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Effect of Pressure on Local Order in Liquid Dimethyl Sulfoxide

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Raman spectroscopy was used to study intermolecular interactions, dynamics and the structure of neat liquid dimethyl sulfoxide (DMSO). Isotropic and anisotropic spectra were recorded in the SO stretching vibration region at temperatures between 30 and 70 °C and under pressures up to 2200 bar. To separate the temperature and density effects, the density of DMSO was also determined over the same region of temperature and pressure. By analyzing the isotropic and anisotropic spectra, the Raman noncoincidence effect was measured. This coupling parameter which reflects intermolecular interactions exhibits a nonlinear increase with density but is relatively insensitive to temperature. With increasing density, drastic changes in the first moment and the shape of the isotropic SO band were detected. The SO stretching vibration band shifts to lower wavenumbers, whereas its full width at half-height increases significantly with increasing pressure. The isotropic SO stretching band is resolved into three components which show markedly different intensity changes upon pressurization. The results are discussed in terms of pressure-induced formation of stronger molecular aggregates leading to an enhanced local order in liquid DMSO at elevated pressures. In a general sense, the results of this study provide yet another example of the dominance of volume effects over kinetic effects on the dynamic structure of liquids.

Introduction

Liquid dimethyl sulfoxide (DMSO) is a unique and poorly understood fluid. At ambient pressure it transforms to the solid phase at 18.55 °C and to the gas phase at 189.0 °C.[1] Beside this large temperature range of liquid phase stability, DMSO is characterized by an unusually high molar entropy of vaporization of 124 J K^{-1} mol^{-1} which is even higher than that of water (109 J K^{-1} mol^{-1})[1]. According to Trouton's rule, normal nonassociated liquids exhibit an entropy of vaporization of about 85 J K^{-1} mol^{-1}, whereas positive deviations occur for partially ordered liquids. In the case of water, hydrogen bonding induces local order in the liquid state, and it is speculated by Schläfer and Schaffernicht[1] that hydrogen bonding also occurs in liquid DMSO, although this idea appears to be improbable from a chemical point of view. Martin et al.[2] review the physical and chemical properties of liquid DMSO and estimate the probability for hydrogen bonds in this fluid. Using the concept of "hard" and "soft" acids and bases they claim that the "hard" proton is not able to bond to the "soft" S atom and that hydrogen bonding to the O atom is also unlikely because of the low acidity of the methyl protons ($pK_a = 31.3$). Contrarily, recent results of molecular dynamics computer simulations of liquid DMSO[3,4] suggest that weak hydrogen bonds to O atoms are present in liquid DMSO and that two DMSO molecules associate in an antiparallel, head-to-tail fashion.

As pointed out by Amey,[5] DMSO aggregates with dipole vectors arranged in a parallel or antiparallel way are not in agreement with the Kirkwood correlation factor *g* of liquid DMSO which can be obtained from dielectric data. The Kirkwood correlation factor *g* is a measure of short-range interactions in liquids which hinder orientation between a molecule and its surrounding neighbors. Calculating a Kirkwood correlation factor near unity for liquid DMSO, Amey concludes that DMSO behaves like a normal nonassociated polar liquid in which strong, but nonspecific dipole−dipole forces are present. Dielectric measurements by Kaatze et al.[6] suggest that the Kirkwood correlation factor of neat liquid DMSO is about 0.5. From this result, a distinct effect of antiparallel ordering of the molecular dipoles is concluded.

To answer the question if aggregates and local order exist in liquid DMSO, X-ray and neutron diffraction studies have also been performed. On the basis of X-ray experiments, Itoh and Ohtaki[7] suggest that the liquid structure of DMSO is similar to that of the solid phase. Bertagnolli et al.[8] have determined the intermolecular atom pair correlation function of liquid DMSO by X-ray and neutron diffraction and found indications for a short-range order which is similar to the corresponding one in the solid phase. In contrast, little evidence for a preference for particular molecular orientations was found by Luzar et al.[9] who employed neutron diffraction experiments together with a computer simulation study.

Infrared and Raman vibrational studies on DMSO were performed for the pure liquid and solutions at ambient pressure and mostly at room temperature. In the infrared study of Figueroa et al.[10] indications for cyclic dimers are found at low concentrations of DMSO in carbon tetrachloride. Forel and Tranquille[11] report infrared and Raman spectra of neat DMSO and propose the existence of dimers and higher polymers in the liquid phase. Fini and Mirone[12] present the isotropic and the anisotropic spectrum of liquid DMSO in the SO stretching vibration region which are explained by the presence of molecular clusters. Sastry and Singh[13] report dilution studies of DMSO in carbon tetrachloride and assign the parallelly polarized Raman spectra in the SO stretching vibration region to monomer DMSO molecules, cyclic dimer and linear polymer

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TABLE 1: Densities[17] at 1 Bar and Tait Parameters of DMSO

T/°C	ρ(1 bar)/g cm^{-3}	B/bar	C
30	1.0904	2155	0.1056
40	1.0804	2357	0.1173
50	1.0704	1794	0.09724
60	1.0603	1667	0.1000
70	1.0503	1510	0.09407

DMSO aggregates. Gill et al.[14] also find indications for monomer, dimer, and linear associated species of DMSO in solution, but they assign the different components of the SO vibrational band in a different way than Sastry and Singh.[13]

In view of the inconclusive results about the liquid structure of DMSO, it is appropriate to carry out high-pressure experiments on liquid DMSO. Intermolecular interactions are expected to increase with increasing pressure and the data obtained will yield unique information about the association behavior of DMSO molecules in the liquid phase. Pressure studies on liquid DMSO have to be performed at higher temperatures to prevent pressure-induced solidification. One calculates that it is possible to increase pressure, e.g., up to about 2200 bar at 70 °C, within the liquid phase of DMSO. By increasing the temperature of a system at constant pressure, both thermal energy and density is changed, whereas only density is changed, when pressure is applied. There is a series of examples where temperature effects on system properties are mainly due to a change in density.[15] To investigate the effect of temperature on the liquid phase of DMSO at constant density, the density of DMSO has to be known as a function of temperature and pressure.

The main aim of this work is to investigate the short-range structure of liquid DMSO at high pressures by Raman spectroscopy. Intermolecular interactions will be probed by measuring the noncoincidence value of the SO stretching vibration band of DMSO which reflects a coupling of neighboring oscillators. This parameter will be compared with theoretical predicted values. Furthermore, by resolving the isotropic SO band of DMSO into a minimal number of components which can be assigned to molecular clusters differing in association strength, the degree of molecular association will be studied as a function of pressure.

Experimental Section

DMSO was purchased from Fisher Scientific and had a purity of 99.9% with a fraction of 0.07% water. It was used without further treatment.

High-pressure density measurements were performed using a home-built high-pressure relative density meter.[16] Relative densities were measured at 30, 40, 50, 60, and 70 °C under pressures up to 2200 bar. At each temperature the relative densities as a function of pressure were calibrated using the corresponding absolute density at 1 bar from the literature.[17] The densities ρ as a function of pressure p were fitted with the Tait equation for each isotherm[18]

$$1 - \frac{\rho_r}{\rho} = C \ln \frac{B + p}{B + p_r} \tag{1}$$

B and C are fit parameters; ρ_r is the density at the reference pressure $p_r = 1$ bar. The obtained Tait parameters and the densities at 1 bar used for fitting are summarized in Table 1. An error of about ±5% is estimated for the high-pressure densities.

High-pressure Raman experiments were carried out using a home-built high-pressure cell. Details of the complete high-pressure setup is given elsewhere.[19,20] Raman spectra were recorded at 30, 40, 50, 60, and 70 °C as a function of pressure within the liquid-phase region of DMSO. The light source for excitation was the 488 nm line of an argon ion laser (Spectra-Physics series 2000) which was operated at 0.6 W. The scattered Raman radiation was analyzed by a double monochromator (Spex 1403) with a slit width of 24 μm and detected by a liquid nitrogen-cooled CCD detector (Princeton Instruments) consisting of a 1024 × 1024 pixel chip. Stokes Raman spectra were collected in the interval of 1160−940 cm^{-1} with parallel (i.e., vertical−vertical, $I_{VV}(\tilde{\nu})$) and perpendicular (i.e., vertical−horizontal, $I_{VH}(\tilde{\nu})$) polarization. Wavelength calibration of the detector was achieved by using the lines of a neon lamp. The error in locating peak frequencies is estimated to be ±0.3 cm^{-1}.

The Raman spectra were analyzed with Grams/32 software (Galactic Industries Corp.). This included the subtraction of a constant background and the normalization to counting time. Isotropic and anisotropic Raman spectra were then calculated as

$$I_{iso}(\tilde{\nu}) = I_{VV}(\tilde{\nu}) - \frac{4}{3} I_{VH}(\tilde{\nu}) \tag{2}$$

$$I_{aniso}(\tilde{\nu}) = I_{VH}(\tilde{\nu}) \tag{3}$$

and fitted to 50:50 combinations of Gaussian and Lorentzian functions.[12]

Results and Discussion

Noncoincidence Effect. The noncoincidence effect (NCE) which is a measure for intermolecular interactions is defined as the difference between the first moments of the anisotropic and the isotropic peaks of a vibrational mode

$$\Delta\tilde{\nu} = \tilde{\nu}_{aniso} - \tilde{\nu}_{iso} \tag{4}$$

The NCE reflects a resonant transfer of vibrational excitation between neighboring molecules. Most often it is due to transition dipole-transition dipole coupling. Recently, it has been shown that even pressure-induced conformational changes in molecules can be detected by measuring the NCE as a function of density.[21] According to a model by Fini et al.,[12,22,23] the NCE in dipolar aprotic liquids can be explained by the presence of molecular clusters in which molecules are oriented in an at least partially ordered way leading to parallel and antiparallel directions of the molecular dipole vectors. The frequency of the isotropic band is then assigned to the mode in which all cluster molecules vibrate in phase, whereas the anisotropic band is attributed to the mode in which the molecules of a given direction vibrate out of phase with the molecules of the opposite direction.

The isotropic and the anisotropic Raman spectra of liquid DMSO at 50 °C and 1000 bar in the SO stretching vibration region are shown in Figure 1. According to Fini and Mirone,[12] the isotropic SO stretching band at about 1043 cm^{-1} can be attributed to the in-phase vibration of cluster molecules. The smaller peak at about 953 cm^{-1} reflects a methyl rocking mode.[24] The anisotropic SO stretching band consists of three components. The first at about 1028 cm^{-1} is assigned to a methyl rocking mode, the second reflects the depolarized part of the SO in-phase vibration and coincides with the first moment of the isotropic SO stretching band, and the third component at about 1056 cm^{-1} is assigned to the out-of-phase vibration of cluster molecules.[12,24] Thus, the overall data analysis is based on that suggested by Fini and Mirone.[12] However, Fini and Mirone[12] determined the in-phase vibrational wavenumber from

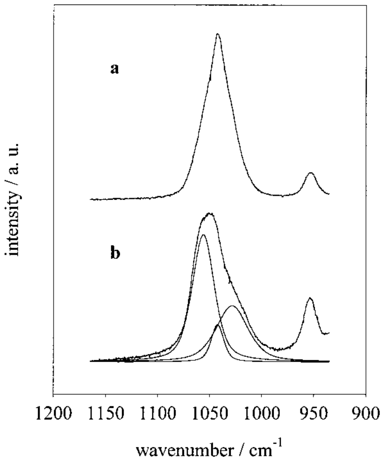

Figure 1. Isotropic (a) and anisotropic (b) Raman spectra of liquid dimethyl sulfoxide at 50 °C and 1000 bar. For the reason of clearity, the anisotropic intensity is increased compared to the isotropic spectrum.

the maximum of the isotropic SO band, whereas in this study the first moment of this band in the region 980−1100 cm^{-1} is used as in-phase vibrational wavenumber. The use of the first moment of a band instead of its maximum wavenumber has been shown to be important for calculating the noncoincidence effect of a vibrational band.[25]

Sastry and Singh[13] recorded the parallelly polarized spectrum of DMSO in the SO stretching vibration region which consists of isotropic and anisotropic contributions. Decomposing this spectrum, three bands at about 1058, 1040, and 1025 cm^{-1} were found and assigned to associated species of DMSO molecules. The authors also find an additional peak at 1070 cm^{-1} for diluted DMSO which disappears at higher concentrations and which is attributed to monomer DMSO molecules. Thus, the assignment of the observed band at about 1028 cm^{-1} (Figure 1b) is not unambiguous. Furthermore, Rintoul and Shurvell[26] report that there would be an additional, very weak band at 1018 cm^{-1}, which they have assigned to a methyl rocking mode. Since these authors did not find any degree of polarization for this mode, this band should only appear in the anisotropic Raman spectrum. However, three peaks were found to be sufficient to reproduce the anisotropic SO band shape in this study (Figure 1b).

With increasing density, the wavenumber of the in-phase vibration of DMSO is found to decrease in an almost linear way, whereas the wavenumber of the out-of-phase vibration is decreasing in the lower density range only. At higher densities ($\rho > 1.12$ g cm^{-3}), a slight increase of this wavenumber with density is detected. Within the experimental error, there is no temperature effect on the in-phase and out-of-phase wavenumbers at constant density. Kelm et al.[27] report an increase of the Raman vibrational wavenumber of the SO stretching mode with increasing temperature in neat DMSO at ambient pressure. This increase is in agreement with our study and can now be attributed to the decrease in density, when temperature is raised at constant pressure.

The NCE, as the difference between the wavenumbers (first moments) of the out-of-phase and the in-phase SO stretching vibration, is calculated and plotted in Figure 2 as a function of density. There is a clear increase of the NCE with density, although in the lower density region ($\rho < 1.12$ g cm^{-3}) this dependence is not as pronounced as that for higher densities. At 30 °C and 1 bar the density of DMSO is 1.0904 g cm^{-3} which corresponds to an NCE of 13.5 cm^{-1}. This value is in good agreement with that found by Fini and Mirone,[12] which is 14 cm^{-1} at ambient temperature and pressure. Simulating the liquid structure of DMSO using the Monte Carlo method and calculating the transition dipoles by performing ab initio molecular orbital calculations, Torii and Tasumi[28] calculated an NCE of 11 cm^{-1}. Compared to the CO stretching mode of acetone[29] with an NCE of about 6 cm^{-1}, DMSO exhibits a very large splitting of the in-phase and out-of-phase SO wavenumbers. As discussed by Torii and Tasumi,[28] the main reasons for this difference are the differences in vibrational wavenumber and in liquid structure between acetone and DMSO.

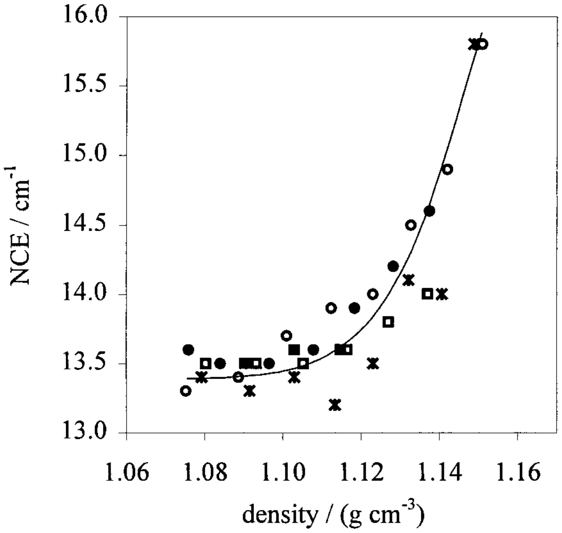

Figure 2. The noncoincidence effect (NCE) of the SO stretching mode of liquid dimethyl sulfoxide as a function of density (■ 30 °C, □ 40 °C, ● 50 °C, ○ 60 °C, * 70 °C).

A theory to predict the NCE has been developed by Logan for symmetric polar modes of neat liquids and binary mixtures.[30,31,32] According to his theory, the NCE of a neat liquid can be calculated from

$$\Delta\omega = \frac{48}{25\pi\epsilon_0}\left(\frac{d\mu}{dQ}\right)^2 \frac{\xi}{m\omega\sigma^3} \qquad (5)$$

where $\Delta\omega$ is the noncoincidence value in the dimension of angular frequency, $d\mu/dQ$ is the dipole moment derivative, Q is the normal coordinate, m is the reduced mass, ω is the vibrational angular frequency of the free molecule, σ is the hard-sphere diameter, and the parameter ξ is given by the equation

$$\frac{\mu_0^2\rho}{3kT\epsilon_0} = \frac{(1+4\xi)^2}{(1-2\xi)^4} - \frac{(1-2\xi)^2}{(1+\xi)^4} \qquad (6)$$

where μ_0 is the permanent dipole moment and ρ is the number density. Logan obtained this equation by using the mean spherical approximation according to which the liquid is composed of spherical molecules with a permanent dipole moment. The parameter ξ is directly related to the integral

$$\xi = \frac{\pi\rho\sigma^3}{6}\int_0^\infty h_D(R)\frac{dR}{R} \qquad (7)$$

in which $h_D(R)$ is the second-order coefficient of the pair correlation function of the liquid and R is the distance between a pair of molecules.

Using Logan's formula (eq 5), it is possible to calculate the NCE for liquid DMSO. With a dipole derivative[28] of 1.542 × 10^{-6} C kg$^{-1/2}$, a vibrational angular frequency[24] of 2.074 × 10^{14} s^{-1}, and a molecular diameter[33] of 5.6 × 10^{-10} m, one obtains $\Delta\omega/(2\pi c) = \xi 24$ cm^{-1}. The parameter ξ is found numerically to be 0.16 using eq 6 for conditions of 30 °C and 1 bar (dipole moment[17] $\mu_0 = 1.30 \times 10^{-29}$ C m and number density $\rho = 8.404 \times 10^{27}$ m^{-3}). Thus, a noncoincidence value of 4 cm^{-1} is predicted by Logan's theory which is about 70% too small. Even with a smaller reported molecular diameter[34] of $\sigma = 4.64 \times 10^{-10}$ m, one obtains an NCE of only 7 cm^{-1} which is still too small. This result is not surprising in view of the simple model of spherical molecules and the strong dependence of the NCE on the molecular diameter according to eq 5. A much better agreement between experimental and theoretical NCE value is achieved, if the liquid structure factor is calculated by eq 7 which reflects the individual structure of a liquid. Using a value of 0.600 for the integral obtained by Monte Carlo computer simulations,[28] one calculates an NCE value of 11 cm^{-1} that is now in very good agreement with the experimental value.

By using eq 6 one can qualitatively evaluate the effect of increasing density on the NCE in terms of decreasing intermolecular distances. Solving this equation for 50 °C over the density range 1.06−1.16 g cm^{-3} (see Figure 2), the parameter ξ is found to increase almost linearly from 0.157 to 0.162 which is a change of +3%. From the experiment, a change of +17% is found for the NCE in the same density region. Thus, the enhanced vibrational coupling of neighboring DMSO molecules observed experimentally under high-pressure cannot be attributed to shorter intermolecular distances only. The main contribution to the nonlinear increase of the NCE with increasing density will be a pressure-induced change in liquid structure. As pointed out by Wang and McHale,[35] the presence of short-range structural order can have a major effect on the magnitude of the NCE. Thus, if the DMSO molecules are arranged in a more ordered way under elevated pressures, the coupling between two oscillating molecules is stronger leading to the observed nonlinear density dependence of the NCE. Furthermore, it is interesting to compare these experimental data for DMSO with those obtained for other polar liquids exhibiting strong noncoincidence effects. For example, the NCE as a function of number density for liquid acetone,[29] *N*,*N*-dimethylacetamide[36] and methyl benzoate[21] shows linear dependence and the changes of the NCE per unit number density are smaller. In a phenomenological sense, the observed NCE results for DMSO provide further evidence for the strongly interacting character of this unusual liquid.

Isotropic Band Shape. The isotropic SO vibrational band (Figure 1a) has been analyzed in the preceding paragraph in terms of first moment in order to determine the in-phase vibrational wavenumber of DMSO molecules and the Raman noncoincidence effect. However, it seems to be worthwhile to analyze also the unusual shape of this band, since it cannot be fitted to a single combination of a Gaussian and a Lorentzian function within the experimental error. Indeed, using 50:50 combinations of Gaussian and Lorentzian functions it is found that the lowest number of peaks is three to reproduce the isotropic SO vibrational band shape (Figure 3). To address the physical meaning of this decomposition into three components, we suggest a simple physical model for the liquid structure of DMSO which is based on the presence of molecular clusters in this liquid which differ in intermolecular association strength. The existence of molecular clusters of different form in liquid DMSO is proposed in numerous publications.[3,4,6,8,10,11,13,26,37] One can now assume that clusters with weak, intermediate, and strong intermolecular interactions are present in liquid DMSO resulting in three different wavenumbers for the SO vibrational mode which correspond to the three components of the isotropic SO vibrational band (Figure 3). The high-wavenumber component is then attributed to the presence of DMSO clusters with weak intermolecular interactions, whereas the two other components with an intermediate and a low wavenumber are due to molecular clusters with intermediate and strong intermolecular forces, respectively.

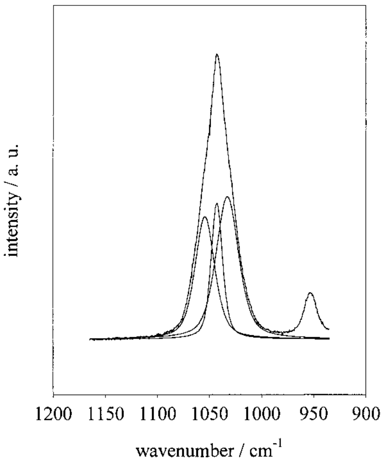

Figure 3. Decomposition of the isotropic SO stretching band of liquid dimethyl sulfoxide, e.g., at 50 °C and 1000 bar. Each band component is a 50:50 combination of a Gaussian and a Lorentzian function.

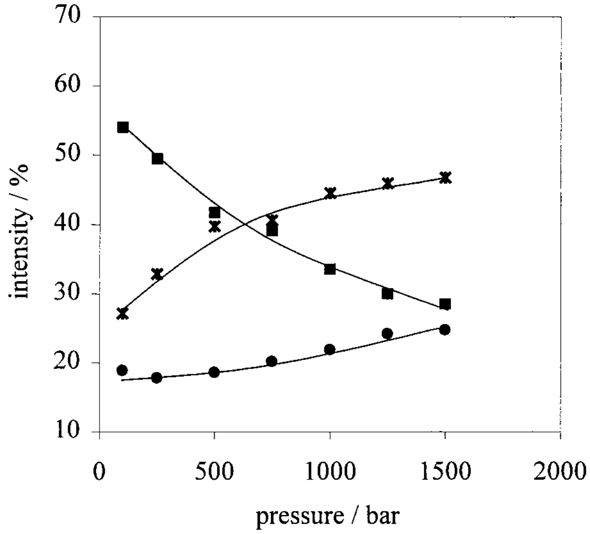

Figure 4. Relative integrated intensities of the three components of the isotropic SO stretching band of liquid dimethyl sulfoxide at 50 °C as a function of pressure (■ high-, ● intermediate-, * low-wavenumber component).

In Figure 4, the intensities of the three components of the isotropic SO band of liquid DMSO relative to the total band area are plotted as a function of pressure for 50 °C. Similar plots are obtained for all other temperatures studied. There is a drastic change in intensity for the high-wavenumber and the low-wavenumber component, whereas the intensity of the intermediate component is relatively insensitive to pressure. Analyzing the corresponding wavenumbers of the three resolved bands of the in-phase SO mode, a slight increase with pressure for the wavenumber of the high-wavenumber component is found, but no major wavenumber change is detected for the other two. Using a simple phenomenological model, the intensities of the three band components can be correlated with concentrations in order to interpret Figure 4. Then, it is found that the concentration of loosely associated DMSO molecules is reduced by pressure, whereas the concentration of clusters with strong intermolecular interactions is increased significantly. Thus, pressure favors molecular association in liquid DMSO

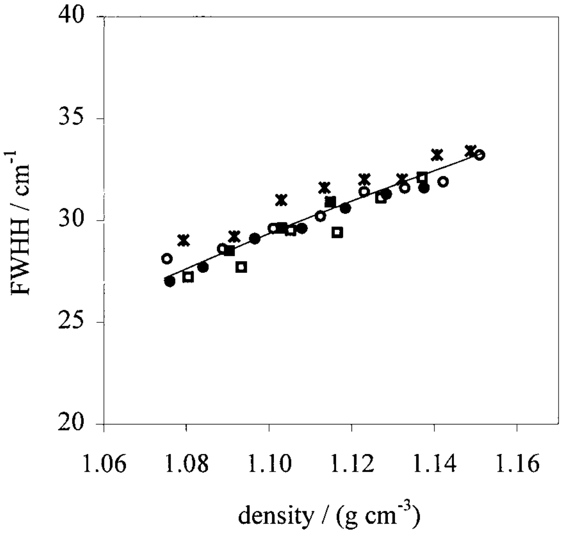

Figure 5. The full width at half-height (fwhh) of the isotropic SO stretching band of liquid dimethyl sulfoxide as a function of density (■ 30 °C, □ 40 °C, ● 50 °C, ○ 60 °C, * 70 °C).

leading to an enhanced local order of the liquid structure, in agreement with the interpretation of the NCE behavior as discussed earlier in this work.

As a logical consequence of the decomposition of the in-phase SO band into three components (Figure 3), the out-of-phase component of the anisotropic SO band (Figure 1b) should also be represented with three peaks resulting in three different values of the NCE. This would require a seven-component fit of the anisotropic band shape (three components for the out-of phase vibration, three components for the depolarized part of the in-phase vibration, and one component for the methyl rocking mode) which can only lead to random fitting results. Thus, taking the first moment of the isotropic SO vibrational band and representing in-phase and out-of-phase vibration with only one respective wavenumber, as it has been carried out in the preceding paragraph, is a reasonable way for analyzing the NCE of the SO vibrational mode of liquid DMSO.

Isotropic Bandwidth. For completeness, the width of the whole isotropic SO stretching band of liquid DMSO (Figure 1a) has also been studied. Vibrational bandwidth studies have already been performed for the symmetric CH and the CS stretching modes of DMSO[34,38,39]. The full width at half-height (fwhh) of the isotropic SO band as a function of density is plotted in Figure 5 which shows no discernible temperature effect over the range of 30−70 °C. Broadening of this band is caused only by an increase in density. This behavior is quite different from that found for the CO stretching mode of acetone.[29] In this case, the bandwidth at half-height decreases with increasing density and increases with increasing temperature at constant density. According to the Kubo model,[40] the vibrational relaxation time is proportional to the reciprocal bandwidth of an isotropic vibrational band. Thus, with increasing density, the vibrational relaxation time of the SO stretching mode in DMSO is reduced.

In the isolated binary collision model developed by Fischer and Laubereau,[41] the vibrational relaxation rate ($1/\tau_{\mathrm{vib}}$) is determined by the dephasing rate ($1/\tau_{\mathrm{p}}$) and the energy relaxation rate ($1/\tau_{\mathrm{e}}$). Phase relaxation dominates for low temperatures and is given by

$$\frac{1}{\tau_{\mathrm{p}}} = \frac{9}{2}\frac{\mu\gamma^4}{M^2}\frac{kT}{\omega^2 L^2}\frac{1}{\tau_{\mathrm{BC}}} \tag{8}$$

where τ_{BC} is the time between collisions of an oscillator A−B and an atom C (ω is the angular frequency of the oscillator, L is a measure for the range of the interaction potential, and the term $\mu\gamma^4/M^2 = m_{\mathrm{A}}{}^2 m_{\mathrm{C}}/[m_{\mathrm{B}}{}^2(m_{\mathrm{A}} + m_{\mathrm{B}})(m_{\mathrm{A}} + m_{\mathrm{B}} + m_{\mathrm{C}})]$ is a function of the masses of the atoms A, B, and C). Employing this model, the decrease of the vibrational relaxation time is related to a decrease of the time τ_{BC} between collisions in the liquid which is reasonable, since at higher densities intermolecular distances are shorter. The time between two collisions in a rough-sphere liquid can be estimated from[42]

$$\frac{1}{\tau_{\mathrm{BC}}} = 4\pi\sigma^2 \rho \frac{2-\eta}{2(1-\eta)^3}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{9}$$

where σ is the hard-sphere diameter, ρ is the number density, ρ is the packing fraction, and m is the molecular mass. Using this formula, the time between collisions in liquid DMSO is decreasing from 1.0×10^{-13} s at a density of 1.06 g cm^{-3} to 7.8×10^{-14} s at a density of 1.16 g cm^{-3} for $T = 50$ °C ($\sigma = 4.64 \times 10^{-10}$ m).[34] Thus, the increase of the full width at half-height of the isotropic SO band of liquid DMSO with density can be understood in a qualitative way.

Summary

Pressure increases the NCE of the SO vibrational mode, whereas the effect of temperature on the NCE at constant pressure is only due to a change in density. There are positive deviations from the theoretically predicted values which become larger at higher densities. This nonlinear dependence of the NCE on the density of DMSO is related to a pressure-induced structural change of the liquid phase. At elevated pressures the DMSO molecules arrange in a more ordered way resulting in an enhanced coupling between oscillating molecules.

By resolving the isotropic SO vibrational band into three components, it is suggested that this band reflects vibrations of clusters which differ in intermolecular association strength. On the basis of this assumption, a pressure-induced decrease of the concentration of clusters with loosely associated molecules and a pressure-induced increase of the concentration of clusters with strongly associated molecules is found. From this it is concluded that pressure favors the formation of aggregates in the liquid phase of DMSO which results in a more ordered local structure compared to the structure at ambient pressure.

Finally, the isotropic bandwidth at half-height of the SO in-phase vibration is only a function of density in the temperature range studied. It increases with increasing density reflecting the increased vibrational relaxation rate at higher densities. The dominance of density effects has also been observed in a number of other studies dealing with different aspects of the dynamic structure of liquids.[43,44]

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