$$

It is assumed that the surfactant molecules are located at the surface ( $x=0$ ) initially. That is,

$$f(x, t=0) = \delta(x) \quad (8a)$$

or

$$\rho(y, \tau=0) = \sqrt{\beta} \delta(y) \exp(U) \quad (8b)$$

The interaction potential of interest here is a step function potential given by

$$W = \begin{cases} -Q, & x < x_0 \\ 0, & x > x_0 \end{cases} \quad (9a)$$

or

$$U = \begin{cases} -\beta Q, & y < y_0 \\ 0, & y > y_0 \end{cases} \quad (9b)$$

Due to the shape of the potential function, Eq.(7) is solved separately in two regions and the solutions are connected by the matching conditions at the boundary.

In the first region,  $x < x_0$  or  $y < y_0$ , Eq.(7) becomes

$$\bar{\rho}_1'' - z \bar{\rho}_1 = -\sqrt{\beta} \delta(y) \exp(U) \quad (10)$$

A general solution may be expressed in terms of the homogeneous solutions as follows:

$$\bar{\rho}_1 = A(y) \exp(-\sqrt{zy}) + B(y) \exp(\sqrt{zy}) \quad (11)$$

where  $A(y)$  and  $B(y)$  are the expansion coefficients to be determined by the standard technique and the result is

$$\begin{aligned} \bar{\rho}_1 = & [A_0 + \frac{1}{2} (\beta/z)^{1/2} \theta(y) \exp(-\beta Q)] \exp(-\sqrt{zy}) \\ & + [B_0 - \frac{1}{2} (\beta/z)^{1/2} \theta(y) \exp(-\beta Q)] \exp(\sqrt{zy}) \end{aligned} \quad (12)$$

where  $A_0$  and  $B_0$  are integration constants to be determined by the matching conditions and  $\theta(y)$  is the Heaviside step function. In the second region,  $x > x_0$  or  $y > y_0$ , Eq.(7) becomes

$$\bar{\rho}_2'' - z \bar{\rho}_2 = 0 \quad (13)$$

and the solution is given by

$$\tilde{\rho}_1 = C_0 \exp(-\sqrt{z}y) \quad (14)$$

In order to determine three constants we need to have three relations. Two of these are provided by the matching conditions at  $x = x_0$  (or  $y = y_0$ ). These are the continuity requirements for the probability distribution function and for the flux. That is,

$$\tilde{\rho}_1 = \tilde{\rho}_2 \text{ at } y = y_0 \quad (15)$$

and

$$\tilde{\rho}_1' = \tilde{\rho}_2' \exp(-\beta Q) \text{ at } y = y_0 \quad (16)$$

The flux continuity relation, Eq.(16), is obtained by integrating Eq.(7) over a thin strip about  $y = y_0$  and then taking the zero width limit.<sup>7</sup> Another relationship is given by the boundary condition at the surface. Since we are considering here the irreversible desorption process at the surface, we assume that the reflecting boundary condition is satisfied:

$$\tilde{\rho}_1' = 0 \text{ at } y = 0 \quad (17)$$

This boundary condition is a special case of the radiation boundary condition.<sup>8</sup>

The solution satisfying Eqs.(15) ~ (17) becomes

$$\tilde{f}_1(y, z) = (\beta/z)^{1/2} \{ \exp(-\sqrt{z}y) + \tanh(\beta Q/2) \exp(-\sqrt{z}(2y_0 - y)) \} \\ \times \{ 1 - \tanh(\beta Q/2) \exp(-2\sqrt{z}y_0) \}^{-1}, \quad (y < y_0) \quad (18a)$$

$$\tilde{f}_2(y, z) = (\beta/z)^{1/2} \{ 1 - \tanh(\beta Q/2) \} \exp(-\sqrt{z}y) \\ \times \{ 1 - \tanh(\beta Q/2) \exp(-2\sqrt{z}y_0) \}^{-1}, \quad (y > y_0) \quad (18b)$$

The inverse Laplace transformation can be performed analytically if the solution in Eq.(18) is expressed in the series expansion form as follows:

$$\tilde{f}_1(y, z) = (\beta/z)^{1/2} \sum_{n=0}^{\infty} \{ \exp(-\sqrt{z}y) + \tanh(\beta Q/2) \\ \times \exp(-\sqrt{z}(2y_0 - y)) \} [\tanh(\beta Q/2)]^n \exp(-2n\sqrt{z}y_0) \\ = (\beta/z)^{1/2} \exp(-\sqrt{z}y) + \sum_{n=1}^{\infty} (\beta/z)^{1/2} [\tanh(\beta Q/2)]^n \\ \times \{ \exp[-(2ny_0 - y)\sqrt{z}] + \exp[-(2ny_0 + y)\sqrt{z}] \} \quad (19a)$$

$$\tilde{f}_2(y, z) = (\beta/z)^{1/2} \{ 1 - \tanh(\beta Q/2) \} \\ \times \sum_{n=0}^{\infty} [\tanh(\beta Q/2)]^n \exp[-(2ny_0 + y)\sqrt{z}] \quad (19b)$$

Then, the inverse Laplace transformation gives

$$f_1(y, \tau) = (\beta/\pi\tau)^{1/2} \exp(-y^2/4\tau) \\ + (\beta/\pi\tau)^{1/2} \sum_{n=1}^{\infty} [\tanh(\beta Q/2)]^n \\ \times \{ \exp[-(2ny_0 - y)^2/4\tau] + \exp[-(2ny_0 + y)^2/4\tau] \} \quad (20a)$$

$$f_2(y, \tau) = (\beta/\pi\tau)^{1/2} \{ 1 - \tanh(\beta Q/2) \} \\ \times \sum_{n=0}^{\infty} [\tanh(\beta Q/2)]^n \exp[-(2ny_0 + y)^2/4\tau] \quad (20b)$$

The remaining probability,  $P(t)$ , defined near the surface region as

$$P(t) \equiv \int_0^{x_0} f_1(x, t) dx \quad (21)$$

can be easily evaluated to become

$$P(t) = \operatorname{erf}(x_0/2\sqrt{Dt}) + \sum_{n=1}^{\infty} [\tanh(\beta Q/2)]^n \\ \times \{ \operatorname{erf}[(2n+1)x_0/2\sqrt{Dt}] - \operatorname{erf}[(2n-1)x_0/2\sqrt{Dt}] \} \\ = [1 - \tanh(\beta Q/2)] \sum_{n=0}^{\infty} [\tanh(\beta Q/2)]^n \\ \times \operatorname{erf}[(2n+1)x_0/2\sqrt{Dt}] \quad (22)$$

where  $\operatorname{erf}(x)$  is the error function. As it stands, the above expression for the remaining probability is not suitable for investigating the long time behavior. If we notice that the flux through  $x = x_0$  is given by

$$J(x_0, t) \equiv -\partial f_2/\partial x|_{x=x_0} \quad (23)$$

the remaining probability can be expressed in terms of the flux as

$$\tilde{P}(z) = (1 - \tilde{J}(x_0, z)/\beta)/z \quad (24)$$

with

$$\tilde{J}(x_0, z) = \beta [1 - \tanh(\beta Q/2)] \exp(-x_0 \sqrt{\beta z}) \\ \times [1 - \tanh(\beta Q/2) \exp(-2x_0 \sqrt{\beta z})]^{-1}$$

In the long time limit of  $x_0 \sqrt{\beta z} \ll 1$ , Eq.(24) can be simplified as

$$\tilde{P}(z) \approx \{ 1 - [1 + x_0 \sqrt{\beta z} \exp(\beta Q)]^{-1} \} / z \quad (25)$$

which can be inverted analytically to give

$$P(t) \approx \exp[Dt/x_0^2 \exp(2\beta Q)] \operatorname{erfc}(\sqrt{Dt}/x_0 \exp(\beta Q)) \\ \xrightarrow{t \rightarrow \infty} (x_0^2/\pi Dt)^{1/2} \exp(\beta Q) \quad (26)$$

where  $\operatorname{erfc}(x)$  is the complementary error function. These are the same expressions obtained earlier by Bilkadi, *et al.*<sup>6</sup> [Eqs.(2.20) and (2.22) of their paper.]

### Three-dimensional Case

The Smoluchowski equation in three-dimensional case with spherical symmetry is given by

$$\partial f(r, t)/\partial t = r^{-2} \frac{\partial}{\partial r} \{ r^2 D [\partial/\partial r + \beta \partial W/\partial r] \} f(r, t) \quad (27)$$

Again, we introduce the following variable transformations,

$$\tau = \beta Dt \\ q = \sqrt{\beta} r \\ U = \beta W \quad (28)$$

and a reduced distribution function  $\rho(q, \tau)$  defined by

$$\rho = q \exp(U/2) f \quad (29)$$

The interaction potential is given by

$$U = \begin{cases} -\beta Q, & a < q < q_0 \\ 0, & q > q_0 \end{cases} \quad (30)$$

where  $\sigma = a/\sqrt{\beta}$  is the radius of a sphere located at the origin and the desorption process occurs from its surface. Then, Eq.(27) becomes

$$\partial \rho / \partial \tau = \rho'' - (U'/4 - U''/2 - U'/q) \rho \quad (31)$$

If we take the Laplace transformation by using the following initial condition

$$f(r, 0) = \delta(r - \sigma) / 4\pi\sigma^2$$

or

$$\rho(q, 0) = \beta^{3/2} \exp(U/2) \delta(q - a) / 4\pi a \quad (32)$$

and the interaction potential given by Eq.(30), the Smoluchowski equation can be reduced to

$$\begin{aligned} \tilde{\rho}_1'' - z \tilde{\rho}_1' &= -\beta^{3/2} \exp(U/2) \delta(q - a) / 4\pi a, & a < q < q_0 \\ \tilde{\rho}_1'' - z \tilde{\rho}_1' &= 0, & q > q_0 \end{aligned} \quad (33)$$

The continuity requirements for the probability distribution function and for the flux become

$$\tilde{\rho}_1 = \tilde{\rho}_2 \exp(\beta Q/2) \quad \text{at } q = q_0 \quad (34)$$

$$\tilde{\rho}_1' - \tilde{\rho}_1/q = (\tilde{\rho}_2' - \tilde{\rho}_2/q) \exp(-\beta Q/2) \quad \text{at } q = q_0 \quad (35)$$

and the reflecting boundary condition is given by

$$\tilde{\rho}_1' - \tilde{\rho}_1/q = 0 \quad \text{at } q = a \quad (36)$$

The solution of Eq.(33) satisfying Eqs.(34) ~ (36) can be obtained as

$$\begin{aligned} \tilde{\rho}_1(q, z) &= (\beta^{3/2}/4\pi) \{ (\sqrt{z}q_0 \coth(\beta Q/2) - 1) \exp[-\sqrt{z}(q - q_0)] \\ &\quad + (\sqrt{z}q_0 + 1) \exp[\sqrt{z}(q - q_0)] \} \exp(-\beta Q/2) \\ &\quad \times \{ (\sqrt{z}a + 1) [\sqrt{z}q_0 \coth(\beta Q/2) - 1] \exp[\sqrt{z}(q_0 - a)] \\ &\quad - (\sqrt{z}a - 1) (\sqrt{z}q_0 + 1) \exp[-\sqrt{z}(q_0 - a)] \}^{-1}, \end{aligned} \quad (37)$$

( $a < q < q_0$ )

$$\begin{aligned} \tilde{\rho}_2(q, z) &= (\beta^{3/2}/4\pi) \sqrt{z}q_0 [\coth(\beta Q/2) + 1] \exp(-\beta Q) \\ &\quad \times \exp(-\sqrt{z}(q - q_0)) \\ &\quad \times \{ (\sqrt{z}a + 1) [\sqrt{z}q_0 \coth(\beta Q/2) - 1] \exp[\sqrt{z}(q_0 - a)] \\ &\quad - (\sqrt{z}a - 1) (\sqrt{z}q_0 + 1) \exp[-\sqrt{z}(q_0 - a)] \}^{-1}, \end{aligned} \quad (38)$$

( $q > q_0$ )

The remaining probability becomes

$$\begin{aligned} \tilde{P}(z) &= \beta^{-3/2} \int_a^{q_0} \tilde{f}_1(q, z) 4\pi q^2 dq \\ &= z^{-1} \{ 1 - \sqrt{z}q_0 (\sqrt{z}q_0 + 1) [\coth(\beta Q/2) - 1] \\ &\quad \times \{ (\sqrt{z}a + 1) [\sqrt{z}q_0 \coth(\beta Q/2) - 1] \exp[\sqrt{z}(q_0 - a)] \\ &\quad - (\sqrt{z}a - 1) (\sqrt{z}q_0 + 1) \exp[-\sqrt{z}(q_0 - a)] \}^{-1} \} \end{aligned} \quad (39)$$

In the long time limit (small  $z$ ), the above expression can be simplified as

$$\tilde{P}(z) \approx a(q_0 - a) \exp(\beta Q) / (\sqrt{z}q_0 + 1) \quad (40)$$

which may be inverted analytically to give

$$P(\tau) \approx a(1 - a/q_0) \exp(\beta Q) \times [(\pi\tau)^{-1/2} - q_0^{-1} \exp(\tau/q_0^2) \operatorname{erfc}(\sqrt{\tau}/q_0)] \quad (41)$$

$$\tau \rightarrow \infty \rightarrow a(1 - a/q_0) q_0^2 \exp(\beta Q) (4\pi\tau^3)^{-1/2} \quad (42)$$

## Discussion

We have solved the Smoluchowski equation for a step potential in one- and three-dimensional cases. One-dimensional case was treated earlier by Bilkadi, *et al.*<sup>8</sup> via different procedure. Their expressions for the solution and the remaining probability are rather involved and only the long time behavior of the remaining probability can be shown explicitly. In the present work we have obtained explicit analytic expressions for the solution [Eq.(20)] and the remaining probability [Eq.(22)] as well as the long time behavior [Eq.(26)] of the remaining probability which is the same expression obtained by Bilkadi, *et al.*

Three-dimensional case with spherical symmetry is considered here and the long time behavior of the remaining probability has been obtained in a simple expression. In both one- and three-dimensional cases the long time behaviors of the remaining probabilities obey the well known  $t^{-d/2}$  behavior where  $d$  denotes the dimensionality.

The boundary condition adopted here is the reflecting boundary condition which is a limiting case of the radiation boundary condition given by<sup>8</sup>

$$-\hat{n} \cdot D(\vec{r} + \beta \vec{r} W) f(\vec{r}, t) = h f(\vec{r}, t) \quad \text{at } r = \sigma \quad (43)$$

where the parameter  $h$  corresponds to the intrinsic rate constant and  $\hat{n}$  is the unit vector outward normal to the surface. The reflecting boundary condition is a particular case of  $h \rightarrow 0$  and the absorption or Smoluchowski boundary condition is the case of  $h \rightarrow \infty$ . If we adopt the radiation boundary condition, the remaining probability in one-dimensional case becomes, following the similar procedure as before,

$$\begin{aligned} P(\tau) &= 1 - (1 - 1/\gamma) \sum_{n=0}^{\infty} \gamma^{-n} F_n(\tau) \\ &\quad * \sum_{k=0}^n n! (-2h)^k [k!(n-k)!]^{-1} H_k(\tau) \end{aligned} \quad (44)$$

where

$$\gamma \equiv \coth(\beta Q/2) \quad (45)$$

$$A(\tau) * B(\tau) \equiv \int_0^\tau A(t) B(\tau - t) dt \quad (46)$$

$$F_n(\tau) \equiv \exp\{(2n+1)h\sqrt{\beta}x_0 + h^2\tau\} \times \operatorname{erfc}\left[\left(n + \frac{1}{2}\right)\sqrt{\beta}x_0\tau^{-1/2} + h\tau^{1/2}\right] \quad (47)$$

$$H_k(\tau) \equiv (2/\pi)^{1/2} k(2\tau)^{-1+k/2} \exp(h^2\tau/2) D_{k-1}(h\sqrt{2\tau}) \quad (48)$$

and  $D_k$  represents the parabolic cylinder function.<sup>9</sup> If we let

$h \rightarrow 0$ , 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

$$P(\tau) = 1 - [1 - h\sqrt{\beta x_0} (h\sqrt{\beta x_0} + 1)^{-1} + h\sqrt{\beta x_0} \exp(2\beta Q) \times (h\sqrt{\beta x_0} + 1)^{-2}] \times \exp(\tau h^2 \exp(2\beta Q) / (h\sqrt{\beta x_0} + 1)^2) \times \text{erfc}[\tau^{1/2} h \exp(\beta Q) / (h\sqrt{\beta x_0} + 1)] + \sqrt{\beta x_0} \exp(\beta Q) (h\sqrt{\beta x_0} + 1)^{-1} (\pi \tau)^{-1/2} \quad (49)$$

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.

**Acknowledgement.** This work was supported by a grant from

the Korea Science and Engineering Foundation.

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## Concentration Dependence of the $\nu_1$ Isotropic Raman Band of Nitromethane in Chloroform-d, Pyridine-d<sub>5</sub>, 1,3,5-Trifluorobenzene, and Hexafluorobenzene

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Concentration dependences of the isotropic Raman band width and the peak position for the  $\nu_1$  (C-H stretching) mode of nitromethane in chloroform-d, pyridine-d<sub>5</sub>, 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  $\text{CH}_3\text{NO}_2/\text{C}_6\text{F}_6$  solution, an abnormally small value (2) of  $N$  indicates strong intermolecular interaction.

## Introduction

Vibrational relaxation in liquid has attracted much attention recently.<sup>1-11</sup> 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.<sup>5,6</sup> 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<sup>12</sup> 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,<sup>7,8</sup> pressure,<sup>7,8</sup> and concentration<sup>1,9</sup> dependences of the isotropic Raman band width provide useful information on the fun-

damental nature of the process. Several mechanisms such as the phase relaxation,<sup>11</sup> the resonant energy transfer,<sup>13</sup> and the energy relaxation<sup>4</sup> 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,<sup>14</sup> 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,<sup>15</sup> and its validity examined experimentally for various binary liquid systems.<sup>9,10,16</sup>

In the present work, the concentration dependences of the isotropic Raman band width of the  $\nu_1$  (C-H stretching) mode of nitromethane in  $\text{CDCl}_3$ , pyridine-d<sub>5</sub>, 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