Raman Noncoincidence Effect and Intermolecular Interactions in Liquid Dimethyl Sulfoxide: Simulations Based on the Transition Dipole Coupling Mechanism and Liquid Structures Derived by Monte Carlo Method

Hajime Torii* and **Mitsuo Tasumi**

Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received June 1, 1994)

Model calculations are performed on the Raman noncoincidence effect (frequency difference between the isotropic and anisotropic components) observed in the region of the S=O stretching band of liquid dimethyl sulfoxide (DMSO). Liquid structures are obtained by Monte Carlo simulations, by using potential functions without specific interactions involving the hydrogen atoms of the methyl groups. Intermolecular coupling between the S=O stretches is evaluated by the transition dipole coupling mechanism. The magnitude and the direction of the transition dipole are calculated by ab initio molecular orbital calculations at the second-order Møller–Plesset perturbation level with a basis set extended from 6-31G(2d,p). The calculated sign and magnitude of the Raman noncoincidence are in reasonable agreement with the observed, indicating that the observed large Raman noncoincidence can be mostly explained by the liquid structures obtained without specific interactions involving the hydrogen atoms of the methyl groups. The pair distribution function of liquid DMSO is also calculated to the second order in the orientation correlation of molecules. The origin of the Raman noncoincidence effect is discussed by comparing the cases of liquid DMSO, acetone, and methanol.

Understanding of the liquid structure and intermolecular interactions in the liquid phase is important for detailed studies of the microscopic aspects of solvation, dissipation processes, and chemical reactions. Intermolecular interactions and the extent of structural order in liquid dimethyl sulfoxide (DMSO) have been investigated by various methods such as measurements of thermodynamic[1—3] and dielectric[4,5] properties, X-ray and neutron scattering experiments,[6—9] and computer simulations.[9—11] Because of its high boiling point (189 °C), a large value of the entropy of vaporization (124 $\mathrm{J\,mol^{-1}\,K^{-1}}$), and other unusual thermodynamic properties, DMSO is considered to be a "strongly associated" liquid.[1,2] In spite of these extensive studies, however, the liquid structure of DMSO has not been clarified at the molecular level.

It has been considered that the properties of DMSO as a strongly associated liquid originate from the formation of hydrogen bonds involving the hydrogen atoms of the methyl groups.[1—3] The X-ray and neutron scattering experiments[8] have shown the presence of intermolecular O···H distances in the range of 2—3 Å. This experimental result as well as the sharp first peak in the radial distribution function of the C···O pair derived from computer simulations[10,11] has been considered to support the view that the hydrogen atoms of the methyl groups are involved in hydrogen bonding.[10,11] However, Luzar et al. have shown[9] that the sharp first peak of the C···O radial distribution function partially arises from packing of molecules due to repulsive intermolecular forces and not necessarily from hydrogen bonding.

It has also been suggested[2] that the sulfur and oxygen atoms form linear intermolecular chains in liquid DMSO. The presence of such intermolecular chains may seem to contradict the result of the measurement of dielectric properties that the Kirkwood correlation factor g is only slightly larger than unity.[5] Such a low value of g indicates that the orientation correlation of molecules in liquid DMSO is significantly weaker than in liquid water. However, as claimed by Fini and Mirone,[12] a low value of g does not necessarily mean that the short-range order (such as the one arising from dipole–dipole interactions) does not exist in the liquid. From the previous computer simulations, two different results have been obtained on the orientation correlation of neighboring molecules in liquid DMSO. Rao and Singh[10] have claimed that S=O···S=O chains do not exist and neighboring molecules are aligned roughly in an antiparallel manner, on the basis of the result that the radial distribution functions of the S···S and O···O pairs are very similar. Their claim is not legitimate, however, because the radial distribution functions of these two pairs of atoms become very similar even when the neighboring molecules are aligned parallel linearly in a head-to-tail manner. On the contrary, Vaisman and Berkovitz$^{11)}$ have discussed that DMSO molecules in an S=O···S=O chain are aligned with parallel dipole moments, while the neighboring DMSO molecules from the adjacent chains are oriented with antiparallel dipole moments. Since orientation correlation in the liquid has not been evaluated quantitatively in both of these studies, a definite conclusion has not been obtained.

In view of the limited understanding of the liquid structure of DMSO presently available, we consider that the extent of local order in liquid DMSO should be further examined. We have recently shown that information on the local order in liquids can be obtained from simulations of the Raman noncoincidence effect.$^{13,14)}$ The Raman noncoincidence effect is the phenomenon that the frequencies of the isotropic and anisotropic components of a single Raman band do not coincide.$^{12-21)}$ The sign and the magnitude of the Raman noncoincidence are primarily determined by relative orientation of the nearest neighbors in the liquid, within 6 Å in the case of liquid acetone.$^{14)}$

In the present study, we calculate the isotropic and anisotropic components of the Raman scattering of liquid DMSO in the region of the S=O stretching band, on the basis of the liquid structure obtained by the Monte Carlo method. We use the potential functions derived by Luzar and Chandler.$^{22)}$ Since the hydrogen atoms of the methyl groups are not explicitly included as the interaction sites in these potential functions, we can see whether the local order realized without specific interactions involving the hydrogen atoms of the methyl groups is sufficient to explain the large Raman noncoincidence$^{12)}$ observed in the S=O stretching band of liquid DMSO. Coupling of the S=O stretches between the molecules in the liquid is evaluated by the transition dipole coupling mechanism.$^{13,23)}$ The magnitude and the direction of the transition dipole of the S=O stretch of a DMSO molecule are obtained by ab initio molecular orbital (MO) calculations. We also calculate the pair distribution function of liquid DMSO to the second order in the orientation correlation of molecules.$^{14,20,24,25)}$ On the basis of the results of calculations, we discuss the short-range order in the liquid and the magnitude of the transition dipole in relation to the observed large Raman noncoincidence.

Computational Procedure

Ab initio MO calculations for a DMSO molecule are performed at the second-order Møller–Plesset perturbation (MP2) level by using the Gaussian 92 program.$^{26)}$ Since d orbitals on the sulfur atom are involved in the S=O $(d \leftarrow p)_\pi$ double bond,$^{1,27-29)}$ those orbitals should be included in the basis set to adequately describe the electronic structure of this molecule. We use the 6-31G-(2d,p) basis set augmented by *f* functions on the sulfur atom and diffuse *s* and *p* functions on the sulfur and oxygen atoms for calculating the structure, vibrational modes, and transition dipoles of a DMSO molecule. We also show the results obtained by using smaller basis sets for comparison.

Monte Carlo simulations are performed by using the standard Metropolis sampling scheme and the periodic boundary condition,$^{30,31)}$ in the same way as in our previous studies.$^{13,14)}$ Random numbers are generated by using a subroutine given in Ref. 32. For the purpose of calculating the pair distribution function, we include 1024 molecules in the simulation box, and the liquid structures of every 5000 steps are extracted from the 6×10^6-step simulation (after the system is brought into thermal equilibrium). In order to obtain liquid structures to be used for calculating polarized Raman spectra, simulations are performed over 4×10^6 steps on a smaller 256-molecule system, and configurations of every 10000 steps are extracted, so that polarized Raman spectra can be calculated with the available computational resources. The volume of the simulation box is fixed to the value obtained from the observed density$^{33)}$ of the liquid. The temperature is set to 25 °C. The potential functions derived by Luzar and Chandler$^{22)}$ to describe the liquid structure of DMSO, named P1 and P2 by those authors, are used. In the P1 potential function, only the sulfur and oxygen atoms are assumed to have partial charges, while the carbon atoms of the methyl groups are also assumed to have partial charges in the P2 potential function. In both of these potential functions, the hydrogen atoms of the methyl groups are not included as the interaction sites.

Polarized Raman spectra are calculated by treating each molecule as an oscillator having a transition dipole, in the same way as in our previous study.$^{13)}$ The averages of the spectra for the 400 configurations obtained from the Monte Carlo simulations are taken. Normal modes of the 256-molecule system for each configuration, which result from the coupling of the S=O stretches of all the molecules in the system, are obtained by solving the eigenvalue problem of the 256×256 $\boldsymbol{F}$ matrix. The diagonal elements of this $\boldsymbol{F}$ matrix are set to 0.657 mdyn Å^{-1} amu^{-1} (1 dyn$=10^{-5}$ N), which corresponds to the vibrational frequency of 1056 cm^{-1}. The off-diagonal elements are determined on the basis of the transition dipole coupling mechanism. The transition dipole of each molecule, whose magnitude and direction are obtained from the ab initio MO calculations mentioned above, is assumed to be located at the center of the S=O bond. The absolute magnitude of the Raman tensor need not be specified for the purpose of calculating band profiles. The Raman tensor of each molecule is assumed to be axially symmetric with respect to the S=O bond. The ratio of the magnitudes of the principal axes of the Raman tensor is adjusted to 14 : 1 so that the observed$^{34)}$ and calculated depolarization ratios are in agreement. All the other details of the calculations of the polarized Raman spectra are the same as in our previous study (Section II and III B of Ref. 13).

The pair distribution function $g\ (\boldsymbol{R}_{ij};\ \boldsymbol{\Omega}_i,\ \boldsymbol{\Omega}_j)$ of liquid DMSO, expanded to the second order in the orientation correlation of molecules in the form[19,25]

$$g\ (\boldsymbol{R}_{ij};\boldsymbol{\Omega}_i,\boldsymbol{\Omega}_j)=g_0(R_{ij})+h_\Delta(R_{ij})\boldsymbol{\Omega}_i\cdot\boldsymbol{\Omega}_j +h_\mathrm{D}(R_{ij})[3(\boldsymbol{R}_{ij}\cdot\boldsymbol{\Omega}_i)(\boldsymbol{R}_{ij}\cdot\boldsymbol{\Omega}_j)/R_{ij}^2-\boldsymbol{\Omega}_i\cdot\boldsymbol{\Omega}_j] \quad (1)$$

is calculated as described in Ref. 25. Here, $\boldsymbol{R}_{ij}$ ($=\boldsymbol{R}_i-\boldsymbol{R}_j$) is the vector from molecule j to i, and R_{ij} is the length of this vector ($R_{ij}=|\boldsymbol{R}_{ij}|$). $\boldsymbol{\Omega}_i$ and $\boldsymbol{\Omega}_j$ are the unit vectors representing the orientation of axes of these molecules. We take the vector $\boldsymbol{\Omega}_i$ to be parallel to the transition dipole of the S=O stretch, which is obtained from the ab initio MO calculations. The vector representing the location of molecule i, $\boldsymbol{R}_i$, is evaluated at the center of the S=O bond. In Eq. 1, $g_0(R)$, $h_\Delta(R)$, and $h_\mathrm{D}(R)$ are the components of the zeroth, first, and second order in terms of the orientation correlation of molecules. A positive value of $h_\Delta(R)$ indicates that molecules are arranged in a parallel manner, while a positive value of $h_\mathrm{D}(R)$ means that the orientation of molecules is stable in terms of dipole–dipole interactions.

Calculations are performed on a Hewlett–Packard workstation at the Research Center for Spectrochemistry of the University of Tokyo, and on an NEC SX-3 supercomputer at the Computer Center of the Institute for Molecular Science.

Results and Discussion

Structure, Vibrational Modes, and Transition Dipoles of a Dimethyl Sulfoxide Molecule. The structure parameters of a DMSO molecule obtained from ab initio MO calculations at the MP2 level with various basis sets are shown in Table 1. The skeleton of a DMSO molecule consisting of the sulfur, oxygen, and carbon atoms is in a pyramidal form, as is evident from the sum of the angles $2\theta(\mathrm{OSC})+\theta(\mathrm{CSC})$ smaller than 360°. Since d orbitals on the sulfur atom are involved in the π bonding between the sulfur and oxygen atoms, the double-bond character of the S=O bond cannot be correctly described without *d* functions on the sulfur atom.[29] As shown in Table 1, the S=O bond length is calculated to be 1.677 Å with the 6-31G basis set, which is longer by about 0.17 Å than the bond length obtained with the 6-31G* basis set (1.510 Å). The S–C bond length also decreases significantly (from 1.894 to 1.806 Å) by changing the basis set from 6-31G to 6-31G*. In order to obtain the quality of the "split valence plus polarization" basis set for describing the double-bond character of the S=O bond, two sets of *d* functions and one set of *f* functions are needed on the sulfur atom. By changing the basis set from 6-31G* to 6-31G(2d) or 6-31G(2d,p), the S=O bond length decreases by about 0.01 Å (from 1.510 to 1.500 or 1.499 Å). By further augmenting the basis set with *f* functions on the sulfur atom (basis set I), the S=O bond length is calculated to be as short as 1.490 Å. Diffuse functions also have a significant effect on the S=O bond length. By adding one diffuse sp shell on both the sulfur and oxygen atoms to basis set I (thus resulting in basis set II in Table 1), the S=O bond length changes by more than 0.01 Å. Considering the reliability and feasibility of the calculations, we have decided to use basis set II for calculating vibrational modes and transition dipoles in the present study. This basis set consists of 6-31+G(2df) for the sulfur atom, 6-31+G(2d) for the oxygen atom, and 6-31G(2d,p) for the carbon and hydrogen atoms.

The vibrational frequencies and infrared intensities calculated at the MP2 level with basis set II are shown in Table 2, and are compared with the experimental results taken from Refs. 6 and 35. Since the calculated force constants are not scaled, most of the calculated frequencies are higher than the observed. Nonetheless, the calculated pattern of the infrared intensities in the whole frequency region is in good agreement with the experimental result,[35] indicating that the calculated vibrational modes and dipole derivatives are reliable. The assignments of individual modes can be made uniquely as shown in this Table 2. The S=O stretch has the strongest infrared intensity. This strong intensity arises from the large magnitude of the transition dipole, which is one of the origin of the large Raman noncoincidence effect observed for this mode in the liquid.

From the above ab initio MO calculations, the transition dipole of the S=O stretch is calculated to be 1.883 $\mathrm{D\,Å^{-1}\,amu^{-1/2}}$ in magnitude and to make an angle of 13.65° with the S=O bond. Since the skeleton of a DMSO molecule is in a pyramidal form, it is reasonable that the transition dipole is tilted from the O→S vector toward the sum of the two S→C vectors.

Polarized Raman Spectra and Pair Distribution Functions of Liquid Dimethyl Sulfoxide. In Fig. 1 are shown the isotropic and anisotropic components of the S=O stretching Raman band calculated by using the liquid structures of DMSO obtained with the P2 potential function. There are 256 normal modes for each of the 400 configurations of the liquid taken from the Monte Carlo simulation, because 256 molecules are included in the simulation box and one vibrational degree of freedom (the S=O stretch) is taken into account for each molecule in the simulation of the polarized Raman spectra. The spectra shown in Fig. 1 therefore consist of 102400 (=256×400) normal modes in total. The intensities of the isotropic and anisotropic components for these normal modes are calculated by using Eqs. 2—6 of Ref. 13. Each of these normal modes is assumed to give rise to a Gaussian Raman band with a half width at half maximum of 12.5 $\mathrm{cm^{-1}}$, so that the width of the calculated total Raman band profile is in reasonable agreement with the observed.[12,35] We note

Table 1. Calculated Molecular Structure Parameters of Dimethyl Sulfoxide[a,b,c]

	Basis set					
	6-31G	6-31G*	6-31G(2d)	6-31G(2d,p)	Basis I[d]	Basis II[e]
r(S =O)	1.677	1.510	1.500	1.499	1.490	1.503
r(S –C)	1.894	1.806	1.809	1.809	1.804	1.800
r(C –H$_1$)	1.093	1.091	1.094	1.087	1.087	1.087
r(C –H$_2$)	1.095	1.093	1.095	1.088	1.088	1.088
r(C –H$_3$)	1.094	1.093	1.096	1.088	1.088	1.089
θ(OSC)	105.6	107.4	106.8	106.7	107.0	106.4
θ(CSC)	97.0	95.7	95.2	95.0	95.0	95.7
θ(SCH$_1$)	106.6	107.4	107.2	107.1	107.1	106.9
θ(SCH$_2$)	107.9	109.3	108.9	108.7	108.9	108.6
θ(SCH$_3$)	108.9	110.3	110.5	110.3	110.1	109.9
θ(H$_1$CH$_2$)	110.2	109.2	109.5	109.7	109.7	109.9
θ(H$_1$CH$_3$)	111.1	109.7	109.7	109.9	109.9	110.0
τ(OSCH$_1$)	70.4	67.6	68.1	68.2	68.0	68.2

a) In units of Å (bond lengths) and degrees (bond angles). b) The results calculated at the MP2 level. c) H$_2$ and H$_3$ are *trans* to the C and O atoms, respectively, with respect to the S–C bond. d) 6-31G(2d,p) basis set augmented by *f* functions on the S atom. e) 6-31G(2d, p) basis set augmented by *f* functions on the S atom and diffuse *s* and *p* functions on the S and O atoms.

Table 2. Vibrational Frequencies, Infrared Intensities, and Assignments of the Normal Modes of Dimethyl Sulfoxide

Obsd[a]		Calcd[c]			
Freq./cm^{-1}	IR int.	Freq./cm^{-1}	Sym.	IR int./km mol^{-1}	Assignment (PED)[d,e]
2998	s	3242	a′	0.7	CH$_3$ asym str$_{//}$ (100)
		3242	a″	0.1	CH$_3$ asym str$_{//}$ (99)
		3235	a′	3.5	CH$_3$ asym str$_\perp$ (101)
		3231	a″	0.0	CH$_3$ asym str$_\perp$ (100)
2917	m	3115	a′	3.4	CH$_3$ sym str (100)
		3113	a″	0.9	CH$_3$ sym str (99)
1435	s	1527	a′	20.3	CH$_3$ asym bend$_\perp$ (87)
1414	m	1507	a″	0.1	CH$_3$ asym bend$_\perp$ (88)
		1502	a′	3.9	CH$_3$ asym bend$_{//}$ (87)
1402	m	1489	a″	9.5	CH$_3$ asym bend$_{//}$ (87)
1303	m	1375	a′	10.3	CH$_3$ sym bend (103)
(1290)		1355	a″	2.0	CH$_3$ sym bend (104)
1070	vs	1102	a′	149.9	S=O str (89)
1008	m	1057	a′	15.3	CH$_3$ rock$_{//}$ (70)
945	s	982	a′	10.5	CH$_3$ rock$_\perp$ (59), S=O str (12)
918	m	960	a″	6.1	CH$_3$ rock$_\perp$ (72)
883	w	927	a″	2.7	CH$_3$ rock$_{//}$ (85)
683	s	723	a″	11.3	S–C str (91), CH$_3$ rock$_\perp$ (11)
661	m	697	a′	4.8	S–C str (99)
378	s	377	a′	7.0	OSC bend (71), CH$_3$ rock$_\perp$ (26)
329	s	318	a″	8.4	OSC bend (107), CH$_3$ rock$_\perp$ (19)
305	w	296	a′	0.4	CSC bend (95), OSC bend (44)
248[b]		255	a′	0.4	CH$_3$ tor (106)
214[b]		208	a″	0.0	CH$_3$ tor (112), CH$_3$ rock$_\perp$ (12)

a) Ref. 35 (dilute solution in CCl$_4$ or CS$_2$). b) Ref. 6 (neutron inelastic scattering). c) Calculated at the MP2 level with basis set II. (See footnote e of Table 1.) d) Abbreviations: str, stretching; bend, bending; rock, rocking; tor, torsion; sym, symmetric; asym, asymmetric. e) The symbols // and ⊥ denote the direction of vibration with respect to the CSC plane.

that the isotropic and anisotropic Raman bands shown in Fig. 1 are different from the spectrum of "density of states". There are many normal modes for which the intensities of the isotropic and anisotropic components are negligibly small [Eqs. 3 and 4 of Ref. 13].

The calculated frequencies of the isotropic and anisotropic components are summarized in Table 3, and are compared with the experimental results taken from Ref. 12. The calculated frequencies obtained by using the P1 potential function are also given in this Ta-

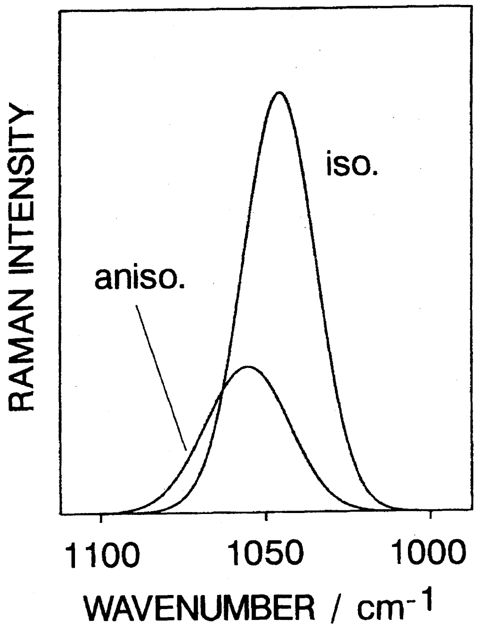

Fig. 1. Calculated isotropic and anisotropic components of the S=O stretching Raman band.

Table 3. Calculated and Observed Frequencies of the S=O Stretching Band of Liquid Dimethyl Sulfoxide

		Frequency/cm^{-1}		
	Potential	ν_{iso}	ν_{aniso}	$\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$
Obsd[a)]		1042	1056	14
Obsd[b)]		1044	1057	13
Calcd	P1	1044	1055	11
Calcd	P2	1046	1056	10

a) From Table 1 Ref. 12. b) Extrapolated from the frequencies in solution of high concentration (Fig. 2 of Ref. 12).

ble 3. Fini and Mirone[12)] have observed the isotropic and anisotropic components in dilute to concentrated solutions of DMSO as well as in the neat liquid, and have confirmed that the frequency separation of these two components arises from intermolecular interactions between DMSO molecules. As shown in Table 3, the calculated sign and magnitude of the frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ are in reasonable agreement with the observed. This result indicates that the observed large Raman noncoincidence can be mostly explained by the liquid structures obtained without specific interactions involving the hydrogen atoms of the methyl groups.

The frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ of the S=O stretching band of liquid DMSO shown above is larger than that of the C=O stretching band of liquid acetone, which is about 6 cm^{-1}.[13,16)] There are two important factors determining the magnitude of the Raman noncoincidence; one is the magnitude of transition dipole giving rise to the coupling of vibrations between molecules, and the other is the relative orientation of neighboring molecules in the liquid.

The magnitude of transition dipole of the S=O stretch of DMSO is 1.883 D Å^{-1} amu$^{-1/2}$ as shown above, which is smaller than that of the C=O stretch of acetone (2.08 D Å^{-1} amu$^{-1/2}$) by a factor of 0.9. Although the transition dipole is smaller in the case of the S=O stretch of DMSO, its effect on the Raman noncoincidence is larger, because its vibrational frequency is lower. The contribution of the transition dipole coupling to the frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ is proportional to $|\partial\mu/\partial Q|^2/(f_{\mathrm{d}})^{1/2}$, where $|\partial\mu/\partial Q|$ is the magnitude of transition dipole, and f_{d} is the diagonal force constant.[19)] The diagonal force constant of the S=O stretch of DMSO is 0.657 mdyn Å^{-1} amu^{-1} as noted in the previous section, while that of the C=O stretch of acetone is 1.733 mdyn Å^{-1} amu^{-1} (Ref. 13). Hence, if we change the values of $|\partial\mu/\partial Q|$ and f_{d} of the C=O stretch of acetone to those of the S=O stretch of DMSO and use the liquid structure of acetone, the calculated frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ would increase from 6 to 8 cm^{-1}. Since this value is smaller than the frequency separation calculated for the S=O stretching band of liquid DMSO given in Table 3, the difference in the liquid structures between acetone and DMSO is also important for the difference in the frequency separations $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ between these two liquids.

According to Logan's formula,[20)] the contribution of the orientation correlation of molecules to the frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ is approximately proportional to $\rho H_{\mathrm{D}}(\infty)$, where ρ is the number density of the liquid, and

$$H_{\mathrm{D}}(r)=\int_0^r \mathrm{d}R\frac{h_{\mathrm{D}}(R)}{R} \tag{2}$$

The three components (g_0, h_Δ, and h_{D}) of the pair distribution functions of liquid DMSO calculated by using the P1 and P2 potential functions are shown in Figs. 2 and 3, respectively. In both cases, $h_{\mathrm{D}}(R)$ in the region of the nearest neighbors ($R \leqq 6$ Å) is positive, indicating that the relative orientation of neighboring molecules conforms to the concept of dipole–dipole interactions. The nearest neighbors are classified into those of negative $h_\Delta(R)$ in the 3—4 Å region and those of positive $h_\Delta(R)$ in the 4—6 Å region. The molecules are arranged side by side and oriented in an antiparallel manner in the former group, while the molecules are arranged head-to-tail in the latter group. The negative value of $h_{\mathrm{D}}(R)$ around $R \cong 7$ Å results from intermolecular interactions among more than three molecules, in which relative orientations of pairs of molecules are perturbed by the existence of other molecules. The positive and negative values of $h_{\mathrm{D}}(R)$ beyond the shell of the nearest neighbors mostly cancel with each other in evaluating the integral $H_{\mathrm{D}}(\infty)$. As a consequence, $H_{\mathrm{D}}(\infty)$ is primarily determined by the relative orientation of the nearest neighbors in the liquid. We should also note, however, that the differences between the profiles of $h_{\mathrm{D}}(R)$ in Figs. 2 and 3 are not strongly reflected in the magnitude of the Raman noncoincidence, since the con-

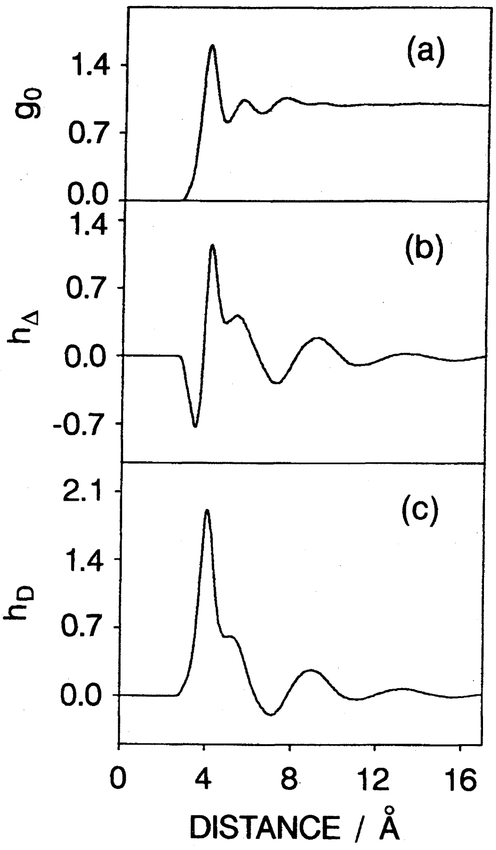

Fig. 2. Three components of the pair distribution function [a: $g_0(R)$, b: $h_\Delta(R)$, c: $h_D(R)$] of liquid dimethyl sulfoxide calculated by using the P1 potential function.

tributions of the nearest neighbors are evaluated only on the average in the integral $H_D(\infty)$. From $h_D(R)$ shown in Figs. 2 and 3, we estimate $H_D(\infty)$ to be 0.600 and 0.484, respectively, for the liquid structures obtained by using the P1 and P2 potential functions. These values are larger than 0.415, which is the value of $H_D(\infty)$ obtained for liquid acetone.[14] The number density ρ of liquid DMSO (8.44×10^{-3} Å^{-3}) is also larger than that of liquid acetone (7.90×10^{-3} Å^{-3}). Because of these factors as well as the factor of $|\partial\mu/\partial Q|^2/(f_d)^{1/2}$, the frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ for the S=O stretching band of liquid DMSO is calculated to be as large as 10—11 cm^{-1} as shown in Table 3.

The difference between the observed and calculated frequencies in Table 3 may originate from the absence of polarization effect[9] (due to many-body interactions) in the potential functions used in the Monte Carlo simulations or from a perturbation on the S=O stretch by the CH_3 rock in the 1020—1000 cm^{-1} region. We also note that the magnitude of transition dipole we have employed in this study may be slightly too small. At the Hartree–Fock level (which does not include the effect of electron correlation) with basis set II, it is calculated to be 2.005 D Å^{-1} amu$^{-1/2}$, which is larger by 6.5% than the value employed in this study (1.883 D Å^{-1} amu$^{-1/2}$).

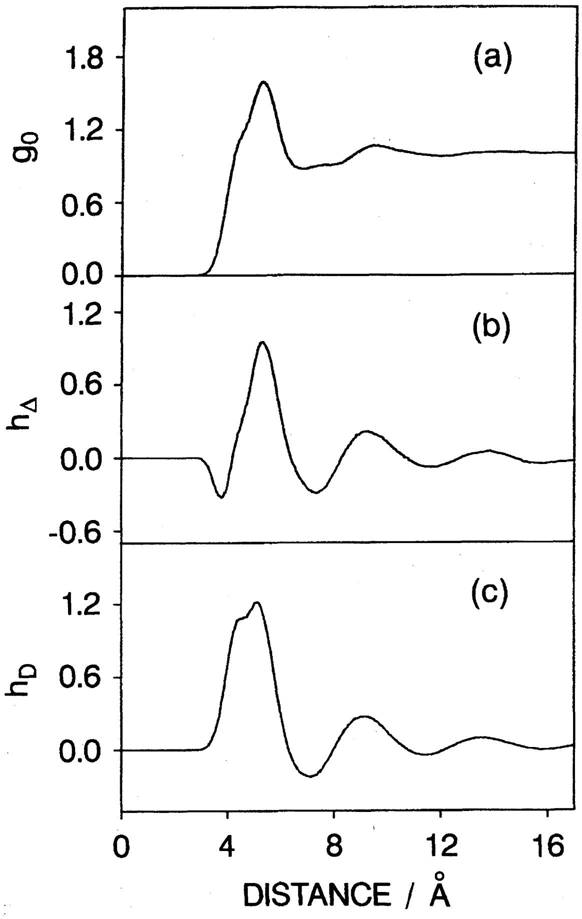

Fig. 3. Three components of the pair distribution function [a: $g_0(R)$, b: $h_\Delta(R)$, c: $h_D(R)$] of liquid dimethyl sulfoxide calculated by using the P2 potential function.

In the case of liquid methanol, relative orientation of the neighboring molecules is primarily determined by hydrogen bonding, and not by dipole–dipole interactions. As a consequence, the sign of the frequency separation $\nu_{\mathrm{aniso}}-\nu_{\mathrm{iso}}$ is reversed in the C–O stretching band of liquid methanol as compared with the case of the C=O stretching band of liquid acetone.[13,17] In the S=O stretching band of liquid DMSO, such reversed order of the isotropic and anisotropic components does not exist. The results of the present study show that the Raman noncoincidence effect of the S=O stretching band of liquid DMSO mostly originates from the local order in the liquid due to dipole–dipole interactions, and that the observed large Raman noncoincidence can be explained without assuming any specific clustering of DMSO molecules.

As shown above, the second-order term $[h_D(R)]$ in the pair distribution function contributes to the sign and the magnitude of the Raman noncoincidence in the form of the integral $H_D(\infty)$ defined in Eq. 2. Since the positive and negative values of $h_D(R)$ beyond the shell of nearest neighbors mostly cancel with each other in the integral $H_D(\infty)$, the sign and the magnitude of the Raman noncoincidence are primarily determined by the relative orientation of nearest neighbors in the liquid.[14)] The Raman noncoincidence effect is therefore a useful tool for examining the extent of local order in the liquid, and provides information complementary to those obtained by other methods for the studies of liquid structures.

References

1) D. Martin, A. Weise, and H. -J. Niclas, *Angew. Chem., Int. Ed. Engl.*, **6**, 318 (1967).
2) A. J. Parker, *Q. Rev., Chem. Soc.*, **16**, 163 (1962).
3) H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960).
4) R. L. Amey, *J. Phys. Chem.*, **72**, 3358 (1968).
5) J. F. Casteel and P. G. Sears, *J. Chem. Eng. Data*, **19**, 196 (1974).
6) G. J. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady, and E. F. X. Lyden, *J. Chem. Phys.*, **50**, 2140 (1969).
7) S. Itoh and H. Ohtaki, *Z. Naturforsch., A*, **42A**, 858 (1987).
8) H. Bertagnolli, E. Schultz, and P. Chieux, *Ber. Bunsenges. Phys. Chem.*, **93**, 88 (1989).
9) A. Luzar, A. K. Soper, and D. Chandler, *J. Chem. Phys.*, **99**, 6836 (1993).
10) B. G. Rao and U. C. Singh, *J. Am. Chem. Soc.*, **112**, 3803 (1990).
11) I. I. Vaisman and M. L. Berkowitz, *J. Am. Chem. Soc.*, **114**, 7889 (1992).
12) G. Fini and P. Mirone, *Spectrochim. Acta, Part A*, **32**, 625 (1976).
13) H. Torii and M. Tasumi, *J. Chem. Phys.*, **99**, 8459 (1993).
14) H. Torii, *J. Mol. Struct. (THEOCHEM)*, **311**, 199 (1994).
15) G. Fini and P. Mirone, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1776 (1974).
16) W. Schindler, P. T. Sharko, and J. Jonas, *J. Chem. Phys.*, **76**, 3493 (1982).
17) T. W. Zerda, H. D. Thomas, M. Bradley, and J. Jonas, *J. Chem. Phys.*, **86**, 3219 (1987).
18) V. M. Shelley and J. Yarwood, *Chem. Phys.*, **137**, 277 (1989).
19) J. L. McHale, *J. Chem. Phys.*, **75**, 30 (1981).
20) D. E. Logan, *Chem. Phys.*, **103**, 215 (1986).
21) D. E. Logan, *Mol. Phys.*, **58**, 97 (1986).
22) A. Luzar and D. Chandler, *J. Chem. Phys.*, **98**, 8160 (1993).
23) H. Torii and M. Tasumi, *J. Chem. Phys.*, **96**, 3379 (1992).
24) L. Blum, *J. Chem. Phys.*, **57**, 1862 (1972).
25) J. P. Hansen and I. R. McDonald, "Theory of Simple Liquids," 2nd ed, Academic Press, London (1986).
26) M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, "Gaussian 92," Gaussian, Inc., Pittsburgh, PA (1992).
27) K. K. Andersen, W. H. Edmonds, J. B. Biasotti, and R. A. Strecker, *J. Org. Chem.*, **31**, 2859 (1966).
28) P. Haake, W. B. Miller, and D. A. Tyssee, *J. Am. Chem. Soc.*, **86**, 3577 (1964).
29) P. G. Mezey and A. Kapur, *Can. J. Chem.*, **58**, 559 (1980).
30) N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).
31) M. P. Allen and D. J. Tildesley, "Computer Simulation of Liquids," Oxford University Press, Oxford (1989).
32) W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, "Numerical Recipes, The Art of Scientific Computing," Cambridge University Press, Cambridge (1989).
33) J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, **39**, 2240 (1961).
34) M. I. S. Sastry and S. Singh, *J. Raman Spectrosc.*, **15**, 80 (1984).
35) M. -T. Forel and M. Tranquille, *Spectrochim. Acta, Part A*, **26A**, 1023 (1970).