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The Electric-field Analyses of a System with an Axial Symmetry and Its Application to the Infrared Intensity

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The method of solving the Laplace equation for a system with axial symmetry is formulated in terms of the finite element method. The molecule having C_{3v} point symmetry is assumed to have axial symmetry, and the van der Waals radii of the component atoms are used to estimate the shape of the central molecule. The method is applied to the IR intensity of the C≡N stretching mode of acetonitrile in various states. The observed intensities are adequately explained by the use of the local and reaction fields, except for the intensity in a solution diluted infinitely in chloroform. The intensity in chloroform can, however, reasonably be explained by taking the hydrogen bond into consideration.

It should be possible to determine the electric properties relevant to the estimation of the IR intensity in a liquid phase with a polar molecule by means of the Laplace equation. Ordinarily, however, the Laplace equation under a boundary condition is not easy to solve analytically, except for a system with spherical symmetry (spherical model). The finite element method, which has been developed for just such a problem,[1,2] is used for the present study.

In this paper we regard a system with a central molecule with C_{3v} point symmetry as having axial symmetry. Under this assumption, we can treat any system by the finite element method; the difficulty in placing the precise shape of the central molecule into the Laplace equation is thereby eliminated. The present study is, thus, more general than that previously reported for a uniformly polarized ellipsoid.[3]

Since the quantities obtained directly from the Laplace equation are the potential, Ψ, and the macroscopic field, E_m, we propose a method of obtaining the local radiation field, E_L, or the reaction field, E_R, derived by the permanent dipole moment; E_L depends partially on the polarization charge stored on the boundary between the central molecule and the media, while E_R depends completely on it.

The absolute infrared intensity, Γ_a, is given by:[4]

$$\Gamma_a = \frac{8\pi^3}{3hc} N_a m_1^2, \tag{1}$$

where h is the Planck constant, c is the velocity of light, N_a is the Avogadro constant, and m_1 is the transition dipole moment, defined as follows:

$$m_1 = \mu_1 + \alpha_1 E_R, \tag{2}$$

where μ_1 and α_1 originate from the dipole moment and the polarizability derivatives respectively. It is well known that Γ_a is related to the observed intensity, Γ, as follows:

$$\Gamma = \Gamma_a E_L^2/n, \tag{3}$$

where n is the refractive index.

The value of E_L has been estimated mainly from the spherical model, and a quantitative discussion of Eq. 2 has been undertaken by several authors.[5,6] Kakimoto and Fujiyama[5] have calculated E_R on the basis of the model of dipole-dipole interaction and referred to the values of μ_1 and α_1. Since their method is essentially different from ours, the values of E_R obtained from their method should also differ from ours.

The intensity of the IR band of the C≡N stretching mode of acetonitrile diluted infinitely in chloroform (≈0% chloroform solution) has been reported to be stronger[7] than that to be expected qualitatively. Since our method can easily be expanded to a hydrogen-bonded system, it is also applicable to a quantitative treatment of this abnormal behavior.

Method

The Laplace equation for a system with axial symmetry is given, in terms of the cylindrical coordinates as follows:

$$\varepsilon_r \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Psi}{\partial r}\right) + \varepsilon_z\left(\frac{\partial^2 \Psi}{\partial z^2}\right) = 0, \tag{4}$$

where ε_r and ε_z are the dielectric constants of the r and z directions respectively; in the present system, we have the following conditions: $\varepsilon_r \neq \varepsilon_z$ in the central molecule and $\varepsilon_r = \varepsilon_z = \varepsilon_2$ in the media. The functional equivalent to Eq. 4 in one of the elements is given by:[1]

$$\chi_e = \frac{1}{2}\iint\left[\varepsilon_r\left(\frac{\partial \Psi}{\partial r}\right)^2 + \varepsilon_z\left(\frac{\partial \Psi}{\partial z}\right)^2\right] r\mathrm{d}r\mathrm{d}z. \tag{5}$$

On the basis of the isoparametric elements,[1,2] the trial function, Ψ, and the variables, r and z, are assumed to be:

$$\begin{aligned}\Psi = {} & (2L_1-1)L_1\Psi_1 + (2L_2-1)L_2\Psi_2 + (2L_3-1)L_3\Psi_3 \\ & + 4L_1L_2\Psi_4 + 4L_2L_3\Psi_5 + 4L_3L_1\Psi_6 = \mathbf{N}\Psi_e,\end{aligned} \tag{6}$$

and:

$$r = \mathbf{N}|r_1r_2r_3r_4r_5r_6| = \mathbf{N}\mathbf{r}_e, \tag{7}$$

and:

$$z = \mathbf{N}|z_1z_2z_3z_4z_5z_6| = \mathbf{N}\mathbf{z}_e \tag{8}$$

where $\mathbf{N}$ is the displacement model, where L_i is defined as $\Delta L_i/\Delta\mathrm{ABC}$, and where Ψ_j, r_j, and z_j are the nodal values of the potential, r and z respectively, as is shown in Fig. 1. According to the definition of L_i, we can introduce the transformation $\xi = L_1$, $\eta = L_2$, and $1-\xi-\eta = L_3$. By the use of $\mathbf{N}$, ξ, and η, we obtain the derivatives in Eq. 5 as follows:

$$\begin{vmatrix} \dfrac{\partial \Psi}{\partial r} \\ \dfrac{\partial \Psi}{\partial z} \end{vmatrix} = \mathbf{J}^{-1} \begin{vmatrix} \dfrac{\partial \mathbf{N}}{\partial \xi} \\ \dfrac{\partial \mathbf{N}}{\partial \eta} \end{vmatrix} \Psi_e, \tag{9}$$

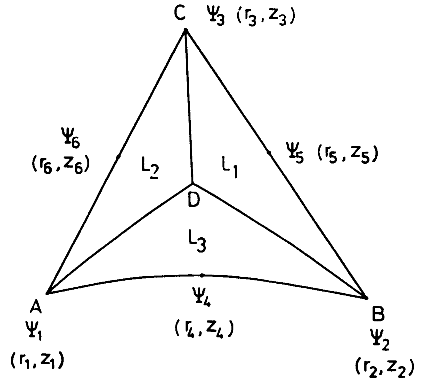

Fig. 1. The isoparametric element and the definition of $\boldsymbol{\Psi}_i$, r_i, or z_i.

where:

$$\mathbf{J} = \begin{vmatrix} \dfrac{\Sigma\partial N_i}{\partial\xi} r_i & \dfrac{\Sigma\partial N_i}{\partial\xi} z_i \\ \dfrac{\Sigma\partial N_i}{\partial\eta} r_i & \dfrac{\Sigma\partial N_i}{\partial\eta} z_i \end{vmatrix}. \tag{10}$$

By substituting Eq. 9 into Eq. 5, we obtain the functional as a function of $\boldsymbol{\Psi}_e$:

$$\chi_e = \frac{1}{2}\tilde{\boldsymbol{\Psi}}_e \mathbf{Q}_e \boldsymbol{\Psi}_e, \tag{11}$$

where:

$$\mathbf{Q}_e = \iint\left(\varepsilon_r \frac{\partial\tilde{\mathbf{N}}}{\partial\xi}\tilde{\mathbf{J}}^{-1}\mathbf{J}^{-1}\frac{\partial\mathbf{N}}{\partial\xi} + \varepsilon_z \frac{\partial\tilde{\mathbf{N}}}{\partial\eta}\tilde{\mathbf{J}}^{-1}\mathbf{J}^{-1}\frac{\partial\mathbf{N}}{\partial\eta}\right)\mathbf{N}\mathbf{r}_e \det[\mathbf{J}]d\xi d\eta. \tag{12}$$

According to the stationary condition of $\delta\chi_e=0$, we obtain this equation:

$$\mathbf{Q}_e\boldsymbol{\Psi}_e = 0. \tag{13}$$

Since Eq. 13 holds for all elements, we obtain a final equation constructed from all the nodal values (see Appendix) as follows:

$$\mathbf{A}\boldsymbol{\Psi} = 0. \tag{14}$$

Equation 14 is solved under a given boundary condition, and we get the electric field from Eq. 9. E_m is obtained under the boundary condition of $\boldsymbol{\Psi}_\infty = E_\infty z(=z)$ at r, $|z|\to\infty$.

Analyses of E_L and E_R

Although E_m is a field already compensated for by that of polarization, E_S, the extent of the compensation depends on the shape of the central molecule. Generally, the extent of a prolate top molecule is smaller than that of an oblate one.[3] This is reflected in E_L through the self-field of polarization, E_S^V, in a vacuum. For instance, the value of E_L in the present study is smaller than that to be expected from the spherical model, especially in liquid acetonitrile; E_L in the spherical model[8] is: $E_L=(\varepsilon_\infty+2)\,E_\infty/3$ $(\varepsilon_\infty=n^2)$. Since this discrepancy is inevitable, we define E_L as follows:

$$E_L = E_m - E_S^V. \tag{15}$$

We calculate E_S^V by means of the general method, which corresponds to the field analysis of permanent polarization or of a magnet with axial symmetry.

The polarization charge, ρ_p, stored on a boundary results from induced polarization, so that ρ_p is given according to Gauss' expression as follows:

$$\rho_p = \mathbf{P}\cdot\mathbf{n} = \{(\varepsilon_r-1)E_r + (\varepsilon_z-1)E_z\}\cdot\mathbf{n}, \tag{16}$$

where $\mathbf{n}$ is the normal vector at the boundary. In the present problem, Eq. 16 is, thus, the boundary condition, and the functional is given by:

$$\chi_e = \frac{1}{2}\iint\left[\varepsilon_r\left(\frac{\partial\boldsymbol{\Psi}}{\partial r}\right)^2 + \varepsilon_z\left(\frac{\partial\boldsymbol{\Psi}}{\partial z}\right)^2\right]r\mathrm{d}r\mathrm{d}z + \int_C \rho_p\boldsymbol{\Psi}r\mathrm{d}C, \tag{17}$$

where the linear integral is carried out along the boundary, C, between the central molecule and the media. The formulation of Eq. 17 is similar to that of Eq. 5; accordingly, we obtain the following equation (see Appendix):

$$\mathbf{A}\boldsymbol{\Psi} = \mathbf{B}, \tag{18}$$

where $\mathbf{A}$ is the matrix given in Eq. 14, except that $\varepsilon_r=\varepsilon_z=1$ in all regions, and $\mathbf{B}$ is the column matrix determined from the linear integral in Eq. 17. Since $\mathbf{B}$ is known from the boundary condition of Eq. 16, E_S^V can be obtained from $\boldsymbol{\Psi}$ in Eq. 18.

The polarization charge, ρ_μ, stored on the boundary by the dipole-moment field is obtained from an equation similar to Eq. 16. Then we get E_R from Eq. 18. However, since E_R is zero if $\varepsilon_1=\varepsilon_2$ and depends on $\varepsilon_1-\varepsilon_2$, where ε_1 represents the dielectric constant of the central molecule, E_R can be obtained by the simple method to be described below.

We first calculate the potentials of $\boldsymbol{\Psi}_{\varepsilon\infty}$ and $\boldsymbol{\Psi}_{\varepsilon s}$, which are obtained, respectively, under the conditions of $\varepsilon_1=\varepsilon_2=\varepsilon_\infty$ and $\varepsilon_1\neq\varepsilon_2=\varepsilon_s$ (static dielectric constant). Second, we calculate this equation:

$$\boldsymbol{\Psi}_R = \boldsymbol{\Psi}_{\varepsilon s} - \boldsymbol{\Psi}_{\varepsilon\infty}. \tag{19}$$

$\boldsymbol{\Psi}_R$ may be regarded as the potential, as for E_R. This method is simple because we have an analytical solution of $\boldsymbol{\Psi}_{\varepsilon\infty}$; we assume the position of the point dipole to be the center of the C≡N bond of acetonitrile. $\boldsymbol{\Psi}_{\varepsilon s}$ is obtained under the boundary condition of $\dfrac{\mu}{\varepsilon_1}\dfrac{z}{(r^2+z^2)}$ at r, $z\to0$. It should be noted that the central molecule interacts with the media through the static dielectric constant;[9] the molecules around the central molecule are oriented so as to produce ε_s.

Since E_L and E_R in the central molecule are generally heterogeneous, it is necessary to average them. As long as we regard α_1 in Eq. 2 as the molecular constant, it is clear that the average of E_R over the z axis of the central molecule should be used as the reaction field. This process is given by:

$$\bar{E}_R = \frac{\int_b^a E_R\mathrm{d}z}{D} = -\frac{\boldsymbol{\Psi}(a)-\boldsymbol{\Psi}(b)}{D}, \tag{20}$$

where a and b are the coordinates of the boundary on the z axis and where D is the distance between them. The average of the E_L values, $\bar{E}_L$, is also given by Eq. 20.

Equation 20 does not have a serious influence on E_L and E_R under the boundary conditions described above, but it does play an important role if E_R varies drastically.

Results and Discussion

The shape of acetonitrile, as estimated from the van der Waals radii[10] of the component atoms, is given in Fig. 2. The values of ε_∞ are obtained from the refractive indices,[11] and those of ε_s from the standard Table;[12] apart from the formulation, we use the condition of $\varepsilon_r = \varepsilon_z = \varepsilon_l$. The dipole moment of acetonitrile, 3.39 D,[13] is used.

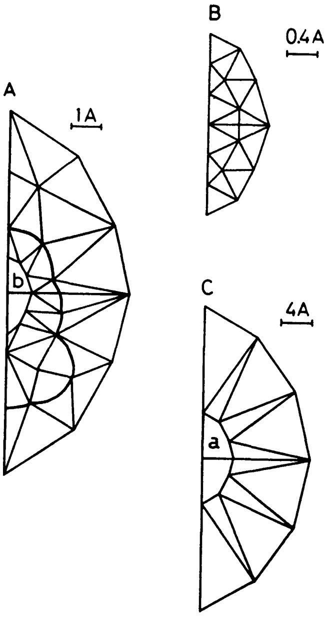

Fig. 2. The molecular shape (broad solid line) and the elements used for E_R. A and B are the expansion of a and b, respectively.

Table 1. Observed and calculated intensities (cm^2/mol) of the C≡N stretching of acetonitrile

State	$\Gamma^{a)}$	$\bar{E}_L/E_\infty$	Γ_a	$\bar{E}_R \times 10^{-5}$	Γ_c
Liquid	444	1.20	415	0.906	396
≈0% In CCl_4	222	1.25	208	0.125	240
Gas	159	1.00	159	−0.493	144
≈0% In $CHCl_3$	500	1.24	470	0.535	317
H. B.$^{b)}$	500	1.27	448	1.080	436

$\bar{E}_R$ in D/cm^3. a) From Ref. 7. b) From the hydrogen-bondmodel.

The intensities of the C≡N stretching mode in various states[5,7] are given in Table 1. As has been mentioned above, E_∞ is assumed to be 1.0, and the value of $\bar{E}_L$ in a liquid is smaller than that of 1.27 obtained from the spherical model. Accordingly, the values of $\bar{E}_L$ in Table 1 vary more gently with the dielectric constants than those to be expected from the spherical model. Since E_R is taken to be zero if $\varepsilon_1 = \varepsilon_2$, the value of $\bar{E}_R$ in the gaseous state becomes negative. The value of $\bar{E}_R$ in a liquid is also smaller than that to be expected from the spherical model, 0.11×10^6 D/cm^3.

In order to estimate the values of the two parameters, μ_1 and α_1, we use the values of Γ_a defined by Eq. 3 and obtained using $\bar{E}_L$ in Table 1, except for the value of Γ_a for a ≈0% chloroform solution; the values thus obtained, $\mu_1 = 0.0295$ (D) and $\alpha_1 = 0.113$ (A^3), are used to calculate the intensity of $\Gamma_c = 8\pi^3/(3hc)N_a(\mu_1 + \alpha_1 \bar{E}_R)^2$ in Table 1. The agreement between Γ_a and Γ_c is satisfactory in each state, except for a ≈0% chloroform solution. The most important features are that the intensity in the gaseous state is explained simultaneously and that the value of α_1 agrees well with the observed value.[5,14]

The value of $\bar{E}_R$ for a ≈0% chloroform solution in Table 1 is reasonable if the interaction between the central molecule and the media takes place through the static electric force. However, Table 1 shows the imperfection in this static electric model. On the other hand, it is reasonable to expect that the hydrogen bond is formed between the nitrogen atom of actonitrile and the hydrogen atom of chloroform in a dilute solution and that, accordingly, the two molecules coordinate, as is shown in Fig. 3.

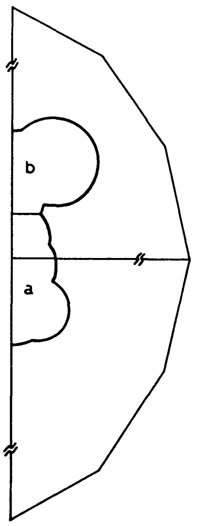

Fig. 3. The hydrogen-bond model of acetonitrile with chloroform. The shapes of acetonitrile and chloroform are given in a and b, respectively.

According to this hydrogen-bond model, the dipole-moment field, $\bar{E}_\mu$, which arises from the chloroform is added to $\bar{E}_R$; $\bar{E}_s$ should be recalculated under the condition of $\varepsilon_s = \varepsilon_\infty$ in the region of the chloroform. To calculate $\bar{E}_\mu$, the dipole moment of the chloroform, 1.55 debye,[13] is set at the center of the hydrogen and chlorine atoms on the z axis in the region of b in Fig. 3. The distance of the hydrogen bond of [C-H···N] is assumed to be 2.8 Å.

In the molecular shape of acetonitrile shown in Fig. 3, $\bar{E}_L$ and $\bar{E}_R$ are 1.27 and 0.331×10^5 D/cm^3 respectively, and $\bar{E}_\mu$ is 0.750×10^5 D/cm^3, resulting in $\Gamma_c = 436$ (cm^2/mol) by the use of the same values of μ_1 and α_1 as have been presented above; they are also given in Table 1. The refinement of Γ_c shows that E_μ is quite important in the intensity of the hydrogen-bonded system. The conclusion to be drawn from the fact that μ_1 is constant in various states is that the intensity in the present system depends only on the electric properties.

The numerical calculations were carried out by the use of the computer, FACOM 230-45S, of Toyama University.

Appendix

We will here outline in more detail the matrix **A** or **B** in Eq. 18 according to our computer program. **A** is constructed by the interconnection of each element. We define the nodal points for two elements (a and b), as is shown in Fig. A-1; the nodal points are numbered arbitrarily. The matrices, $\mathbf{Q}(6\times 6)$, of these elements, a and b, are denoted, respectively, by $\mathbf{Q}'$ and $\mathbf{Q}''$, which are defined as follows:

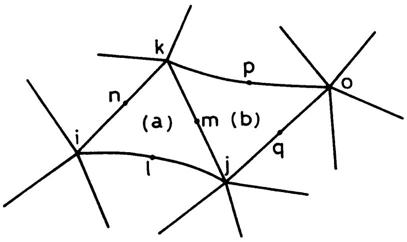

Fig. A-1. The two adjacent elements a and b. The numberings of the nodes (●) are given by i, j, ⋯.

$$\mathbf{Q}' = \left|\begin{array}{c} \mathrm{i\ j\ k\ l\ m\ n} \\ Q'_{\mathrm{rs}} \end{array}\right| \qquad \text{(A-1)}$$

and:

$$\mathbf{Q}'' = \left|\begin{array}{c} \mathrm{j\ o\ k\ q\ p\ m} \\ Q''_{\mathrm{rs}} \end{array}\right| \qquad \text{(A-2)}$$

where $1\leq \mathrm{r,s} \leq 6$. According to the condition of $\delta\chi=\sum\delta\chi_{\mathrm{e}}$, we have a matrix element of **A** as follows:

$$\mathbf{A}\boldsymbol{\Psi} = \begin{array}{ccccc}
\mathrm{i} & \mathrm{j} & \mathrm{k} & \mathrm{m} & \\
\cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \\
Q'_{11}\cdots\cdots & Q'_{12}\cdots\cdots & Q'_{13}\cdots\cdots & Q'_{15}\cdots\cdots & \Psi_{\mathrm{i}} \\
 & \cdots\cdots & \cdots\cdots & \cdots\cdots & \\
 & Q'_{22}+Q''_{11}\cdots & Q'_{23}+Q''_{13}\cdots & Q'_{25}+Q''_{16}\cdots & \Psi_{\mathrm{j}} \\
 & & \cdots\cdots & \cdots\cdots & \\
 & & \cdots\cdots & \cdots\cdots & \\
\text{Sym.} & & Q'_{33}+Q''_{33}\cdots & Q'_{35}+Q''_{36}\cdots & \Psi_{\mathrm{k}} \\
 & & & \cdots\cdots & \\
 & & & Q'_{55}+Q''_{66}\cdots & \Psi_{\mathrm{m}} \\
 & & & \cdots\cdots & \\
 & & & \cdots &
\end{array} \qquad \text{(A-3)}$$

All the matrix elements of **A** in Eq. A-3 are obtained in a similar manner.

We get the **B** column matrix by means of numerical integration. We define the following linear integral in an element:

$$\chi_{\mathrm{B}} = \int_C \rho_{\mathrm{p}} \Psi r \mathrm{d}C \qquad \text{(A-4)}$$

It then follows that:

$$\delta\chi_{\mathrm{B}}/\delta\Psi_{\mathrm{e}} = \int_C \rho_{\mathrm{p}} \mathbf{N} r \mathrm{d}C$$
$$= \int_C \rho_{\mathrm{p}} |(2L_1-1)L_1\ (2L_2-1)L_2\ 0\ 4L_1L_2\ 0\ 0\ | r \mathrm{d}C \qquad \text{(A-5)}$$

where C is the boundary defined in Fig. A-2. This process is carried out for the elements with the C boundary in the central molecule.

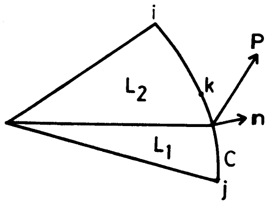

Fig. A-2. Linear integral along the boundary C. **P** is the induced polarization in the central molecule on C, and **n** is the normal vector. L_1 and L_2 are defined in Fig. 1.

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