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Intermolecular interaction of carbon disulfide under pressure (high presssure and effective negative solvation pressure)

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Raman spectra of liquid carbon disulfide (CS_2) were measured under high pressures and in dilution with ethanol and with heptane. The pressure and concentration dependences of molecular vibration modes ν_1 and $2\nu_2$ of CS_2 are discussed. The intermolecular distance changes simultaneously with concentration and pressure. In addition, dilution also varies the environment around the CS_2 molecule. The derivative of intermolecular interaction energy is obtained from the frequency shift from gas phase to liquid phase of ν_1 and $2\nu_2$ vibrations. The results show that dilution acts as negative pressures effectively, where the intermolecular distance between CS_2 molecules increases in the mixing of ethanol and heptane. This effective pressures and pressures give the change in intramolecular double bond betwen carbon and sulfur atoms. But these give different effect for the damping of vibrations.

1 INTORDUCTION

The Raman shift of libratinal mode in liquid CS_2 under high pressure and in dilution with ethanol was measured [1, 2, 3]. The result shows that the restoring force of orientation of molecule increases with increasing pressure because of the stronger intermolecular interaction [5, 6].

Pressure and dilution are used in studies of the liquid state. Their principal effect is to change intermolecular distance and intermolecular interaction systematically. Especially dilution varies the microscopic environment because CS_2 molecules are replaced by the solvent molecules. We measured Raman spectra of the ν_1 and $2\nu_2$ bands in liquid CS_2 under high pressure and in dilution with ethanol and with heptane to investigate intermolecular interaction. The ν_1 vibration is the stretching mode. The $2\nu_2$ vibration is the first Raman active overtone of the bending mode. Further for investigating the intermolecular interaction in detail in liquid, CS_2 is a good molecule because C^{+}=S^{-} intramolecular double bond has large dipole moment 2.6 [D] [4]. The intermolecular interaction potential U between a CS_2 molecule and its neighboring molecules is resolved into the summation of four contributions: electrostatic, induction, dispersion, and repulsion. Pressure changes the intermolecular distance. On the other side, CS_2 molecules make place for solvent molecules in dilution. Dilution changes the value of the dipole moment and the polarizability of neighboring molecules. We will show that the change of the derivative of intermolecular interaction potential and that the effective pressure is negative under dilution with ethanol and heptane.

2 EXPERIMENTS AND RESULTS

Carbon disulfide is a linear molecule like CO_2 and crystallizes at ∼1.3 GPa (at room temperature) or ∼173 K (at atmospheric pressure). We measured polarized Raman scattering spectra of CS_2 under high pressures and in dilution with ethanol and with heptane. The hydrostatic pressure was applied in a diamond anvil

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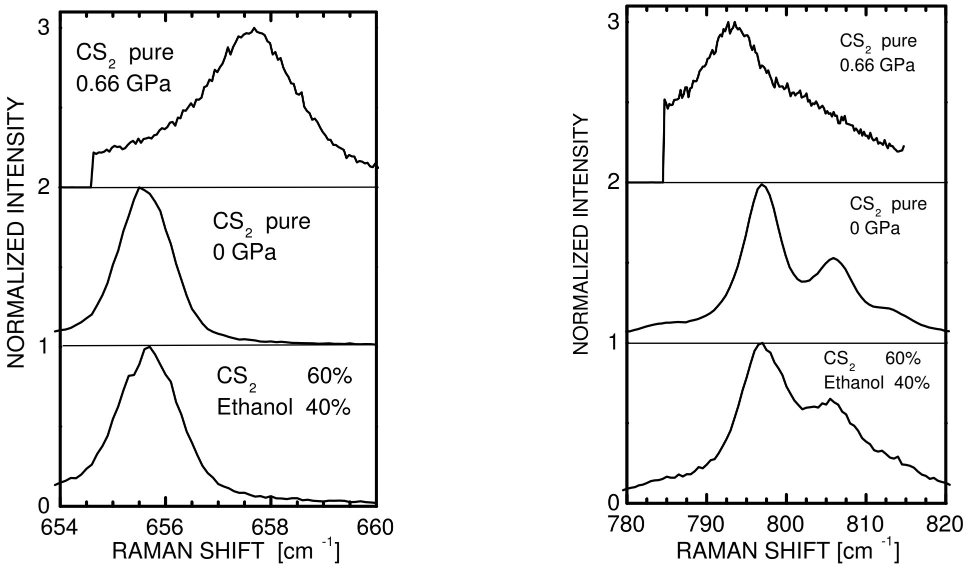
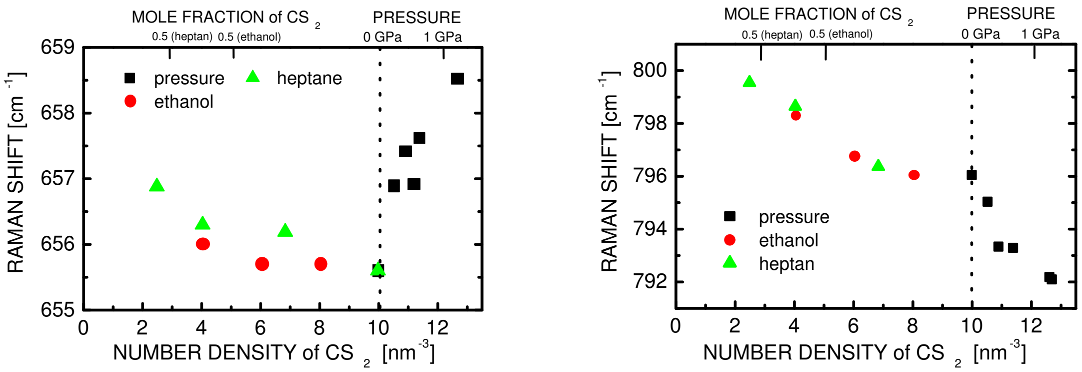
cell (DAC) up to 1.3 GPa, and pressures are determined using ruby scale. The 488 nm line of Ar^+ laser (NEC, GLG 3480) was used as an excitation source for the measurement.

Typical spectra of the ν_1 and $2\nu_2$ vibrations are plotted in Fig. 1. In Fig. 1 a) the band of the ν_1 vibration shifts to higher frequency and broadens as the pressure increases and does not change in dilution. The $2\nu_2$ band is drawn in Fig. 1 b). The satellites on the high frequency sides have been assigned to hot band transition from excited level of the ν_2 and ν_1 modes [7]. In dilution and under high pressures, the band of $2\nu_2$ vibration shifts and broadens.



a) b)

Fig. 1 Polarized Raman spectra of ν_1 vibration and $2\nu_2$ vibration of CS_2 at 0 GPa and 0.66 GPa, dilution with ethanol. a) ν_1 vibration and b) $2\nu_2$ vibration.

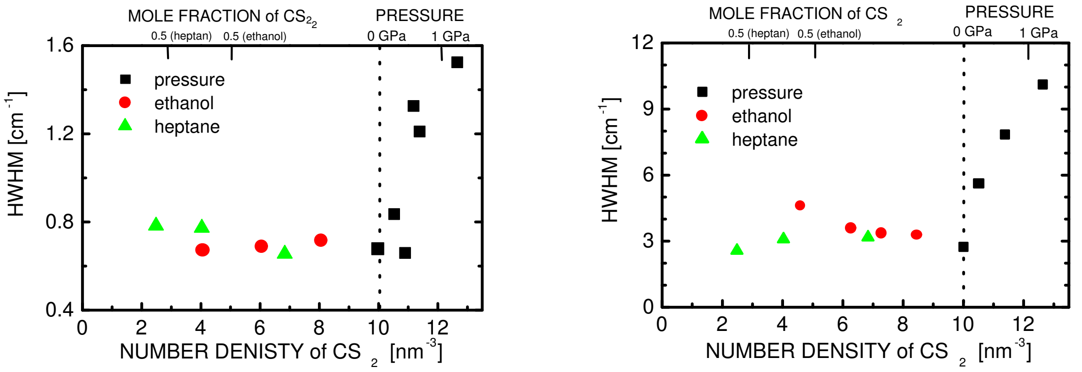


a) b)

Fig. 2 The number density dependence of observed frequencies of a) ν_1 vibration and b) $2\nu_2$ vibration in liquid CS_2. The peak frequencies, where the number density is less than 10 nm^{-3}, are measured by dilution with ethanol. The peak frequencies, where the number density is larger than 10 nm^{-3}, are measured under high pressure.

The observed peak frequencies ν_1 and $2\nu_2$ are plotted against number density in Fig. 2. We measured the X-ray scattering function for liquid CS_2 under high pressure at room temperature and obtained the peak of correlation function which is ascribed predominantly to sulfur and sulfur interactions from neighboring molecules. The number density under pressure is estmated from the values of peaks of correlation function.

The peak frequencies of CS_2, where the number density is less than 10 nm^{-3}, are measured in dilution. The peak frequencies, where the number density is larger than 10 nm^{-3}, are measured under high pressure. Figure 2 shows that the peaks of ν_1 bands shift to higher frequencies under pressure (at the rate 1.1 cm^{-1}/nm^{-3}) in dilution (ethanol: -0.07 cm^{-1}/nm^{-3}, heptane: -0.17 cm^{-1}/nm^{-3}). Increasing pressure takes $(\nu_1)_0$ closer to the gas-phase frequency of 664.27 cm^{-1} [8]. As one can see in Fig. 2, there is almost no difference between dilution with ethanol and heptane. The peak frequencies of $2\nu_2$ bands decrease with pressure (-1.7 cm^{-1}/nm^{-3}) and increase with dilution (-0.51 cm^{-1}/nm^{-3}). Decreasing dilution, the peak frequency of $(2\nu_2)_0$ is closer to 795.50 cm^{-1} of gas phase [8].



a) b)

Fig. 3 half-band width of a) ν_1 band vibrations and b) $2\nu_2$ band vibrations

The half-bandwidth δ_1 of ν_1 band and δ_2 of $2\nu_2$ band are drawn in Fig. 3. Especially the half-bandwidths are estimated from the low-frequency half of the band. The bandwidth increases under high pressure, but there is almost no change in dilution. The time constant τ_v for the relaxation of the vibrational phase is obtained from the half-bandwidth δ_1 by the equation $\tau_v = 1/2\pi\delta_1$. The dephasing time τ_v is proportional to $1/\eta$, where η is the viscosity of fluid. The dephasing time depends on the frequency and violence of collisions. Sometimes broadening occurs because energy is transferred between molecules by the interaction of dipoles. Viscosity η of CS_2, ethanol and heptane is 0.37, 1.19 and 0.41 [cP] respectively [9]. The viscosity increases with pressure increases. Carbon disulfide freezes around 13 GPa at room temperature, where the viscosity is about 10 times the viscosity at 0 GPa [9]. There is almost no change of viscosity in dilution. Figure 3 shows that the change of bandwidth reflects that of viscosity of liquid.

The frequencies free of Fermi resonance are needed to discuss the effect of intermolecular interaction. It occurs when two molecular vibration modes of same symmetry are coupled by anharmonic part of Hamiltonian H_a. The frequency separation $\Delta = 2\nu_2 - \nu_1$ is obtained from observed frequencies ν_1, $2\nu_2$ [10] as following

$$\Delta = (\Delta_0^2 + 4W^2)^{\frac{1}{2}}, \tag{1}$$

where $\Delta_0 = (2\nu_2)_0 - (\nu_1)_0$ is the separation of the resonance-free levels, $W = \langle\psi^0_{\nu_1}|H_a|\psi^0_{2\nu_2}\rangle$ is the matrix element of Fermi resonance and H_a is anharmonic part of Hamiltonian. The perturbed wave functions can be expressed as a linear combination of harmonic wave functions.

$$\psi_{\nu_1} = s\psi^0_{\nu_1} - t\psi^0_{2\nu_2}, \qquad \psi_{2\nu_2} = t\psi^0_{\nu_1} + s\psi^0_{2\nu_2} \quad . \tag{2}$$

The values of “s” and “t” can be expressed as

$$s^2 = \frac{\Delta + \Delta_0}{2\Delta}, \qquad t^2 = \frac{\Delta - \Delta_0}{2\Delta} \quad . \tag{3}$$

Here, W and Δ_0 are estimated to be 28.5 cm^{-1} and 129.5 cm^{-1} [2]. The gas-phase frequencies give W^{gas}= 28.6 cm^{-1} and Δ_0^{gas}=132.0 cm^{-1} [8]. The good agreement between the value W and W^{gas} confirms that W is little affected by interaction and W is assumed to be independent of pressure. The resonance-free frequencies $(\nu_1)_0$ and $(2\nu_2)_0$ are calculated from the equations

$$(\nu_1)_0 = \nu_1 + \frac{\Delta - (\Delta^2 - 4W^2)^{\frac{1}{2}}}{2}, \quad (2\nu_2)_0 = 2\nu_2 - \frac{\Delta - (\Delta^2 - 4W^2)^{\frac{1}{2}}}{2}. \tag{4}$$

3 DISCUSSIONS

The frequency shift of a molecular vibration from gas phase to the liquid phase has been explained as a combined effect of molecular anharmonicity and interaction potential, using a simple model with a single vibration. The vibrational Hamiltonian of a molecule in the liquid phase is

$$H = H_0 + H_a + U, \tag{5}$$

where H_0 and H_a are the harmonic and anharmonic parts of the Hamiltonian of an isolated molecule and U is the intermolecular interaction potential between CS$_2$ and neighboring molecules. The intermolecular interaction energy U between a single CS$_2$ molecule and neighboring molecules may be resolved into the summation of four contributions: electrostatic, induction, dispersion, and repulsion. The four contributions of the interaction energy between CS$_2$ molecule and neighboring molecule are expressed:

$$\begin{aligned} \phi_i^{el} &= \frac{\mu_{CS_2}\mu_i}{4\pi\epsilon_0 R_i^3}k_i, \qquad \phi_i^{ind} = \frac{\alpha_{CS_2}\mu_i^2}{(4\pi\epsilon_0)^2 R_i^6}, \\ \phi_i^{dis} &= -\frac{3I_{CS_2}I_i}{2(I_{CS_2}+I_i)} \cdot \frac{\alpha_{CS_2}\alpha_i}{(4\pi\epsilon_0)^2 R_i^6}, \quad \text{and} \quad \phi_i^{rep} = \frac{C_i}{R_i^6}. \end{aligned} \tag{6}$$

Here α, μ and I are the polarizability, dipole moment, and ionization energy of the bond, R_i is the intermolecular distance between the two molecules and k_i is geometric factor of describing the relative orientation of the two molecules. i denotes neighboring molecules.

In case that U and H_a are perturbations of H_0, the frequency shift from gas phase to the liquid phase of CS$_2$ is described by second-order perturbation theory [2, 11]. The frequency shift of CS$_2$ under pressure is obtained from the experiment by Ikawa *et al.* [2] as follows,

$$\Delta(\nu_1)_0 = (\nu_1^{gas})_0 - (\nu_1^{liq})_0 = -0.082\frac{\partial U^{(0)}}{\partial q_1} + \Delta_a \tag{7}$$

and

$$\Delta(2\nu_2)_0 = (2\nu_2^{gas})_0 - (2\nu_2^{liq})_0 = 0.128\frac{\partial U^{(0)}}{\partial q_1} + 0.81\Delta_a. \tag{8}$$

Here, $(\nu_1)_0 = 664.27$ cm^{-1} and $(2\nu_2)_0 = 795.50$ cm^{-1} are the frequencies of gas phase and Δ_a is positive constant which consists of higher order derivatives of the intermolecular interaction potential U. The frequency shift depends on the derivative of intermolecular interaction potential $\partial U^{(0)}/\partial q_1$. The value of $\partial U^{(0)}/\partial q_1$ and Δ_a calculated from Eqs.(7) and (8) are plotted against number density of CS$_2$ in Fig. 4.

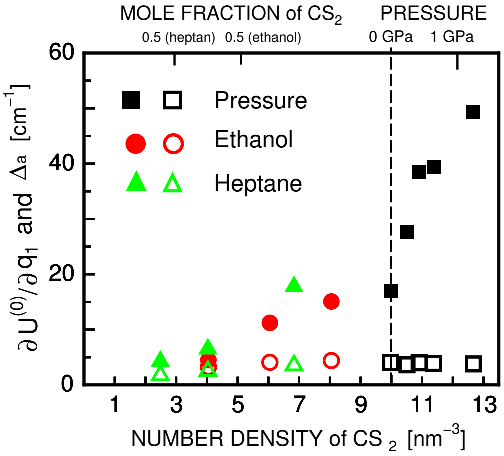


Fig. 4 Calculated values of derivative of the interaction potential $\partial U^{(0)}/\partial q_1$ (full symbols) and Δ_a (open symbols). $\partial U^{(0)}/\partial q_1$ is the derivative of intermolecular interaction potential. The values Δ_a consist of higher order derivatives of the intermolecular interaction potential U.

As shown in Fig.4, the values of $\partial U^{(0)}/\partial q_1$ increases under high pressure and in dilution. $\partial U^{(0)}/\partial q_1$ corresponds to force which is caused by the intermolecular interaction in liquid. Pressure shortens intermolecular distance between CS$_2$ and neighboring molecules R_i. Dilution changes the environment around CS$_2$ molecule, because CS$_2$ molecules are replaced by the solvent molecules that have smaller dipole moment. Ethanol is a polar molecule with a large dipole moment ($\mu_{Ethanol}$=1.4 [D]). Heptane has no dipole moment. The dipole moment C$^+$=S$^-$ of intramolecular bond of CS$_2$ is larger than heptane and ethanol. The parameters μ_i, α_i and R_i in Eq.(6) are independent of coordinate q_1 of the CS$_2$ molecule. The effects of electrostatic energy, induction energy, and dispersion energy between CS$_2$ - CS$_2$ are stronger than those between CS$_2$ - solvent molecule. Dilution not only changes the number of solvent molecules around the CS$_2$ molecule but also weakens intermolecular interaction potential. Figure 4 shows that the derivative of intermolecular interaction to grows intense, as the number density rises from 2.5 to 12.7 nm^{-3}. Dilution and pressure influence the intermolecular interaction potential. The values of electrostatic, induction, dispersion energy between CS$_2$ -ethanol are less than that between CS$_2$-CS$_2$ in Eq.(6).

Figure 4 shows that the values of the derivative of intermolecular interaction potential increase with increasing CS$_2$ density. The rate in liquid CS$_2$ under high pressure is larger than in dilution. But it has smaller change in both CS$_2$ and its dilution liquid than that under pressure. The value of $\partial U^{(0)}/\partial q_1$ is influenced by intermolecular distance R_1 rather than the parameter μ_i and α_i. It is considered that the effect of intermolecular interaction potential in dilution is less than that at atmospheric pressure. $\partial U^{(0)}/\partial q_1$ corresponds to force which is caused by the intermolecular interaction in liquid and indicates the intensity of the intermolecular interaction between CS$_2$ and neighboring molecules. As the mole fraction of CS$_2$ in the solution decreases, the value of $\partial U^{(0)}/\partial q_1$ gets smaller. The roles of these solvent are to change the microscopic environment around CS$_2$ molecule and to weaken the storong interaction between CS$_2$ and neighboring molecules. Dilution makes the intermolecular interaction weaker than at 0 GPa. Solvation seem to behave like pressure as a kind of parameter. The effective negative solvation pressure is considered to be generated by dilution in the region where the value of $\partial U^{(0)}/\partial q_1$ in dilution is less than that of pure CS$_2$ at 0 GPa. Results indicate that dilution controlled the intermolecular interaction like real pressure and effective negative solvation pressure was generated by dilution because pressure and dilution changes the environment around CS$_2$ molecule.

The deformation of the geometry induced by intermolecular interaction is described by second-order perturbation theory[2, 11]. The change Δd of the C = S bond length from the length in gas-state to it in liquid-state is

$$\Delta d = \frac{1}{\omega_1}\left(\frac{h}{8\pi^2 c\omega_1 m_s}\right)^{\frac{1}{2}}\frac{\partial U^{(0)}}{\partial q_1}, \tag{9}$$

where h is Planck's constant, ω_1 the harmonic frequency in wave number, c the speed of light in vacuum, and m_s the mass of the sulfur atom. The Δd , which is calculated from the values of $\partial U^{(0)}/\partial q_1$ in Figure4, is plotted in Fig. 5.

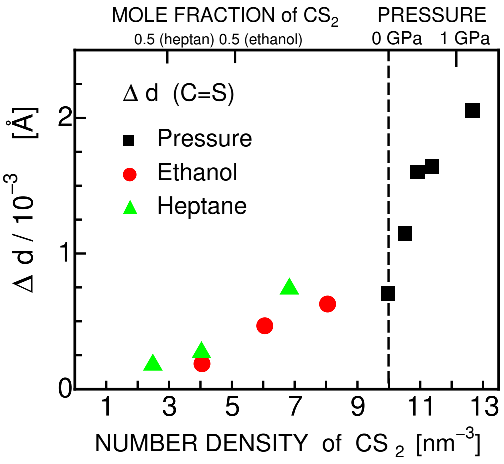


Fig. 5 The shrinkage of C=S bond length from the gas-phase distance due to the effect of pressure and dilution. Δ d is positive constant

The shrinkage from the gas-phase bond length increases with increasing number density of CS$_2$. This value rises 0.2×10^{-3} to $2.6 \times 10^{-3}\mathring{A}$ as the number density rises from 2.5 to 12.7 nm^{-3} in mixture with heptane. C = S bond length changes in dilution and under pressure. It is considered that the C = S bond length is influenced by the microscopic environment and the intermolecular interaction potential. Its conponents are electrostatic energy, induction energy, dispersion energy and repulsion energy, whose effects vary with pressure and dilution.

4 CONCLUSION

The vibrational frequencies were measured under high pressure and in dilution with ethanol and with heptane, to change the intermolecular distance of CS$_2$ molecules systematically. We obtained the derivative of intermolecular interaction potential and the change of C = S bond length from the frequency shift from gas phase to liquid phase of ν_1 and $2\nu_2$ vibrations as a function of number density of CS$_2$. Dilution varies the microscopic environment and changes the effect of the intermolecular interaction potential like real pressure. The interaction between CS$_2$ molecules is extremely stronger than that between CS$_2$ molecule and ethanol or heptane. It is considered that dilution acts like real pressure and this effective negative solvation pressure was generated by diluting CS$_2$ with ethanol and with heptane.

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