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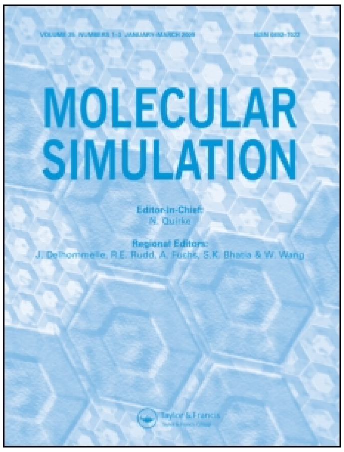

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MONTE CARLO SIMULATION STUDY OF FREE ENERGY CURVES FOR ELECTRON TRANSFER REACTIONS IN POLAR SOLUTIONS BY CONSIDERING THE ELECTRONIC POLARIZABILITY

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We have conducted Monte Carlo simulations of polar solutions with a spherical hard core model by properly taking into account the electronic polarizability of solvent molecules. We have calculated the free energy curve as a function of the reaction coordinate of electron transfer reactions in cases where the reactant is neutral and charged. From the analysis of the free energy curvature ratio between the two cases, we have found that the electronic polarizability contributes to enhance the non-linear response of solvent polarizations and that this enhancement is greatly strengthened if the translational motion of solvent molecules is frozen.

KEY WORDS: Monte Carlo simulation of polar solution, free energy curve, curvature ratio, non-linear response, electronic polarizability, density fluctuation.

1. INTRODUCTION

One of the most important topics in the study of electron transfer reactions has been the energy gap (free energy difference between the initial and final states) dependence of the activation energy of the reaction. This relation is called an energy gap law. Experimentally it has been elucidated that the energy gap law for the charge recombination (CR) reaction ($A^{\pm}\cdots B^{\mp} \rightarrow A\cdots B$) is nearly parabolic [1,2] but that the energy gap law for the photoinduced charge separation (CS) reaction ($A^{*}\cdots B \rightarrow A^{\pm}\cdots B^{\mp}$) is not a simple parabolic form; the activation energy decreases very rapidly in the normal region and that remains small until the large energy gap [3,4]. Therefore, this experimentally apparent energy gap law differs between the two types of electron transfer reactions. From a theoretical point of view, so far as the thermal equilibrium is assumed in the initial state and a linear response approximation of the polarization to the external field is adopted, the energy gap law becomes parabolic, irrespective of the type of electron transfer reactions. This theorem was first proved by Marcus [5]. Recently, we made a theoretical proposal that if a non-linear response of solvent polarization around a charged reactant takes place, different energy gap laws between the CS and CR reactions can be obtained [6–9], which are favorable to explain the experimental data. However, many of the computer simulation studies for the motion of solvent molecules around position-fixed reactants demonstrated that the non-linearity of the solvent polarization is rather small [10–12]. Very recently we noticed that there must be a certain distribution of the distance between the donor and acceptor molecules, and that this distribution might be different between the CS and CR reactions [13]. From the analysis by taking into account the distance distribution adequately for each type of the electron transfer reaction, we found that a considerable part of the difference of the apparent energy gap laws between the CS and CR reactions as seen in the experimental data can be removed [13]. However, the residual part of the difference must be ascribed to the other factors, such as the non-linearity of the solvent polarization and/or the non-equilibrium effect [13].

On the other hand, we theoretically showed that when many-particle correlations of solvent are strong, a non-linear response of polarization results. It is noticeable that the electronic polarizability of solvent molecules can cause the many-particle interaction, and so it is expected to play a significant role in enhancing the non-linear response effect.

Under such a situation, we conduct, in this paper, Monte Carlo simulations by taking into account the electronic polarizability of solvent molecules explicity which was not taken into account exactly in most of the former simulations. Finally, we shall demonstrate that the electronic polarizability really contributes to enhance the non-linear effect of the solvent polarization. We shall also demonstrate that if the translational motion of solvent molecules is frozen, the non-linear enhancement by the electronic polarizability is greatly strengthened.

2. PROPERTIES OF REACTION COORDINATES

Before going to the Monte Carlo simulation, it will be worth noting what is the correct reaction coordinate of the electron transfer reaction in polar solutions. We consider the case that the interaction between the donor and acceptor is weak. Then, the electron transfer reaction is possible only when the energy at a certain configuration of solvent molecules in the initial state is equal to that at the same configuration of solvent molecules in the final state. The overall reaction rate is obtained by collecting all the solvent configurations satisfying the above condition with a suitable weight. In other words, the reaction proceeds through the crossing curve between the hyper-energy-surfaces of the initial and final states spanned over the multi-dimensional space corresponding to the solvent configuration. Practically it is impossible to obtain such hyper-energy surfaces exactly and integrate over the crossing curve. Recently the alternative, powerful method was discovered to calculate free energy surfaces $G^r(x)$ and $G^p(x)$ along the reaction coordinate x as follows [15]:

$$e^{-\beta G^r(x)} = \frac{1}{\beta}\int \delta(H^r - H^p - x)\, e^{-\beta H^r}\, d\Gamma \tag{1}$$

$$e^{-\beta G^p(x)} = \frac{1}{\beta}\int \delta(H^r - H^p - x)\, e^{-\beta H^p}\, d\Gamma\ , \tag{2}$$

where H^r and H^p are Hamiltonians of the solution except the electronic energy in the initial and final states, respectively, Γ is the normalized phase space for solvent molecules and $\beta = 1/k_BT$. As seen from Equations (1) and (2), the crossing point between $G^r(x)$ and $G^p(x)$-ε, where ε is the electronic energy difference between the initial and final states, represents a collection of all the possible solvent configurations which satisfy the energy conservation for the same solvent configuration between the initial and final states with a weight of Boltzmann distribution. Although such a simple, analytical expression was first given by us [15], the similar representations were also given by the others [16–19].

By conducting the further manipulation of Equations (1) and (2), the following relation can be derived [15,20]:

$$\Delta G^{\neq}(-\Delta g) = G^r(\Delta G - \Delta G_s) - G^{r'}, \tag{3}$$

where $\Delta G^{\neq}$ is the activation free energy of the reaction, $-\Delta G$ the energy gap, $-\Delta G_s$ the solvation energy of the reactants due to the charging up and $G^{r'}$ a constant defined by $G^{r'} = \int G^r(x)\,dx$. Equation (3) is useful because the energy gap law is readily obtained once we know the form of $G^r(x)$. Then, the relation of the energy gap laws between CS and CR reactions is equivalent to the relation of $G^r(x)$ and $G^p(x)$ (We consider the case that the reactants are neutral in the initial state and ionized in the final state). Therefore, the difference between $G^r(x)$ and $G^p(x)$ represents the difference of the energy gap laws between the two types of electron transfer reactions. On the other hand, it was demonstrated that if the non-linear response takes place, the free energy curvature $k_n\,(\equiv \partial^2 G^r(x)/\partial x^2)$ is much smaller than $k_c\,(\equiv \partial^2 G^p(x)/(\partial x^2)$ at their minima [15]. Therefore, the curvature ratio k_c/k_n can be a relevant quantity, representing that the more deviates k_c/k_n from unity, the larger is the non-linear response effect and correspondingly the larger is the difference of the energy gap law between CS and CR reactions.

3. METHOD OF MONTE CARLO SIMULATIONS

In this section, we examine whether the free energy curves representing the non-linear response is obtained or not by the Monte Carlo simulation. For this purpose, we adopt a rather simple model. We fix a reactant with a spherical hard core (radius r_0) at the center of the spherical vessel with a radius R. We consider only one reactant for simplicity. We put N solvent molecules with a spherical hard core (radius a) into this vessel and allow to move. The reactant has a point charge ze. The solvent molecule has a point dipole moment μ and the electronic polarizability (denoting α_x, α_y and α_z for each principal axis).

In the actual calculations, the values of the electronic polarizability are chosen by refering to the experimental values of acetonitrile $\alpha_x = \alpha_y = 3.85\,\text{Å}^3$ and $\alpha_z = 5.74\,\text{Å}^3$ [21]. N is usually chosen as 100 in the present calculations. This number is considerably smaller than the previous calculations without the role of the electronic polarizability. We shall discuss the effect of the small number of solvent molecules later. The radius a of solvent molecules is always 2.2 Å. The dipole moment μ is 2.0 Debye. R is chosen as 13.4 Å, and the packing fraction is 0.45. Temperature is 300 K.

Since the electronic motion is much rapider than that of molecules, we solve the following simultaneous equations selfconsistently in each solvent configuration of the simulation:

$$\mathbf{P}_i = \boldsymbol{\mu}_i + \vec{\boldsymbol{\alpha}}_i \mathbf{F}_i \tag{4}$$

$$\mathbf{F}_i = \mathbf{E}_i^c - \sum_j \vec{\mathbf{T}}_{ij} \mathbf{P}_j \tag{5}$$

where

$$T_{ij}^{\alpha\beta} = \frac{1}{r_{ij}^3} (\delta_{\alpha\beta} - 3r_{ij}^{\alpha} r_{ij}^{\beta}/r_{ij}^2), \ (\alpha,\beta = x,y,x) \tag{6}$$

$$\mathbf{E}_i^c = \frac{ze}{r_{i0}^3} \mathbf{r}_{i0} \tag{7}$$

with r_{ij} being the distance between the two dipoles and r_{i0} the distance between the dipole and the central reactant. Equations (6) and (7) are solved by the iteration method. The number of the iteration is usually 5. The Hamiltonian of the solvent is given by [22]

$$\begin{aligned} H = {} & \frac{1}{2}\sum_i \sum_j \boldsymbol{\mu}_j \vec{\mathbf{T}}_{ij} \boldsymbol{\mu}_j - \sum_i \boldsymbol{\mu}_i \mathbf{E}_i^c \\ & - \frac{1}{2}\sum_i \mathbf{F}_i \vec{\boldsymbol{\alpha}}_i (\mathbf{E}_i^c - \sum_{j \neq i} \vec{\mathbf{T}}_{\mathbf{ij}} \boldsymbol{\mu}_j) \end{aligned} \tag{8}$$

and H^r and H^p are obtained from H by substituting the pertinent value of z in E_i^c. We conduct 10^4 Monte Carlo steps (10^6 configurations in the case $N = 100$). We use the latter 9000 steps for statistics. For the calculation of the free energy curve, we make a histogram in such a way that the number of configurations for the energy difference being x is $g\,(x)$. Then, the free energy curve is obtained from $G\,(x) = -kT \ln g\,(x)$. Therefore, $G\,(x)$ is easily calculated by the Monte Carlo simulation method.

4. RESULTS

We have calculated the free energy curves for $z = 0$ and $z = 1$ for some cases of the electronic polarizability. An example is shown in Figure 1. It should be noted that the position of minimum of the free energy curve for $z = 0$ is shifted from $x = 0$. Such a shift never occurs when the electronic polarizability is zero, as proved in our previous theoretical study [15]. The curvatures k_n and k_c are obtained from such free energy curves, by calculating $\partial^2 G\,(x)/\partial x^2$ at the minima for $z = 0$ and $z = 1$, respectively.

The calculated results of the curvatures and the ratio k_c/k_n are listed in Table 1. From this Table 1, it is found that when the translational and rotational motions are in thermal equilibrium, the value of the ratio is about 1.7, nearly irrespective of the value of α_z for $\alpha_z \geqslant 5$ Å^3, and its ratio is somewhat larger than the case of $\alpha_x = \alpha_y = \alpha_z = 0$. Even when the values of α_x, α_y and α_z become as large as 8 Å^3, the ratio does not increase but rather decreases. In the case that the radius of the solute is decreased to 1.6 Å, the ratio increases a little. When the translational motion is frozen and rotational motion is in thermal equilibrium, the ratio increases considerably in all the cases. Furthermore, the ratio can change in some cases depending on the fixed positions of solvent molecules. Due to the imitation of the computation time, we did not calculate all the cases. But, it appears to be a general tendency that the ratio

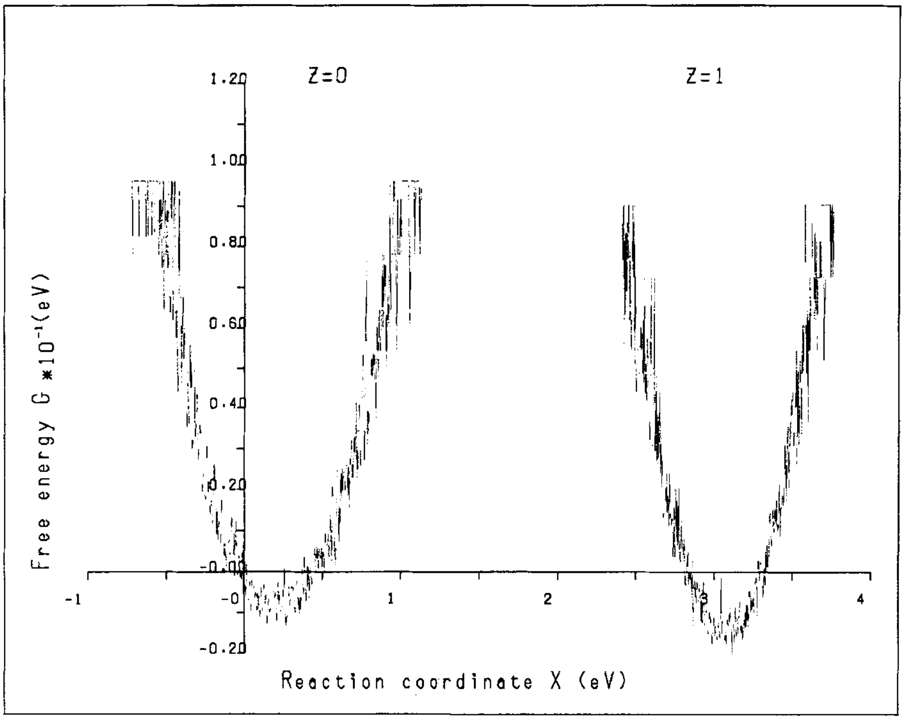

Figure 1 The calculated free energy curve as a function of the reaction coordiante for $z = 0$ and $z = 1$ in the case $\alpha_x = \alpha_y = 0$ and $\alpha_z = 5\,\text{Å}^3$. Relative heights of the free energy curves are arbitrary.

Table 1 The curvatures and ratios as obtained by the Monte Carlo simulation calculations for some cases of the electronic polarizabilities and radius r_0 of the solute molecules.

r_0 (Å)	α_x	α_y (Å^3)	α_z	*Thermal equilibrium for the translation and rotation of solvents*			*Thermal equilibrium for the rotation and frozen for the translation of solvents*		
				k_n (eV^{-1})	k_c (eV^{-1})	k_c/k_n	k_n (eV^{-1})	k_c (eV^{-1})	k_c/k_n
2.2	0	0	0	0.33	0.48	1.45	0.32	0.64[a]	2.00[a]
							0.30	0.58[b]	1.93[b]
	0	0	5	0.33	0.58	1.76			
	0	0	10	0.33	0.57	1.73	0.30[a]	0.86[a]	2.87[a]
							0.24[b]	0.86[b]	3.58[b]
	8	8	8	0.45	0.70	1.56			
1.6	0	0	10	0.32	0.56	1.75	0.23[a]	0.89[a]	3.87[a]
							0.25[b]	0.95[b]	3.80[b]

[a] The position of solvent molecules is fixed to the configuration which was realized at the 10^{4}th Monte Carlo step conducted by the condition of thermal equilbrium around the neutral reactant for each value of α.
[b] The position of solvent molecules is fixed to the configuration which was realized at the 10^{4}th Monte Carlo step conducted by the condition of thermal equilibrium around the charged reactant for each value of α.

is 3 ~ 4 when the translational motion is frozen. This value is a comparable magnitude to the one expected from the analysis of the experimental data of the energy gap laws by taking into account the distance distribution of reactants [13].

5. DISCUSSIONS

According to our results from Monte Carlo simulation using simple model systems of polar solutions, the curvature ratio is enhanced by considering the electronic polarizability of solvent molecules but it never exceeds 2.0 when the translational and rotational motions are in thermal equilibrium. This enhancement effect by the electronic polarizability is greatly strengthened, sometimes the ratio exceeding 3.0, when the translational motion of solvent molecules is frozen. The physical meaning of the translational motion being fixed might be as follows: The longitudinal relaxation time τ_L of the rotation of solvent dipoles is very small, ca. 0.2 ps for acetonitrile and the preexponential factor for the electron transfer rate will be comparable to or smaller than $1/\tau_L$. So, the rotational motion will always look like in thermal equilibrium for the electron transfer. In contrast to this, the translational motion is generally much slower than the rotational motion, ca. by two orders of magnitude. So, it may happen that the translational motion does not proceed so much at the time of the electron transfer. In order to see it in more detail, it is necessary to solve the diffusion-rate equation for the translational motion. This task is in progress.

We conducted the Monte Carlo simulation using a rather small number of solvent molecules $N = 100$. If we consider that the dipole–change and dipole–dipole interactions are long-ranged, the above solvent number appears to be too small to discuss quantitatively. In order to check this point, we conducted the similar Monte Carlo simulation without taking into account the electronic polarizability for a system of $N = 360$. The curvature ratio obtained for the thermal equilibrium of translational and rotational motions of solvent molecules was 1.20, which is rather smaller than 1.45 for a system of $N = 100$ in Table 1. When the translational motions of solvent molecules are frozen at the configurations surrounding the neutral and charged reactants, curvature ratios were 1.68 and 1.70, respectively, which are slightly smaller than 2.00 and 1.93 for $N = 100$ in Table 1. From those results, it may be expected that the non-linear effect in the presence of the electronic polarizability is somewhat decreased when N is large. But, even in this case, our qualitative result that the non-linearity of the solven polarization is enhanced by the electronic polarizability and its enhancement is greatly strengthened by the freezing of the translational motion of solvent molecules would remain valid.

As we discussed in the Introduction, the physical reasoning of the enhancement of the non-linearity by the electronic polarizability should be ascribed to the many-particle interaction produced by the electronic polarizability. Theoretically it was also shown that if the two-particle correlation length is not much larger than all the other many-particle correlation lengths, the anharmonic free energy curve is obtained, representing a strong non-linear response of the polarization [14]. So, it is an interesting problem to calculate the many-particle correlation lengths in an appropriate way using the ensemble of the present Monte Carlo simulation. This work will be made elsewhere.

The physical reasoning of the stronger enhancement of the non-linearity by the freezing of translational motions of solvent will be as follows: When the translational motion is allowed, a large electrostatic energy which arises from interactions between a charged reactant and solvent dipoles can be effectively optimized (or minimized) by the density fluctuation of solvent, without causing a strong dielectric saturation of the solvent around the charged reactant in each iteration step. However, if the translational motion is frozen, this energy optimization route is closed, and the strong dielectric saturation (large non-linear response) of solvent would inevitably result.

In the present calculation, the temperature was fixed at 300 K. In our previous calculations, however, we found that the free energy curvature contributed from the first shell around the charged reactant where the non-linear response is nearly independent of the temperature but that the free energy curvature contributed from the outer shells where the linear response is proportional to the temperature [23]. Therefore, it may be expected that the curvature ratio increases with the temperature if the saturation shell remains the same. This problem will be investigated in a forthcoming paper.

As a conclusion of this paper, it is found by the Monte Carlo simulation that the electronic polarizability and the freezing of the density fluctuation affect the free energy curve considerably, enhancing the non-linear response effect.

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References

[1] N. Mataga, T. Asahi, Y. Kanda, T. Okada and T. Kakitani, "The Bell-Shaped Energy Gap Dependence of the Charge Recombination Reaction of Geminate Radical Ion Pairs Produced by Fluorescence Quenching Reaction in Acetonitrile Solution", *Chem. Phys.*, **127**, 249 (1988).

[2] M.A. Wasielewski, M.P. Niemczyk, W.A. Svec and E.B. Pewitt, "Dependence of Rate Constants for Photoinduced Charge Separation and Dark large Recombination of the Free Energy of Reaction in Restricted-Distance Porphyrin-Quinone Molecules", *J. Am. Chem. Soc.*, **107**, 1080 (1985).

[3] D. Rehm and A. Weller, "Kinetics of Fluorescence Quenching by Electron and H-Atom Transfer", *Israel J. Chem.*, **8**, 259 (1970).

[4] N. Mataga, Y. Kanda, T. Asahi, H. Miyasaka, T. Okada and T. Kakitani, "Mechanism of the Strongly Exothermic Charge Separation Reaction in the Excited Singlet State. Picosecond Laser Photolysis Studies on Aromatic Hydrocarbon-Tetracyanoethylene and Aromatic Hydrocarbon-Pyromellitic Dianhydride Systems in Polar Solutions", *Chem. Phys.*, **127**, 239 (1988).

[5] R.A. Marcus, "On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I", *J. Chem. Phys.*, **24**, 966 (1956).

[6] T. Kakitani and N. Mataga, "Photoinduced Electron Transfer in Polar Solutions. I. New Aspects of the Role of the Solvent Mode in Electron-Transfer Processes in Charge-Separation Reactions", *Chem. Phys.*, **93**, 381 (1985).

[7] T. Kakitani and N. Mataga, "Different Energy Gap Laws for the Three Types of Electron-Transfer Reactions in Polar Solvents", *J. Phys. Chem.*, **90**, 993 (1986).

[8] T. Kakitani and N. Mataga, "Comprehensive Study on the Role of Coordinated Solvent Mode Played in Electron-Transfer Reactions in Polar Solutions", *J. Phys. Chem.*, **91**, 6277 (1987).

[9] Y. Hatano, M. Saitou, T. Kakitani and N. Mataga, "Monte Carlo Study of the Dielectric Saturation in Molecular Solutions. Physical Bases of the C Mode in Electron-Transfer Reactions", *J. Phys. Chem.*, **92**, 1008 (1988).

[10] J.K. Hwang and A. Warshel, "Microscopic Examination of Free-Energy Relationships for Electron Transfer in Polar Solvents", *J. Am. Chem. Soc.*, **109**, 715 (1987).

[11] E.A. Carter and J.T. Hynes, "Solute-Dependent Solvent Force Constants for Ion- and Neutral Pairs in a Polar Solvent", *J. Phys. Chem.*, **93**, 2184 (1989).

[12] R.A. Kuharski, J.S. Bader, D. Chandler, M. Sprik, M.L. Klein and R.W. Impey, "Molecular Model for Aqueous Ferrous-Ferric Electron Transfer", *J. Chem. Phys.*, **89**, 3248 (1988).

[13] T. Kakitani, A. Yoshimori and N. Mataga, "Theoretical Analysis of Energy Gap Laws of Electron Transfer Reactions. Distribution Effect of Donor-Acceptor Distance, in *Electron Transfer in Inorganic, Organic, and Biological Systems, Advances in Chemistry Series*, J. Bolton, N. Mataga and G. McLendon, eds, *American Chemical Soc.*, in press.

[14] A. Yoshimori and T. Kakitani, "Theoretical Study of the Free Energy Curve as a Function of Reaction Coordiante of Electron Transfer by the Cumulant Expansion Methods", *J. Chem. Phys.*, in press.

[15] A. Yoshimori, T. Kakitani, Y. Enomoto and N. Mataga, "Shapes of the Electron-Transfer Rate vs Energy Gap Relations in Polar Solutions", *J. Phys. Chem.*, **93**, 8316 (1989).

[16] R.A. Marcus, "Exchange Reactions and Electron Transfer Reactions Including Isotopic Exchange. Theory of Oxidation-Reduction Reactions Involving Electron Transfer", *Disc. Faraday Soc.*, **29**, 21 (1960).

[17] A. Warshel, "Dynamics of Reactions in Polar Solvents. Semiclassical Trajectory Studies of Electron-Transfer and Proton-Transfer Reactions", *J. Phys. Chem.*, **86**, 2218 (1982).

[18] D.F. Calef and P.G. Wolynes, "Classical Solvent Dynamics and Electron Transfer. I. Continuum Theory", *J. Phys. Chem.*, **87**, 3387 (1983).

[19] D.F. Calef and P.G. Wolynes, "Classical Solvent Dynamics and Electron Transfer. II. Molecular Aspects", *J. Chem. Phys.*, **78**, 470 (1983).

[20] M. Tachiya, "Effect of the Dielectric Saturation on the Rates of Electron Transfer in Polar Solvents", *Chem. Phys. Letters*, **159**, 505 (1989).

[21] Taken from Table IV in J. Applequist, J.R. Carl and K. Fung, "An Atom Dipole Interaction Model for Molecular Polarizability. Application to Polyatomic Molecules and Determination of Atom Polarizabilities", *J. Am. Chem. Soc.*, **94**, 2952 (1972).

[22] M. Mandel and P. Mazur, "On the Molecular Theory of Dielectric Polarization" *Physica* XXIV, 116 (1958).

[23] Y. Hatano, T. Kakitani, A. Yoshimori, M. Saito and N. Mataga, "Theoretical Study of Dielectric Saturation in Molecular Solutions by the Monte Carlo Simulation", *J. Phys. Soc. Japan*, **59**, 1104 (1990).