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Field-Modulating Modes of Solvents for Describing Electrostatic Intermolecular Vibrational Interactions in Solution

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A theoretical method is developed for examining the intermolecular vibrational motions that are responsible for modulating the external electric field at the position of the solute in solution. The derivation is done in the context of the instantaneous normal mode theory by using an algebraic property of the interaction formula, in the same way as in the intensity-carrying mode theory of intramolecular vibrations developed in our previous studies. The vibrational motions derived by the present method are called field-modulating modes (FMMs). These modes play an essential role in electrostatic intermolecular vibrational interactions in solution. As an example of application of the present method, the case of an acetonitrile solution of the nitrate ion (NO_3^-) is studied. Various characteristics of the FMMs, which are important for vibrational polarization of the solute, are examined in detail. The relation of the present picture to vibrational relaxation theories is also discussed.

1. Introduction

Molecules in polar solutions are affected more or less by intermolecular electrostatic interactions. In addition to the (usual) electronic polarization, molecules are polarized to some extent due to distortion of molecular structures. The so-called vibrational polarizability describes such polarization. Recent studies on the vibrational spectra of some molecular ions (cyanine dyes, I_3^-, and NO_3^-) in solution[1−8] have shown that the effects of the structural distortion are clearly seen in those vibrational spectra.

The formula for the vibrational polarizability may be derived as follows. Within the harmonic approximation and to the first order in the external electric field, the potential energy (V) of the solute in a polar solution is expressed as[9]

$$V = \frac{1}{2}\sum_p \omega_p^2 q_p^2 - \sum_k \left[\mu_k^{(0)} + \sum_p \frac{\partial \mu_k}{\partial q_p} q_p\right] E_k \qquad (1)$$

where q_p is the pth (mass-weighted) intramolecular normal mode of the solute, ω_p is its vibrational angular frequency, μ_k is the molecular dipole moment ($\mu_k^{(0)}$ is the value at $q_p = 0$), and E_k is the external electric field. Because of the existence of the second part in the parentheses in eq 1, the position of the potential energy minimum is displaced as

$$\delta q_p = \frac{1}{\omega_p^2}\sum_k \frac{\partial \mu_k}{\partial q_p} E_k \qquad (2)$$

The molecule is polarized according to $\delta\mu_i = \Sigma_p(\partial\mu_i/\partial q_p)\delta q_p$. The vibrational polarizability is therefore expressed as[10,11]

$$\alpha_{ik}^{(v)} = \sum_p \frac{1}{\omega_p^2}\frac{\partial \mu_i}{\partial q_p}\frac{\partial \mu_k}{\partial q_p} \qquad (3)$$

It is clear from the above equations that dipole derivatives ($\partial\mu_k/\partial q_p$) play an important role in describing electrostatic intermolecular vibrational interactions. In our previous studies,[4−6,12−16] the vibrational motions responsible for generating dipole derivatives and other electrical property derivatives (polarizability derivatives and first hyperpolarizability derivatives) have been analyzed for molecules with conjugated π-electron systems. As a method of extracting the vibrational degrees of freedom responsible for generating the electrical property derivatives, the theory of intensity-carrying modes (ICMs) has been developed.[14,16] By using this theory, the nature of the vibrational motions generating electrical property derivatives and their relation to the electronic structure have been clarified.

In relation to the above problem, another important type of vibrational motions that should be clarified are the intermolecular vibrations in solution that give rise to significant changes in the electric field E_k. In the instantaneous normal mode (INM) picture[17,18] and to the first order in E_k, the potential energy of the solution may be expanded as

$$V = \frac{1}{2}\sum_p \omega_p^2 q_p^2 + \frac{1}{2}\sum_r [\Omega_r{}^2 Q_r{}^2 - 2F_r Q_r] - \sum_k \left[\mu_k^{(0)} + \sum_p \frac{\partial \mu_k}{\partial q_p} q_p\right]\left[E_k^{(0)} + \sum_r \frac{\partial E_k}{\partial Q_r} Q_r\right] \qquad (4)$$

where Q_r is the rth (mass-weighted) intermolecular normal mode of the solution, Ω_r is its vibrational angular frequency, F_r is the force along this normal mode at the instantaneous configuration of liquid structure ($Q_r = 0$), and $E_k^{(0)}$ is the external electric field (at the position where the solute molecule is located) at $Q_r = 0$.[19] The modes with large values of $\partial E_k/\partial Q_r$ induce large changes in E_k. It is therefore important to clarify the nature of such modes to understand the electrostatic intermolecular vibrational interactions operating in solution.

One problem that should be considered at this point is that there are many intermolecular normal modes Q_r (too many to

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examine the nature of each), and a large number of them are expected to have large values of $\partial E_k/\partial Q_r$. This problem is related in part to the delocalized nature of the intermolecular normal modes. It is therefore preferable to develop a method for extracting the intermolecular vibrational motions (which may be different from *normal* modes) that are really responsible for the changes in E_k. By using such a method, the nature of the electrostatic intermolecular vibrational interactions obscured in the normal mode picture may be elucidated.

In the present study, we develop such a method by using an algebraic property of the interaction formula, in a way similar to the development of the ICM theory[14,16] of intramolecular vibrations. As an example of application of the method, we show the results of the calculations carried out for an acetonitrile solution of the nitrate ion (NO_3^-). The relation of the present picture to vibrational relaxation theories is also discussed.

2. Theory

In our previous studies,[14,16] the vibrational motions responsible for generating dipole derivatives have been derived by using an algebraic property[20] of the expansion of $\partial\mu_k/\partial q_p$. The vibrational modes thus obtained (in general not equal to intramolecular normal modes) are called infrared (IR) ICMs, since the IR intensity of a given mode is proportional to the square of its dipole derivative. By looking at eq 4 shown above, it is noticed that (μ_k, q_p) and (E_k, Q_r) appear in a symmetric way. It is therefore expected that the vibrational motions inducing large changes in E_k may be obtained in the same way as in the derivation of the IR ICMs. We call such vibrational motions field-modulating modes (FMMs), since they modulate electric field at the position where the solute molecule is located.

For the purpose of deriving FMMs, we take the set of mass-weighted translational and librational (rotational) coordinates of the molecules in solution, denoted by $R_{l,m}$ ($1 \le l \le 3$ for translations and $4 \le l \le 6$ for librations,[21] m denoting the molecule number). $\partial E_k/\partial Q_r$ may be expanded by $\{R_{l,m}\}_{1\le l\le 6, 1\le m\le N}$ as

$$\frac{\partial E_k}{\partial Q_r} = \sum_{m=1}^{N}\sum_{l=1}^{6}\frac{\partial E_k}{\partial R_{l,m}}\frac{\partial R_{l,m}}{\partial Q_r} \tag{5}$$

where N is the number of molecules.

The summation over l and m in eq 5 may be regarded as a scalar product of two $6N$-dimensional vectors $\boldsymbol{e}_k$ and $\boldsymbol{q}_r$, defined as $(\boldsymbol{e}_k)_u = \partial E_k/\partial R_{l,m}$ and $(\boldsymbol{q}_r)_u = \partial R_{l,m}/\partial Q_r$ with $u = 6m + l$. Since $\{R_{l,m}\}_{1\le l\le 6, 1\le m\le N}$ is a set of mass-weighted coordinates, the vectors $\boldsymbol{q}_r$ are normalized and orthogonal to each other by definition. We consider an orthogonal transformation from $\{\boldsymbol{q}_r\}_{1\le r\le n}$ to another set of $6N$-dimensional vectors $\{\boldsymbol{s}_t\}_{1\le t\le n}$. (We denote the number of normal modes included in the derivation of FMMs by n.) Since $\{\boldsymbol{e}_k\}_{1\le k\le 3}$ generates a three-dimensional subspace in the $6N$-dimensional space of intermolecular vibrational motions, we can take $\{\boldsymbol{s}_t\}_{1\le t\le n}$ such that ${}^t\boldsymbol{e}_k\,\boldsymbol{s}_t = 0$ ($1 \le k \le 3$; $4 \le t \le n$) is satisfied. We then define a set of vibrational coordinates S_t as $(\boldsymbol{s}_t)_u = \partial R_{l,m}/\partial S_t$ (with $u = 6m + l$). Since $\partial E_k/\partial S_t = 0$ for $4 \le t \le n$ by definition, and since $\{S_t\}_{1\le t\le n}$ is related to $\{Q_r\}_{1\le r\le n}$ by an orthogonal transformation, we may regard $\{S_t\}_{1\le t\le 3}$ as representing the intermolecular vibrational modes responsible for modulating electric field at the position where the solute molecule is located, i.e., the FMMs.

To obtain the explicit forms of the FMMs, we diagonalize an $n \times n$ matrix $\boldsymbol{M}$ defined as

$$M_{rs} = \sum_{k=1}^{3}\frac{\partial E_k}{\partial Q_r}\frac{\partial E_k}{\partial Q_s} \tag{6}$$

It is easily derived from the algebraic property of the vectors explained in the last paragraph that there are at most three nonzero eigenvalues for $\boldsymbol{M}$. The rest of the eigenvalues are zero. The eigenvectors for the nonzero eigenvalues represent the FMMs. Each nonzero eigenvalue is equal to the square of the electric field modulated by the corresponding FMM.

The above derivation shows that it is possible to represent the intermolecular vibrational motions that modulate electric field at the position of the solute only by three mutually orthogonal vibrational modes for a given configuration of liquid structure. Although the derivation is done in the context of the INM theory, the three vibrational modes thus obtained (the FMMs) are not equal in general to any normal modes. The dimensionality of the vector space of FMMs comes from the fact that $\{\boldsymbol{e}_k\}_{1\le k\le 3}$ generates a three-dimensional space, or in other words, there are three independent elements of $\partial E_k/\partial R_{l,m}$ for each $R_{l,m}$. As a result, if we confine ourselves to only two components of the electric field (e.g., the electric field along the x and y directions of the nitrate ion in the example shown below), we obtain only two FMMs.

As in the derivation of the IR ICMs, any orthogonal set of vibrational coordinates may be taken instead of $\{Q_r\}_{1\le r\le n}$ to derive FMMs. For example, we may include only the motions of the solvent molecules in the derivation of the FMMs and consider the (translational and librational) motions of the solute molecule separately. We take this option in most part of the example shown below.

3. Example of Application: Acetonitrile Solution of the Nitrate Ion

In this section, we show the results of the calculations carried out for an acetonitrile solution of the nitrate ion (NO_3^-). It has been shown in a previous study[7] that this ion is distorted in polar solutions along the NO asymmetric stretching modes, which are strongly IR active and hence give rise to large vibrational polarizabilities. We examine the extent to which this ion is distorted due to intermolecular electrostatic interactions and the nature of the intermolecular vibrational motions responsible for those interactions by using the theoretical picture developed in the present study.

A. Computational Procedure. The liquid structures of the solution were calculated by the molecular dynamics (MD) simulation method. The six-site model of acetonitrile developed by Böhm et al.,[22] which involves electrostatic interactions between fixed partial charges and Lennard-Jones (12−6) interactions, was used. For the nitrate ion, the four-site (electrostatic and exp-6) model developed by Signorini et al.[23] was used after fitting its exp-6 part by the 12−6 form ($\epsilon = 0.338$ kJ mol^{-1} and $\sigma = 3.09$ Å for N; $\epsilon = 0.613$ kJ mol^{-1} and $\sigma = 2.80$ Å for O). Only intermolecular degrees of freedom were considered in the MD simulations. Four-dimensional vectors (quaternions) were used to represent molecular orientations in solving the equations of motion,[24,25] in combination with the leapfrog integration method.[25] 215 molecules of acetonitrile and 1 nitrate ion were contained in a cubic cell. The periodic boundary condition was employed. The side of the cubic cell was fixed to 26.7 Å, taking into account the molecular volume of acetonitrile (87.8 Å^3).[26] The temperature was kept at 298 K by adjusting the total kinetic energy every 200 fs. The time step was set to 2 fs. The system was equilibrated for more than 320 ps, after which a production run of 1 ns was carried out.

From the MD simulations, 50 configurations of liquid structure were taken to calculate INMs. Force constant matrices (F matrices) were constructed in the mass-weighted intermolecular vibrational coordinate system, $\{R_{l,m}\}_{1\le l\le 6,1\le m\le N}$ defined in section 2. The molecular axes were defined so that the x and y axes were the degenerate axes of the C_{3v} (for acetonitrile) or D_{3h} (for the nitrate ion) point group. INMs were obtained by diagonalization of the F matrices thus constructed. For each configuration of liquid structure, there were three modes with zero frequencies that correspond to overall translation of the system. The other $6N-3$ modes had nonzero (real or imaginary) frequencies.

The electric field at the center of the solute molecule due to the partial charges on solvent molecules is expressed as

$$\boldsymbol{E} = -\sum_{j,m} q_{j,m}\frac{\mathbf{r}_{j,m}}{r_{j,m}^3} \tag{7}$$

where $q_{j,m}$ is the partial charge of the jth atom in the mth solvent molecule, $\mathbf{r}_{j,m}$ denotes the position of this atom relative to the center of the solute molecule, and $r_{j,m}$ is the length of this vector. We therefore have

$$\frac{\partial \boldsymbol{E}}{\partial \mathbf{r}_{j,m}} = -q_{j,m}\left[\frac{\boldsymbol{I}}{r_{j,m}^3} - \frac{3}{r_{j,m}^5}\mathbf{r}_{j,m}\,\mathbf{r}_{j,m}\right] \tag{8}$$

where $\boldsymbol{I}$ is a 3 × 3 unit tensor. The coordinate system used for this tensor was then transformed to obtain $\partial E_k/\partial R_{l,m}$ that appears in eq 5. The FMMs were then calculated by using this tensor as shown in section 2.

All the above calculations were carried out with our original programs on a Fujitsu VPP5000 supercomputer at the Research Center for Computational Science of the Okazaki National Research Institutes.

To estimate the extent to which the nitrate ion is distorted due to intermolecular electrostatic interactions, it is also necessary to calculate its vibrational polarization properties. The vibrational frequencies and the dipole derivatives for the intramolecular normal modes of this ion were calculated at the third-order Møller−Plesset perturbation[27] (MP3) level of the ab initio molecular orbital (MO) theory with the 6-31+G(2d,p) basis set.[28−30] The Gaussian 98 program[31] was used for the ab initio MO calculations on an NEC SX-5 supercomputer at the Research Center for Computational Science of the Okazaki National Research Institutes. From the quantities thus obtained, the vibrational polarization properties were calculated by using our original programs on a Compaq XP 1000 workstation in our laboratory.

B. Properties of the FMMs. An example of the vibrational patterns of FMMs is shown in Figure 1. Here we adopt a "covariant" representation of the vibrational patterns, expressed as $\sqrt{I_{l,m}}\,\partial R_{l,m}/\partial S_t$, where $I_{l,m}$ is the total mass of the molecule (for translations) or the moment of inertia (for librations). Figure 1 shows the atomic motions in this representation.

The rational for adopting such a representation is as follows. $\partial Q_r/\partial S_t$ is expanded by $\{R_{l,m}\}_{1\le l\le 6,1\le m\le N}$ as

$$\frac{\partial Q_r}{\partial S_t} = \sum_{m=1}^{N}\sum_{l=1}^{6}\frac{\partial Q_r}{\partial R_{l,m}}\frac{\partial R_{l,m}}{\partial S_t} \tag{9}$$

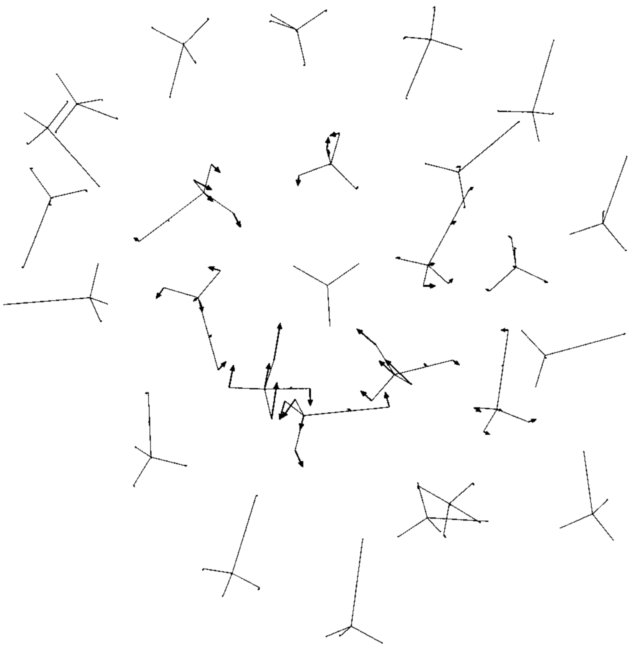

Figure 1. An example of the vibrational patterns of FMMs in a covariant representation (see text) calculated for an acetonitrile solution of the nitrate ion. The nitrate ion is located at the center. The atomic motions are shown by arrows.

Since $\{Q_r\}_{1\le r\le 6N}$ and $\{R_{l,m}\}_{1\le l\le 6,1\le m\le N}$ are related by an orthogonal transformation, we have

$$\frac{\partial Q_r}{\partial S_t} = \sum_{m=1}^{N}\sum_{l=1}^{6}\frac{\partial R_{l,m}}{\partial Q_r}\frac{\partial R_{l,m}}{\partial S_t} \tag{10}$$

Since $\{R_{l,m}\}_{1\le l\le 6,1\le m\le N}$ is a set of mass-weighted coordinates, a natural contravariant representation of the vibrational patterns of normal modes should be in the form $(\partial R_{l,m}/\partial Q_r) \times (1/\sqrt{I_{l,m}})$. The corresponding covariant representation of the tensor $\partial R_{l,m}/\partial S_t$ is therefore in the form $\sqrt{I_{l,m}}\partial R_{l,m}/\partial S_t$. It is necessary to introduce this representation because $I_{l,m}$ for the libration around the z axis of acetonitrile is much smaller than the other types of motions, and its contribution to the FMMs will be unnecessarily exaggerated without the factor of $\sqrt{I_{l,m}}$.

It is seen in Figure 1 that the amplitudes of the motions are large only for the solvent molecules just around the solute molecule (located at the center). This localized nature of the vibration holds also for the other two FMMs. This result demonstrates that the motions of the molecules in the first solvation shell are primarily responsible for modulation of the electric field at the position of the solute. The motions of the solvent molecules outside this region have only small effects on the field modulation.

The localized nature of the FMMs is more clearly seen by plotting the contribution of the molecular motions to the FMMs as a function of the solute−solvent intermolecular distance. The function defined as

$$C_l(r) = \left\langle \sum_{k,t=1}^{3}\sum_{m=1}^{N}\left[\frac{\partial E_k}{\partial S_t}\right]^2\left[\frac{\partial S_t}{\partial R_{l,m}}\right]^2 I_{l,m}\,\delta(r-r_m)\right\rangle \tag{11}$$

represents the contribution of each type of motions to the field modulation, where r_m is the distance between the solute molecule and the mth solvent molecule, and $\langle\ldots\rangle$ denotes statistical

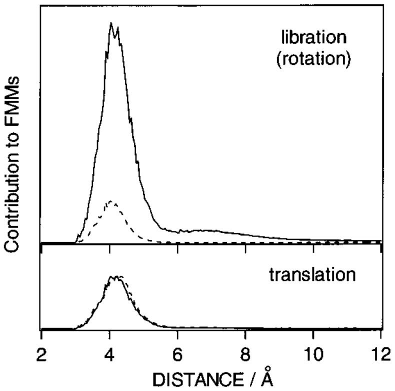

Figure 2. Contribution of molecular translations and librations to the FMMs as a function of the solute−solvent intermolecular distance [$C_l(r)$ defined in eq 11]: (solid lines) translations along and librations around the *x* and *y* axes of acetonitrile molecules; (broken lines) translations along and librations around the *z* axis.

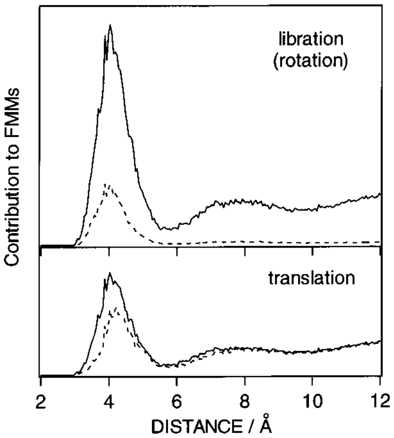

Figure 3. Contribution of molecular translations and librations to normal modes, with the weights of their effects on field modulation, as a function of the solute−solvent intermolecular distance [$D_l(r)$ defined in eq 12]. See also the caption for Figure 2.

average. The result is shown in Figure 2. The following points are noteworthy. (1) Most of the field modulation originates from the motions of the solvent molecules within about 5 Å from the solute. The localized nature of the FMMs seen in Figure 1 is not peculiar to a few configurations of liquid structure but is common to most (or all) configurations. (2) The contribution to the FMMs is especially large for the librations around the *x* and *y* axes. This result is reasonable because the molecular dipole moment changes its direction when the molecule rotates around its *x* or *y* axis. A tail of the function $C_l(r)$ in the $r > 6$ Å region is noticeable only for this type of motion, indicating that the contribution to the FMMs is slightly longer-ranged than the other types of motions. (3) Since we are using a six-site (not three-site) model for acetonitrile, in which hydrogen atoms are treated explicitly, the libration around the *z* axis also contributes to the FMMs. However, the contribution is short-ranged because the molecular dipole moment does not change its direction or location by this type of motion.

Since intermolecular normal modes are delocalized, the localized nature of the contribution to the field modulation is obscured in the normal mode picture. To clarify this point, we calculate another function defined as

$$D_l(r) = \left\langle \sum_{k,t=1}^{3} \sum_{m=1}^{N} \sum_{s=1}^{n} \left[\frac{\partial E_k}{\partial S_t}\right]^2 \left[\frac{\partial S_t}{\partial Q_s}\right]^2 \left[\frac{\partial Q_s}{\partial R_{l,m}}\right]^2 I_{l,m}\, \delta(r-r_m) \right\rangle \tag{12}$$

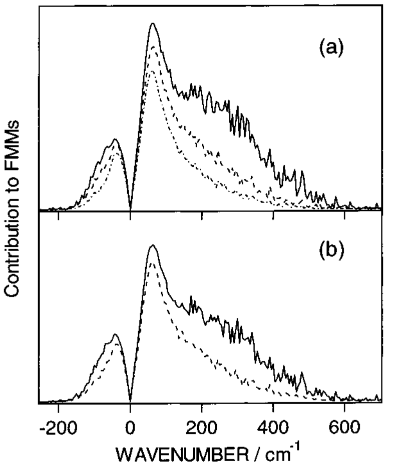

Figure 4. (a) Frequency distributions of the normal modes involved in the expansion of the FMMs [$G_t(\Omega)$ defined in eq 13] in the case where all the three components of the modulated field are taken into account in the calculations of FMMs: (solid line) $t = 1$; (broken line) $t = 2$; (dot−dashed line) $t = 3$. (b) Those in the case where only the components of the modulated field in the *x* and *y* directions of the nitrate ion are taken into account in the calculations of FMMs.

This quantity represents the contribution of each type of molecular motion to normal modes with the weights of their effects on field modulation. The result is shown in Figure 3. It is clearly seen that, except for $l = 6$ (the libration around the *z* axis), significant values of $D_l(r)$ are calculated over the whole range of intermolecular distances. This result demonstrates that the normal modes with large effects on field modulation are delocalized to the extent that they include molecular motions in the $r > 10$ Å region. It may be said, therefore, that the normal mode picture does not provide sufficiently correct information on the intermolecular vibrational motions that are really responsible for field modulation.

The difference in the functional forms of $C_l(r)$ and $D_l(r)$ shown above suggests that the FMMs are expressed as linear combinations of many (not only a few) normal modes. To confirm this point, the frequency distributions of the normal modes involved in the expansion of FMMs, defined as

$$G_t(\Omega) = \left\langle \sum_{k=1}^{3} \sum_{s=1}^{n} \left[\frac{\partial E_k}{\partial S_t}\right]^2 \left[\frac{\partial S_t}{\partial Q_s}\right]^2 \delta(\Omega - \Omega_s) \right\rangle \tag{13}$$

are calculated. Here, the FMMs with the largest, medium, and smallest values of $\Sigma_k(\partial E_k/\partial S_t)^2$ calculated for each configuration of liquid structure are denoted by S_1, S_2, and S_3, respectively. The result is shown in Figure 4a. As is usually done, imaginary frequency modes are plotted on the negative frequency side. It is seen that all the FMMs are made of linear combinations of normal modes in a wide frequency range.[32] The same is true if we include only the electric field in the *x* and *y* directions of the solute, as shown in Figure 4b.

As references to the functions $G_t(\Omega)$ shown above, the densities of states for the six types of motions ($1 \leq l \leq 6$), defined as

$$H_l(\Omega) = \left\langle \sum_{m=1}^{N} \sum_{s=1}^{n} \left[\frac{\partial R_{l,m}}{\partial Q_s}\right]^2 \delta(\Omega - \Omega_s) \right\rangle \tag{14}$$

are shown in Figure 5. It is seen that the frequencies of most normal modes on the real-frequency side, except for those with large contributions of the librations around the *z* axis ($l = 6$), are confined in the $\Omega < 200$ cm^{-1} region. The librations around

TABLE 1: Vibrational Frequencies, IR Intensities, and Vibrational Polarizabilities of the Normal Modes for the Optimized Structure and Frequency Shifts for Displaced Structures of the Nitrate Ion [a]

					displaced structures		
		optimized structure			freq shift (cm^{-1})		
normal mode		freq. / cm^{-1}	IR int. / km mol^{-1}	vib. polar. / au	$\delta q_1 = 0.013$ Å amu$^{1/2}$	$\delta q_2 = 0.013$ Å amu$^{1/2}$	$\delta q_2 = -0.013$ Å amu$^{1/2}$
q_1	NO asym. str. (0,+,−)	1478.8	717.7	8.89	13.1 [b]	12.8	−12.8
q_2	NO asym. str. (2+,−,−)	1478.8	717.7	8.89	−12.5 [b]	−12.2	13.3
q_3	NO sym. str.	1137.9	0.0	0.00	−0.4	−0.4	−0.4
q_4	out-of-plane bend	884.7	9.8	0.34	−0.1	−0.1	−0.1
q_5	in-plane bend (0,+, −)	731.0	0.8	0.04	0.3 [b]	0.3	−0.4
q_6	in-plane bend (2+,−,−)	731.0	0.8	0.04	−0.4 [b]	−0.4	0.4

[a] Calculated at the MP3/ 6-31+G(2d,p) level. [b] The vibrational pattern of this normal mode is not exactly similar to that of the corresponding mode of the optimized structure.

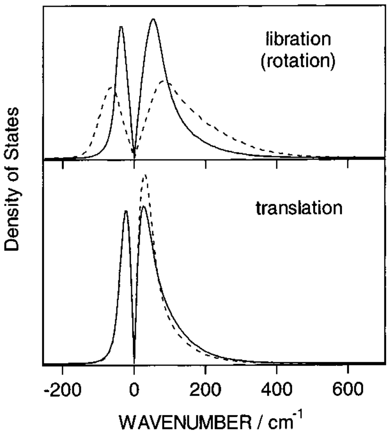

Figure 5. Densities of states for the molecular translations and librations [$H_l(\Omega)$ defined in eq 14]. See also the caption for Figure 2.

the *z* axis appear in a higher-frequency region, probably because the moment of inertia is very small for this type of motion.

It is noticed from the comparison of Figures 4 and 5 that, although the librations around the *x* and *y* axes contribute significantly to the FMMs as shown in Figure 2, the functional forms of $G_t(\Omega)$ and $H_l(\Omega)$ ($l = 4$ and 5) are substantially different. Especially in the case of $G_1(\Omega)$, which is the component with the largest $\Sigma_k(\partial E_k/\partial S_t)^2$, large values are calculated in the 400−200 cm^{-1} region, where the density of states is rather small. It may be said that, among the modes with large amplitudes of the librations around the *x* and *y* axes, those in a higher-frequency region tend to be more effective in modulating electric field.

C. Vibrational Polarization of the Nitrate Ion in Solution. As explained in section 1, vibrational polarization of the solute in solution is determined by the magnitude of external electric field and the vibrational polarizability of the solute itself.

The magnitude of field modulation in the FMM picture is obtained from the values of $|\partial \boldsymbol{E}/\partial S_t|$ and the vibrational amplitudes of the FMMs. In the case of the acetonitrile solution of the nitrate ion shown above, the root-mean-square values of $|\partial \boldsymbol{E}/\partial S_t|$ are in the range of $0.033-0.049 \times 10^{-10}$ esu Å^{-3} amu$^{-1/2}$. The vibrational amplitudes of these FMMs (δS_t) at temperature T are calculated from their “average” vibrational angular frequencies $\bar{\Omega}_t$ as

$$\langle \delta S_t^2 \rangle = \frac{\hbar}{\bar{\Omega}_t} \coth\left(\frac{\hbar \bar{\Omega}_t}{2kT}\right) \qquad (15)$$

The average vibrational frequencies (wavenumbers) are in the range of 150−220 cm^{-1}. From these values, the magnitudes of field modulation are calculated to be $\sim 0.027 \times 10^{-10}$ esu Å^{-2}. This value is slightly smaller than that obtained directly from MD simulations, $\sim 0.043 \times 10^{-10}$ esu Å^{-2}. This is partly because the FMMs obtained above do not involve the motions of the solute molecule, as noted in the last paragraph of section 2. Since the electric field in solution is not uniform, the motions of the solute molecule induce changes in the electric field at its center of mass. If we include those motions in the definition of FMMs, we obtain $\sim 0.034 \times 10^{-10}$ esu Å^{-2} as the magnitudes of field modulation in the FMM picture. The remaining difference is probably due to the anharmonicity of intermolecular vibrations and the existence of multiple potential energy minima in the solution.

The vibrational frequencies, the IR intensities, and the vibrational polarizabilities of the intramolecular normal modes of the nitrate ion calculated at the MP3/6-31+G(2d,p) level are shown on the left half of Table 1. The vibrational polarizabilities are large only for the degenerate pair of the NO asymmetric stretching modes (q_1 and q_2). It is therefore reasonable that distortion of molecular structure occurs particularly along these modes in polar solutions.

From the vibrational polarizability calculated for q_1 and q_2 shown in Table 1 and the magnitude of the modulation of external electric field ($\sim 0.04 \times 10^{-10}$ esu Å^{-2}), it is estimated that the root-mean-square displacements along q_1 and q_2 for the nitrate ion in acetonitrile are ~ 0.013 Å amu$^{1/2}$. The vibrational frequency shifts calculated for displaced structures are shown on the right half of Table 1. A frequency splitting of ~ 25 cm^{-1} is obtained between the two NO asymmetric stretching modes. In a previous study,[7] it has been stated that the accurate value of the frequency splitting is difficult to determine experimentally for the nitrate ion in acetonitrile and other polar solvents except for water. However, considering the frequency splitting of ~ 60 cm^{-1} observed in aqueous solution[7] and from the expectation that nitrate−water interactions are stronger than nitrate−acetonitrile interactions, the frequency splitting of ~ 25 cm^{-1} obtained above may be reasonable.[33] It has also been shown in ref 7 that the structural displacements along the NO asymmetric stretching modes occurring upon the $\pi \rightarrow \pi^*$ electronic excitation are estimated to be 1.3 in the dimensionless unit (which corresponds to about 0.2 Å amu$^{1/2}$) from the observed resonance Raman intensities. Since this value is larger than the displacement calculated above for the ion in the ground electronic state (~ 0.013 Å amu$^{1/2}$), it may be said that the ion in the $\pi\pi^*$ excited state is more sensitive to external electric field.

4. Summary and Outlook

In the present study, we have developed a method for examining the intermolecular vibrational motions that are responsible for modulating external electric field at the position of the solute in solution. Those vibrational motions are called field-modulating modes (FMMs). The FMMs are derived in the context of the INM theory by using an algebraic property of the expansion of $\partial E_k/\partial Q_r$ (eq 5), in the same way as in the ICM theory of intramolecular vibrations developed in previous studies.[14,16] As an example of application of the present method, FMMs have been calculated for an acetonitrile solution of the nitrate ion. The vibrational patterns of the FMMs, the magnitude of the field modulation by the vibrations along the FMMs, and the structural distortion of the solute induced by the field modulation are discussed in detail.

Intermolecular vibrational interactions are important in many situations. When the external electric field E_k in eq 1 depends on intramolecular vibrational modes of other molecules in the liquid, we obtain intermolecular coupling of intramolecular vibrations. If the intrinsic frequencies of the vibrational modes involved in the coupling are sufficiently close to each other (the resonant case), the vibrational modes are delocalized in the liquid. An example of manifestation of such delocalization of vibrational modes in vibrational spectral features is the noncoincidence effect.[34−43] Theoretical aspects of this phenomenon have been discussed.[38−43] In the present study, we have examined the modulation of E_k by intermolecular vibrational motions. As a result of the field modulation, interactions between intramolecular and intermolecular vibrations such as those given in eq 4 are obtained. In addition to the situation analyzed in the present study, this type of interaction is expected to be important also in vibrational relaxation. As is well known, one factor that determines the vibrational relaxation rate is the derivative of the system Hamiltonian with respect to the vibrational modes involved in the process. It has been discussed in previous studies[44−46] that electrostatic interactions play an important role in vibrational relaxation. For example, if we go on to the second order in E_k in eq 4, we obtain

$$V^{(2)} = -\sum_{k,l}\left[\alpha_{kl}^{(0)} + \sum_{p}\frac{\partial \alpha_{kl}}{\partial q_p}q_p\right]\left[E_k^{(0)} + \sum_{r}\frac{\partial E_k}{\partial Q_r}Q_r\right]\times \left[E_l^{(0)} + \sum_{s}\frac{\partial E_l}{\partial Q_s}Q_s\right] \qquad (16)$$

as the second-order term. Since it is first order in intramolecular and second order in intermolecular modes, this term is expected to be important in a vibrational relaxation process into two intermolecular modes. As discussed in section 2, $\Sigma_r(\partial E_k/\partial Q_r)Q_r$ may be replaced by the summation over the FMMs. Therefore, the nature of the vibrational modes involved in the vibrational relaxation process may be examined by using the FMM theory. Discussion on this point will be made further in future studies.

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References and Notes

(1) Johnson, A. E.; Myers, A. B. *J. Phys. Chem.* **1996**, *100*, 7778.

(2) Sato, H.; Hirata, F.; Myers, A. B. *J. Phys. Chem. A* **1998**, *102*, 2065.

(3) Lynden-Bell, R. M.; Kosloff, R.; Ruhman, S.; Danovich, D.; Vala, J. *J. Chem. Phys.* **1998**, *109*, 9928.

(4) Furuya, K.; Inagaki, Y.; Torii, H.; Furukawa, Y.; Tasumi, M. *J. Phys. Chem. A* **1998**, *102*, 8413.

(5) Torii, H.; Furuya, K.; Tasumi, M. *J. Phys. Chem. A* **1998**, *102*, 8422.

(6) Furuya, K.; Torii, H.; Furukawa, Y.; Tasumi, M. *J. Phys. Chem. A* **2000**, *104*, 11203.

(7) Waterland, M. R.; Kelley, A. M. *J. Chem. Phys.* **2000**, *113*, 6760.

(8) Waterland, M. R.; Stockwell, D.; Kelley, A. M. *J. Chem. Phys.* **2001**, *114*, 6249.

(9) We consider the case of a dilute solution where solute−solute interactions may be neglected. It is sufficient to include only one solute molecule in the Hamiltonian.

(10) Bishop, D. M. *Rev. Mod. Phys.* **1990**, *62*, 343.

(11) Bishop, D. M. *Adv. Chem. Phys.* **1998,** *104*, 1.

(12) Torii, H.; Tasumi, M. *J. Phys. Chem. B* **1997**, *101*, 466.

(13) Torii, H. *Chem. Phys. Lett.* **1999**, *306*, 381.

(14) Torii, H.; Ueno, Y.; Sakamoto, A.; Tasumi, M. *J. Phys. Chem. A* **1999**, *103*, 5557.

(15) Torii, H. *Vib. Spectrosc.* **2000**, *24*, 3.

(16) Torii, H. *Nonlinear Optics* **2000**, *26*, 123.

(17) Keyes, T. *J. Phys. Chem. A* **1997**, *101*, 2921.

(18) Stratt, R. M. *Acc. Chem. Res.* **1995**, *28*, 201.

(19) The intramolecular vibrations of the solvent molecules are neglected.

(20) Torii, H.; Tasumi, M. *J. Chem. Phys.* **1992**, *97*, 86.

(21) In the case of linear molecules, $4 \le l \le 5$ for librations. The total dimensionality of the intermolecular vibrational motions discussed hereafter should be changed accordingly.

(22) Böhm, H. J.; McDonald, I. R.; Madden, P. A. *Mol. Phys.* **1983**, *49*, 347.

(23) Signorini, G. F.; Barrat, J.-L.; Klein, M. L. *J. Chem. Phys.* **1990**, *92*, 1294.

(24) Evans, D. J. *Mol. Phys.* **1977**, *34*, 317.

(25) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: Oxford, 1989.

(26) Marcus, Y. *Introduction to Liquid State Theory*; Wiley: London, 1977.

(27) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(28) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(29) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(30) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Gaussian, Inc.: Pittsburgh, PA, 1998.

(32) It should be noted at this point that we may also calculate FMMs from normal modes in a limited frequency range. In that case, it is possible to compare the vibrational patterns of FMMs obtained for different frequency ranges.

(33) Of course, since the modulation of external electric field is time-dependent, the vibrational band will be motionally narrowed to some extent. From the MD simulations, the correlation time of field modulation is estimated to be ∼140 fs. Taking into account this rate of field modulation, the magnitude of band broadening (fwhm) is estimated to be about 9 cm^{-1}.

(34) Fini, G.; Mirone, P.; Fortunato, B. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1243.

(35) Giorgini, M. G.; Fini, G.; Mirone, P. *J. Chem. Phys.* **1983**, *79*, 639.

(36) Zerda, T. W.; Thomas, H. D.; Bradley, M.; Jonas, J. *J. Chem. Phys.* **1987**, *86*, 3219.

(37) Mortensen, A.; Faurskov Nielsen, O.; Yarwood, J.; Shelley, V. *J. Phys. Chem.* **1994**, *98*, 5221.

(38) McHale, J. L. *J. Chem. Phys.* **1981**, *75*, 30.

(39) Logan, D. E. *Chem. Phys.* **1986**, *103*, 215.

(40) Torii, H.; Tasumi, M. *J. Chem. Phys.* **1993**, *99*, 8459.

(41) Torii, H. *J. Mol. Struct. (THEOCHEM)* **1994**, *311*, 199.

(42) Torii, H.; Musso, M.; Giorgini, M. G.; Döge, G. *Mol. Phys.* **1998**, *94*, 821.

(43) Other references on this subject are found in Torii, H. *J. Phys. Chem. A* **1999**, *103*, 2843.

(44) Rey, R.; Hynes, J. T. *J. Chem. Phys.* **1998**, *108*, 142.

(45) Morita, A.; Kato, S. *J. Chem. Phys.* **1998**, *109*, 5511.

(46) Terashima, T.; Shiga, M.; Okazaki, S. *J. Chem. Phys.* **2001**, *114*, 5663.