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Intermolecular interaction of carbon disulfide under pressure (high pressure 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 $\nu_1$ 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 $\nu_1$ 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 between carbon and sulfur atoms. But these give different effect for the damping of vibrations.

1 INTRODUCTION

The Raman shift of librational 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 $\nu_1$ 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 $\nu_1$ 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 $\sim$1.3 GPa (at room temperature) or $\sim$173 K (at atmospheric pressure). We measured polarized Raman scattering spectra of CS$_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 $\nu_1$ and $2\nu_2$ vibrations are plotted in Fig. 1. In Fig. 1 a) the band of the $\nu_1$ 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 $\nu_2$ and $\nu_1$ modes [7]. In dilution and under high pressures, the band of $2\nu_2$ vibration shifts and broadens.

**Fig. 1** Polarized Raman spectra of $\nu_1$ vibration and $2\nu_2$ vibration of CS$_2$ at 0 GPa and 0.66 GPa, dilution with ethanol. a) $\nu_1$ vibration and b) $2\nu_2$ vibration.

**Fig. 2** The number density dependence of observed frequencies of a) $\nu_1$ 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 $\nu_1$ 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 estimated 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 $\nu_1$ 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].

![Fig. 3](image-url)

**Fig. 3** half-band width of a) $\nu_1$ band vibrations and b) $2\nu_2$ band vibrations

The half-bandwidth $\delta_1$ of $\nu_1$ bands and $\delta_2$ 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 $\tau_v$ for the relaxation of the vibrational phase is obtained from the half-bandwidth $\delta_1$ by the equation $\tau_v = 1/2\pi \delta_1$. The dephasing time $\tau_v$ is proportional to $1/\eta$, where $\eta$ 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 $\eta$ 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, and 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 $\nu_1$, $2\nu_2$ [10] as following

$$\Delta = (\Delta_0^2 + 4W^2)^{1/2},$$  \hspace{1cm} (1)

where $\Delta_0 = (2\nu_2)_0 - (\nu_1)_0$ is the separation of the resonance-free levels, $W = \langle \psi_{\nu_1}^0 | H_a | \psi_{2\nu_2}^0 \rangle$ 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.

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\[ \psi_{\nu_1} = s\psi_{\nu_1}^0 - t\psi_{2\nu_2}^0, \quad \psi_{2\nu_2} = t\psi_{\nu_1}^0 + s\psi_{2\nu_2}^0. \]  \tag{2}

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

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

Here, \( W \) and \( \Delta_0 \) are estimated to be 28.5 cm\(^{-1}\) and 129.5 cm\(^{-1}\) [2]. The gas-phase frequencies give \( W^{\text{gas}} = 28.6 \text{ cm}^{-1} \) and \( \Delta_0^{\text{gas}} = 132.0 \text{ cm}^{-1} \) [8]. The good agreement between the value \( W \) and \( W^{\text{gas}} \) 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 \( \text{CS}_2 \) and neighboring molecules. The intermolecular interaction energy \( U \) between a single \( \text{CS}_2 \) 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 \( \text{CS}_2 \) molecule and neighboring molecule are expressed:

\[ \phi_i^{el} = \frac{\mu_{i} \mu_{\text{CS}_2}}{4\pi\varepsilon_0 R_i^3}, \quad \phi_i^{ind} = \frac{\alpha_{i} \mu_{\text{CS}_2}}{(4\pi\varepsilon_0)^2 R_i^6}, \]
\[ \phi_i^{dis} = -\frac{3I_{\text{CS}_2}I_i}{2(I_{\text{CS}_2} + I_i)} \cdot \frac{\alpha_{\text{CS}_2} \alpha_i}{(4\pi\varepsilon_0)^2 R_i^6}, \quad \text{and} \quad \phi_i^{rep} = \frac{C_i}{R_i^6}. \]  \tag{6}

Here \( \alpha, \mu \) 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 \( \text{CS}_2 \) is described by second-order perturbation theory [2, 11]. The frequency shift of \( \text{CS}_2 \) under pressure is obtained from the experiment by Ikawa \textit{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}

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Here, \((\nu_1)_0 = 664.27 \text{ cm}^{-1}\) and \((2\nu_2)_0 = 795.50 \text{ cm}^{-1}\) are the frequencies of gas phase and \(\Delta_a\) is a 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 \(\Delta_a\) calculated from Eqs.(7) and (8) are plotted against number density of CS\(_2\) in Fig. 4.

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 (\(\mu_{\text{Ethanol}} = 1.4 \text{ [D]}\)). Heptane has no dipole moment. The dipole moment \(C^+\equiv S^-\) of intramolecular bond of CS\(_2\) is larger than heptane and ethanol. The parameters \(\mu_i\), \(\alpha_i\) 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 \(R_i\) rather than the parameter \(\mu_i\) and \(\alpha_i\). 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 strong 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 $\Delta d$ of the $C = S$ bond length from the length in gas-state to it in liquid-state is

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

(9)

where $h$ is Planck’s constant, $\omega_1$ the harmonic frequency in wave number, $c$ the speed of light in vacuum, and $\mu_s$ the mass of the sulfur atom. The $\Delta d$, which is calculated from the values of $\partial U^{(0)}/\partial q_1$ in Figure 4, is plotted in Fig. 5.

The shrinkage from the gas-phase bond length increases with increasing number density of CS$_2$. This value rises $0.2 \times 10^{-3}$ to $2.6 \times 10^{-3}$ Å 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 components 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 $\nu_1$ 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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