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Solvent induced dynamic polarization, vibrational dephasing, and infrared band shape of the C = O stretch mode of acetone in acetonitrile: a new theoretical approach

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Abstract

The solvent induced dynamic polarization and the resultant vibrational dephasing have been studied theoretically for acetone in acetonitrile. A molecular dynamics simulation has been used in conjunction with a molecular orbital calculation to obtain the instantaneous C = O stretch frequency that corresponds to the instantaneous polarized structure of the C = O bond. The infrared band shape calculated for the stochastic limit agrees well with the experiment, showing that the solvent induced dynamic polarization is the primary cause of the dephasing of the C = O stretch vibration of acetone in acetonitrile.

1. Introduction

Chemical reactions in solution are influenced profoundly by the solvent–solute interactions. In a nucleophilic substitution reaction, for instance, the polarized structure of the reactant site, where the nucleophile is to attack, plays a crucial role. Such a polarized structure is likely to be induced stochastically through the solvent–solute interactions (the solvent induced dynamic polarization). It is of vital importance to elucidate the nature of the solvent induced dynamic polarization in order to fully understand the molecular mechanisms of chemical reactions in solution.

In a previous paper, we presented a theoretical model in which the dephasing of a solute molecular vibration is caused primarily by the solvent induced dynamic polarization [1]. The effect of vibrational dephasing manifests as the changes in the band shape in the vibrational spectrum. Therefore, we have an experimental access to the solvent induced dynamic polarization through the measurement of the vibrational spectrum. In the present study, we demonstrate theoretically the correlation among the solvent induced dynamic polarization, vibrational dephasing, and the infrared bandshape of acetone in acetonitrile, using a new molecular dynamics (MD) approach.

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The MD simulation has already been used by several groups to study the process of vibrational dephasing [2–4]. In these previous studies, the intramolecular atomic potential functions were obtained from molecular orbital (MO) calculations of the free molecule, except for the diatomic molecule studied in [3]. However, the electron distribution in a chemical bond is readily distorted by the solvent field and the intramolecular potential functions can change significantly depending on the instantaneous solvent configurations. Such dynamic aspects of the solvent–solute interactions were not taken into account in the previous MD studies. In the present study, the solvent–solute interactions are examined in terms of the short-range Lennard–Jones (LJ) and the long-range Coulomb interactions. While the Lennard–Jones interactions are treated with the standard semiclassical perturbation method [2], the Coulomb interactions are treated with a new approach in which the electric field generated by the solvent molecules is calculated on the basis of an MD simulation. Two different components of the electric field are treated separately. One component is due to the fixed charges on the solvent molecules and is determined by the instantaneous solvent configurations (direct field). The other component is due to the electron polarization of the solvent molecules which is much less dependent on the solvent configurations and which is approximated well by a reaction field from the continuous dielectric medium. The instantaneous $C=O$ stretch frequency of acetone under these electric fields is obtained using finite field MO calculations combined with the self-consistent reaction field (SCRF) method [5]. The stochastic band shape theory is then used to calculate the infrared absorption band shape to be compared with the experiment. The time evolution of the electric dipole moment is also calculated to quantify the solvent induced dynamic polarization of the acetone molecule in acetonitrile.

2. Theoretical basis

The infrared absorption bandshape $I_{\mathrm{IR}}(\omega)$, corresponding to a particular normal coordinate Q, is related to vibrational dephasing through the vibrational correlation function C_{vib} and the rotational correlation function C_{rot},

$$I_{\mathrm{IR}}(\omega) \propto \frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-\mathrm{i}\omega t)C_{\mathrm{vib}}(t)C_{\mathrm{rot}}(t)\mathrm{d}t, \tag{1}$$

$$C_{\mathrm{vib}}(t) \equiv \langle Q(t)Q(0)\rangle, \tag{2}$$

$$C_{\mathrm{rot}}(t) \equiv \langle \boldsymbol{n}(t)\cdot\boldsymbol{n}(0)\rangle, \tag{3}$$

where the angular bracket refers to a classical ensemble average, and $\boldsymbol{n}(t)$ is the molecular axis at time t [6]. It is generally the case in liquids and solutions that the population relaxation makes a negligible contribution to dephasing, so that only pure dephasing needs to be considered. Pure dephasing of a vibration arises from the time-dependent fluctuation of the vibrational frequency. If this frequency fluctuation is induced by a Gaussian process, C_{vib} can be related to the ensemble averaged autocorrelation function of the frequency fluctuation as

$$C_{\mathrm{vib}}(t) = \exp(\mathrm{i}\langle\omega\rangle t)\exp\left[-\langle\omega_1^2\rangle\int_0^t(t-\tau)\psi(\tau)\mathrm{d}\tau\right], \tag{4}$$

$$\psi(t) \equiv \langle\omega_1(t_0)\omega_1(t_0+t)\rangle/\langle\omega_1^2\rangle, \tag{5}$$

$$\omega_1(t) \equiv \omega(t) - \langle\omega\rangle, \tag{6}$$

where $\omega(t)$ is the instantaneous vibrational frequency and $\langle\omega\rangle$ is its mean value [6,7]. Therefore from the time evolution of the instantaneous vibrational frequency and the rotational correlation function obtained by a MD simulation, the infrared absorption bandshape can be calculated.

The intermolecular interactions between the solute and solvent molecules are considered in terms of the short-range LJ and the long-range Coulomb interactions. The instantaneous vibrational frequency $\omega(t)$ can be expressed as

$$\omega(t) = \omega_0 + \Delta\omega_{\mathrm{CL}}(t) + \Delta\omega_{\mathrm{LJ}}(t), \tag{7}$$

where ω_0 is the gas phase vibrational frequency, and $\Delta\omega_{\mathrm{CL}}$ and $\Delta\omega_{\mathrm{LJ}}$ are the instantaneous frequency shifts induced by solvents via the Coulomb interactions and the LJ interactions, respectively.

In the present paper, a new approach is proposed in which Coulomb interactions are divided into two components. One is the direct electric field from the fixed charge of each site of the solvent molecules, and the other is the reaction electric field due to the electron polarization of the solvent molecules. The frequency shift $\Delta\omega_{\mathrm{CL}}$ is given by

$$\Delta\omega_{\mathrm{CL}}(t) \simeq \Delta\omega_{\mathrm{RF}} + \sum_{\alpha}\left(\frac{\partial\omega}{\partial E_\alpha}\right)_{\mathrm{RF}} E_\alpha(t) + \frac{1}{2}\sum_{\alpha,\beta=x,y,z}\left(\frac{\partial^2\omega}{\partial E_\alpha\,\partial E_\beta}\right)_{\mathrm{RF}} E_\alpha(t)E_\beta(t), \tag{8}$$

where $\Delta\omega_{\mathrm{RF}}$ is the frequency shift induced by the electron polarization of the solvent with no direct field, $E_\alpha(t)$ is the time-dependent direct electric field on the solute molecule obtained by an MD simulation. The values of $\Delta\omega_{\mathrm{RF}}$, $(\partial\omega/\partial E_\alpha)_{\mathrm{RF}}$, and $(\partial^2\omega/\partial E_\alpha\,\partial E_\beta)_{\mathrm{RF}}$ are determined by using finite field MO calculations combined with the SCRF method.

The frequency shift via the LJ interactions is obtained according to the semiclassical perturbation approach [2]. If the coordinate Q is assumed to be isolated and the couplings with other modes are neglected, the frequency shift $\Delta\omega_{\mathrm{LJ}}(t)$ can be expressed as

$$\Delta\omega_{\mathrm{LJ}}(t) = -\frac{f}{2\mu^2\omega_0^3}\left[\frac{\partial\Delta V_{\mathrm{LJ}}(t)}{\partial Q}\right]_{Q=0} + \frac{1}{\mu\omega_0}\left[\frac{\partial^2\Delta V_{\mathrm{LJ}}(t)}{\partial Q^2}\right]_{Q=0}, \tag{9}$$

where ΔV_{LJ} is the intermolecular potential energy due to the LJ interactions, f and μ are the coefficient of the cubic term and the reduced mass of the $\mathrm{C=O}$ stretch mode in the gas phase, respectively. The derivatives in Eq. (9) are given by

$$\left[\frac{\partial\Delta V_{\mathrm{LJ}}(t)}{\partial Q}\right]_{Q=0} = \sum_{i}\sum_{\alpha=x,y,z}\left[\frac{\partial\Delta V_{\mathrm{LJ}}(t)}{\partial r_{i\alpha}}\right]_{r_{i\alpha}=0}\frac{\partial r_{i\alpha}}{\partial Q}, \tag{10}$$

$$\left[\frac{\partial^2\Delta V_{\mathrm{LJ}}(t)}{\partial Q^2}\right]_{Q=0} = \sum_{i,j}\sum_{\alpha,\beta=x,y,z}\left[\frac{\partial^2\Delta V_{\mathrm{LJ}}(t)}{\partial r_{i\alpha} r_{j\beta}}\right]_{r_{i\alpha},r_{j\beta}=0}\frac{\partial r_{i\alpha}}{\partial Q}\frac{\partial r_{j\beta}}{\partial Q}, \tag{11}$$

where $r_{i\alpha}$ is the displacement of each site of the acetone molecule. We employ Eq. (10) and Eq. (11) for the analysis of the MD data.

3. Computational details

We apply equilibrium molecular dynamics simulations to a system consisting of 127 solvent molecules and a single acetone molecule in a cubic box with the standard periodic conditions. The side length is chosen to yield a number density of 0.0115 $\mathrm{\AA}^{-3}$,which is the density of the solution at room temperature. A home-made program using the leap-frog algorithm is used. The temperature is maintained at about 298 K with the velocity scalings at 2 ps intervals. All the reported quantities have been obtained after a simulation run of 8 ns, following an initial equilibration period over 100 ps, with an integration time step of 2.5 fs.

The acetone molecule is represented as rigid four sites and acetonitrile is represented as rigid three sites with a methyl group treated as one site [8,9]. Each site of the solute interacts with solvent sites via the LJ plus Coulomb terms of the usual form. LJ parameters between unlike sites are obtained using the Lorentz–Berthelot combination rules [10]. The long-range Coulomb potential is truncated by multiplying the following tapering function $f(r)$,

$$f(r)=\begin{cases}1, & r\le r_{\mathrm{c}}-0.5\,\text{Å}\\ \dfrac{r_{\mathrm{c}}-r}{0.5}, & r_{\mathrm{c}}-0.5\,\text{Å}<r<r_{\mathrm{c}}\\ 0, & r_{\mathrm{c}}\le r.\end{cases} \tag{12}$$

Here r_c is the cutoff length which was set to be half of the box size ($r_c = 11.2$ Å for the acetonitrile solution).

In order to calculate $\Delta\omega_{\mathrm{CL}}$, we use finite field MO calculations combined with the SCRF method. According to the Onsager reaction field model, a dipole of moment $\boldsymbol{\mu}$ at the center of a spherical cavity of radius a_0 surrounded by a uniform dielectric medium having a dielectric constant ε has a reaction field $\boldsymbol{R}$ given by [11]

$$\boldsymbol{R}=\frac{1}{4\pi\varepsilon_0}\,\frac{2(\varepsilon-1)}{2\varepsilon+1}\,\frac{\boldsymbol{\mu}}{a_0^3}. \tag{13}$$

If the electron polarization of solvents is assumed to be independent of their configurations, the reaction field induced by the solvent medium is approximated as

$$\boldsymbol{R}_{\mathrm{opt}}=\frac{1}{4\pi\varepsilon_0}\,\frac{2\left(n_{\mathrm{opt}}^2-1\right)}{2n_{\mathrm{opt}}^2+1}\,\frac{\boldsymbol{\mu}}{a_0^3}, \tag{14}$$

where $n_{\mathrm{opt}}$is the reflactive index ($n_{\mathrm{opt}} = 1.35$ for acetonitrile at 589.3 nm). The cavity radius a_0 is calculated self-consistently to be 3.56 Å by using the VOLUME keyword in the Gaussian 94 program [12]. The geometry optimization and frequency calculations are carried out using the GAMESS program [13] with both the $EFIELD and $SCRF groups. The $EFIELD group calculates the frequency under the direct electric field E, while the $SCRF group takes into account of the effect of reaction field. The level of these calculations is the restricted Hartree–Fock (RHF) with the 6-31 + G(d) basis set, which is reported to be sufficiently high for reproducing the frequency shift of the carbonyl stretch band in solution by using the SCRF method [5]. The harmonic frequencies obtained are scaled with a single factor (0.87) which is equal to the ratio of the experimental frequency in the gas phase to the calculated scaled harmonic frequency with no external and reaction field. The frequency shift due to the field perpendicular to the C = O bond is much smaller (about 1%) than that due to the field parallel to the bond and is neglected in the calculation. The calculated frequencies are shown in Fig. 1, together with the result without the reaction field ($EFIELD only).

Third order polynomials in the direct electric field parallel to the C = O bond (plus sign is used for the direction from the carbon to the oxygen atom of the carbonyl group) are least-squares fitted to these frequencies.

$$\omega_{\mathrm{CL}}\equiv\omega_0+\Delta\omega_{\mathrm{CL}}=\begin{cases}1730.79+6.36\times10^{-9}E-1.27\times10^{-19}E^2\\ 1737.3+5.73\times10^{-9}E-1.18\times10^{-19}E^2 \qquad (\text{direct field only}),\end{cases} \tag{15}$$

where the frequency is in cm^{-1} and the direct electric field E is in Vm^{-1}. In the MD simulation, the electric field induced on the acetone molecule at each time step is assumed to be the the average of the fields on the four sites. The molecular dipole moment of acetone M in these electric fields has also been obtained as

$$M=\begin{cases}3.557-2.26\times10^{-10}E+4.11\times10^{-22}E^2\\ 3.377-2.15\times10^{-10}E+2.89\times10^{-22}E^2 \qquad (\text{direct field only}),\end{cases} \tag{16}$$

where M is in Debye.

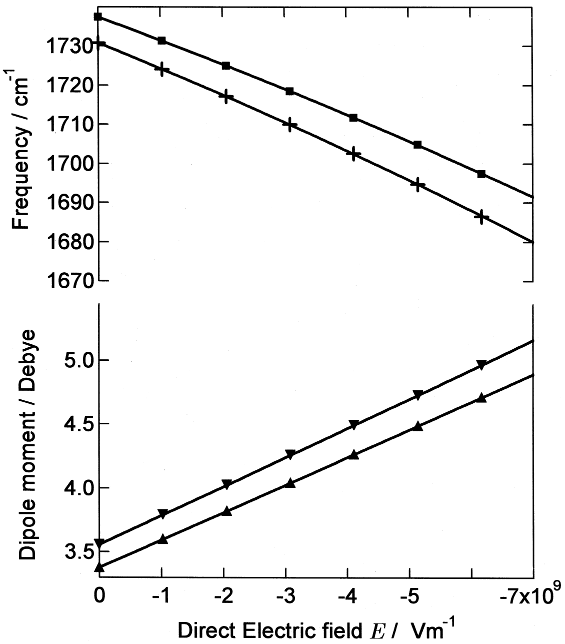

Fig. 1. The electric field dependence of the harmonic C = O stretch frequency and the dipole moment of acetone in acetonitrile. Frequency calculated with direct field only (■), frequency calculated with direct + reaction fields (+); dipole moment calculated with direct field only (▲), dipole moment calculated with direct + reaction fields (▼).

In order to calculate $\Delta\omega_{LJ}$, the gas phase potential curve for the C = O stretch vibration has been obtained from the pointwise ab initio energy calculations at the 21 points along the normal coordinate that were obtained from the geometry optimization and the subsequent normal coordinate calculation. These calculations were carried out using the Gaussian 94 program with the same level, the same basis set and the same scaling factor as those in the calculation of $\Delta\omega_{CL}$.

4. Experimental

The special grade acetone and acetonitrile from Nacalai Tesque Inc. were used as received. The concentration was 0.28 mol dm^{-3}. The infrared absorption spectrum was recorded on a BOMEM MB-120 FTIR spectrometer with a 0.1 mm KBr cell. The wavenumber resolution was 1 cm^{-1}.

5. Results and discussion

The calculated instantaneous vibrational frequencies of the C = O stretch vibration are shown in Fig. 2 for the time range between 500 and 520 ps. It is clearly seen from the figure that the C = O stretch frequency fluctuates very rapidly according to the change in the solvent configurations and that the magnitude of the fluctuation is as large as 20 cm^{-1}. The calculated instantaneous molecular dipole moments of acetone in the same time range are also shown in Fig. 2. The time evolution of the dipole moment corresponds well to the C = O vibrational frequency, indicating that the C = O frequency is stochastically modulated by the solvent induced dynamic polarization. Acetone is polarized to have $M = 5.2$ Debye at 517 ps which corresponds to an

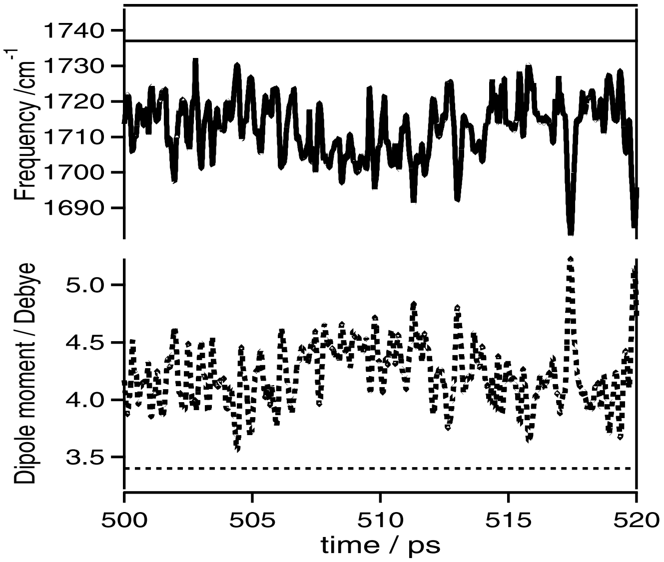

Fig. 2. Instantaneous vibrational frequency of the C = O stretch and the instantaneous molecular dipole moment of acetone. Thick solid line: the instantaneous vibrational frequency; thin solid line: the vibrational frequency in the gas phase; thick dashed line: the instantaneous molecular dipole moment; the thin dashed line: the molecular dipole moment in the gas phase.

almost fully charge separated structure. Such a highly polarized structure appears at about every 1 ns and may well contribute to nuclepohilic reactions of acetone in polar solvents. The correlation between the solvent induced dynamic polarization and reaction rates in solution has already been discussed by us [14,15].

Fig. 3 shows the distribution of the instantaneous vibrational frequency of the acetone C = O stretch and that of the instantaneous molecular dipole moment of acetone. The frequency distribution is represented by a

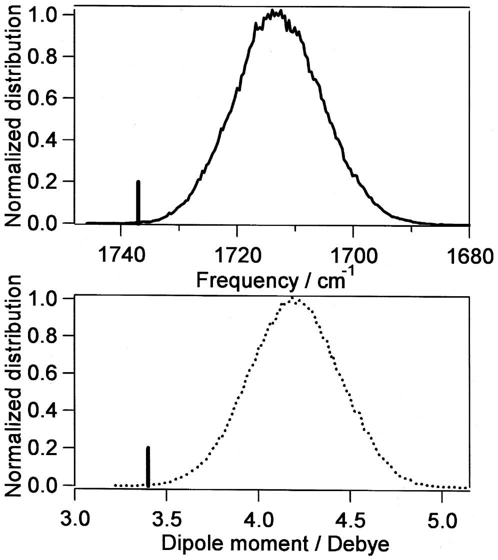

Fig. 3. The distribution of the instantaneous vibrational frequency and the molecular dipole moment. Solid line: the vibrational frequency; dashed line: the magnitude of the molecular dipole moment; thick vertical lines: the values in the gas phase.

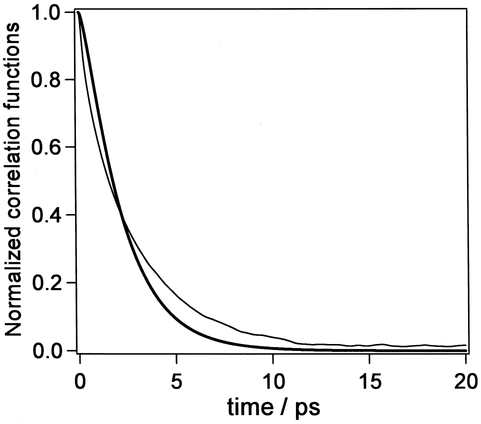

Fig. 4. The autocorrelation functions. Thick solid line: the envelope of the vibration autocorrelation function of the C = O stretch coordinate C_{vib} ; thin solid line: the rotational autocorrelation function of acetone C_{rot}.

Gaussian function with a full width at half-maximum (FWHM) of 18 cm^{-1}, having a peak value at 1713 cm^{-1}, which is 24 cm^{-1} red shifted from the gas phase value (1737 cm^{-1}). The dipole moment distribution is also represented by a Gaussian function with a full width at half-maximum of 0.7 Debye, having a peak value of 4.2 Debye. The value 4.2 Debye is larger by 0.8 Debye than the gas phase value (3.4 Debye). Acetone is significantly more polarized in acetonitrile than in the gas phase.

Next, we compute the autocorrelation function of the C = O stretch coordinate C_{vib} from Eq. (4) and the rotational correlation function C_{rot} from Eq. (3). Fig. 4 shows these autocorrelation functions. They both have initial gaussian and subsequent exponential decays. The exponential decay time constant is 2.1 ps for the vibrational correlation function and 2.8 ps for the rotational correlation function.

Finally, we obtain the infrared absorption bandshape from Eq. (1). Fig. 5 displays the calculated bandshape, together with the experimental result. As is evident from the figure, there is very good agreement between the calculation and the experiment. The bandshape obtained by our calculation is very close to a Lorentzian, showing that the vibrational dephasing in this system can be regarded as in the fast modulation limit.

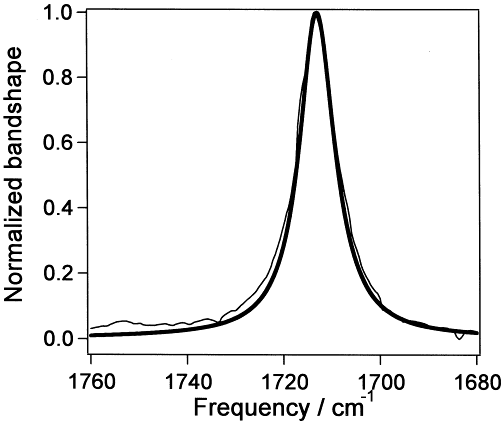

Fig. 5. Infrared absorption bandshape for the C = O stretch vibration of acetone. Thick solid line: calculated result; thin solid line: experimental result.

Table 1
Frequency shifts and band width of acetone in acetonitrile arising from different forces (Coulomb, LJ) and the rotation term (Rot). The results on the right (Obs) are the experimental data. Values in parentheses include only the direct electric field.

	Calc				Obs
	Coulomb	LJ	Rot	Total	
frequency shift (cm-1)	−25.4 (−17.0)	1.4	–	−24.0	−24
band width (cm-1)	5.0 (4.1)	0.2	3.8	8.9	9.6

We analyze the contributions of the Coulomb term (direct field + reaction field, reaction field only), the LJ term, and the rotation term to the frequency shift and the bandwidth by calculating the bandshape considering only one of the three terms. The results are summarized in Table 1, together with the experimental value. Both the frequency shift and the bandwidth are determined predominantly by the Coulomb term, and the contribution of the LJ term is relatively small. The contribution of the rotation to the bandwidth is comparable with the Coulomb term. Thus, we conclude that the vibrational dephasing in the present system is dominated by the Coulomb interactions. We also find that the contribution of the reaction field cannot be neglected and that it is essential to include the contribution of electron polarization when analyzing vibrational band shapes in solution.

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References

[1] H. Hamaguchi, Mol. Phys. 89 (1996) 463.
[2] D.W. Oxtoby, J. Chem. Phys. 68 (1978) 5528.
[3] S. Okazaki, I. Okada, J. Chem. Phys. 98 (1993) 607.
[4] R. Ray, J.T. Hynes, J. Chem. Phys. 108 (1998) 142.
[5] M.W. Wong, K.B. Wiberg, J. Chem. Phys. 95 (1991) 8991.
[6] D.W. Oxtoby, Adv. Chem. Phys. 40 (1979) 1.
[7] M. Toda, R. Kubo (Eds.), Basic Mod. Phys. 5, Statistical Physics (in Japanese), Iwanami Shoten, 2nd edition, 1978.
[8] D.M.F. Edwards, Mol. Phys. 51 (1984) 1141.
[9] A. Brodka, T.W. Zerda, J. Chem. Phys. 104 (1996) 6313.
[10] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, 1987.
[11] L. Onsager, J. Am. Chem. Soc. 58 (1936) 1486.
[12] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople (Gaussian, Inc., Pittsburgh, PA, 1995).
[13] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.
[14] H. Hamaguchi, K. Iwata, Chem. Phys. Lett. 208 (1993) 465.
[15] V. Deckert, K. Iwata, H. Hamaguchi, J. Photochem. Photobiol. 102 (1996) 35.