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VIBRATIONAL SPECTRA OF SOLID AND LIQUID SULFUR

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Abstract.— We have measured the Raman spectra of intermolecular vibrations of sulfur in the temperature regions of orthorhombic-monoclinic, solid-liquid, and polymerization transitions. The evolution of the Raman spectrum at the first phase transition is discussed in terms of the disorder-induced Raman scattering. The Raman spectra in liquid suggest ordering in the liquid phase. The appearance of the S_n -polymer above the polymerization temperature changes the slopes of the exponential Raman spectra in the liquid.

1. Experiment.— The Raman spectra were measured by conventional Raman scattering equipment with a He-Ne laser and by a system designed to obtain spatially-resolved Raman spectra with an Optical Multichannel Analyzer (OMA) and an Ar⁺ laser (5145Å). In the latter case, a sample cell was placed in a vertical oven with the temperature gradient of about 10 deg./mm along the vertical direction. Then, the temperature dependence of the Raman spectra across the liquid-solid phase boundary was obtained from the spatially-resolved Raman spectra with the spatial resolution of 10 μ . The use of the OMA system made it possible to determine the temperature dependence of the Raman spectra very quickly with a small temperature increment of less than 0.5 K. All the data were taken with 99.999 % sulfur sealed in a glass cell in a back scattering configuration.

2. Results.— Figure 1 shows the depolarized Raman spectra of (a) orthorhombic (α), (b) monoclinic (β), and (c) liquid (γ) sulfur that were measured when we increased the temperature from 290 K to above the melting point $T_m = 391$ K. The Raman spectrum for α -sulfur in Fig. 1(a) agrees well with the results of Anderson and Loh.¹⁾ The Raman bands at 83 and 153 cm^{-1} have been assigned to intramolecular vibrations of the S_8 -ring.¹⁾ Intermolecular vibrations are responsible for the other parts of the spectra in Fig. 1. The spectrum in Fig. 1(d) was taken at the same temperature as Fig. 1(b), but the two spectra are quite different.

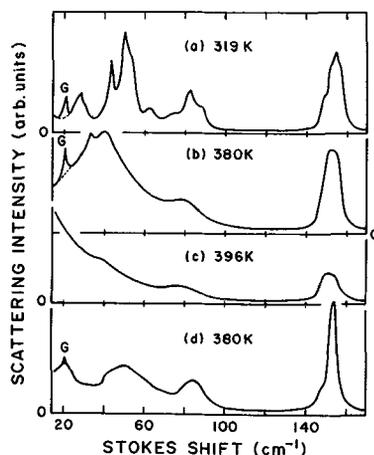


Fig. 1. Depolarized Raman spectra of sulfur. The peak, G, is the monochromator ghost.

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The reason for the difference arises from the fact that the sample for Fig. 1(b) was obtained through the $\alpha \rightarrow \beta$ phase transition at about 369 K while the crystal for Fig. 1(d) was solidified from liquid. The quality of the β -sulfur obtained by the solidification of liquid is expected to be better.

Figure 2 shows the spatially-resolved Raman spectra across the liquid-solid phase boundary. The data were taken for five different temperature regions at 0.5 K intervals simultaneously. Figures 2(a) and 2(b) correspond to the β -, and 2(d) and 2(e) to the ℓ -sulfur region, respectively. Since the resolution in Fig. 2 ($\approx 7 \text{ cm}^{-1}$) is not as high as in Fig. 1 ($\approx 0.75 \text{ cm}^{-1}$), the fine structure in Fig. 1(b) is not resolved in Fig. 2(a) or 2(b). The intermolecular Raman band appears at the same frequency ($\approx 37 \text{ cm}^{-1}$) for $\Delta T \equiv T_m - T = 11 \text{ K}$ (Fig. 1(b)), $\Delta T = 1.0 \text{ K}$ (2(a)), and $\Delta T = 0.5 \text{ K}$ (2(b)). The width of the band, furthermore, stays almost constant from $\Delta T = 11 \text{ K}$ to $\Delta T = 1.0 \text{ K}$, and it increases slightly at $\Delta T = 0.5 \text{ K}$.

Figure 3 shows a logarithmic plot of the Raman spectra of the liquid. The spectral shape is approximated by

$$I \propto \exp(-\hbar\omega/\Delta) \quad (1)$$

where $\hbar\omega$ and Δ denote the Stokes shift and a constant, respectively. Humps at 40 and 80 cm^{-1} , however, are superposed on the exponential curves in the low temperature spectra for $T \leq 510 \text{ K}$. The 80 cm^{-1} hump is due to an intramolecular vibration. The intensity of the hump at 40 cm^{-1} decreases with temperature, and the hump disappears above 440 K . Figure 4 shows the

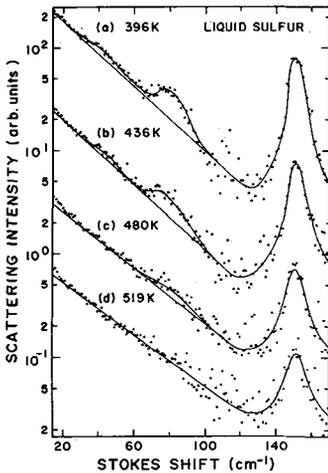


Fig. 3. Logarithmic plot of Raman spectra of ℓ -sulfur. Vertical displacements of the spectra have been made for clarity.

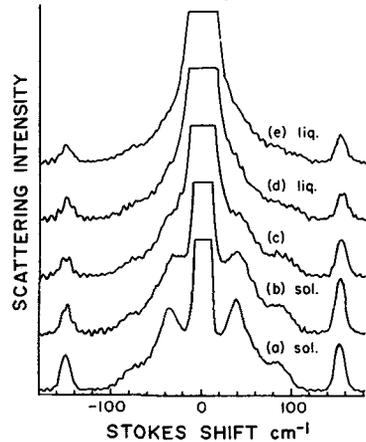


Fig. 2. Spatially-resolved Raman spectra of sulfur across the solid-liquid phase boundary.

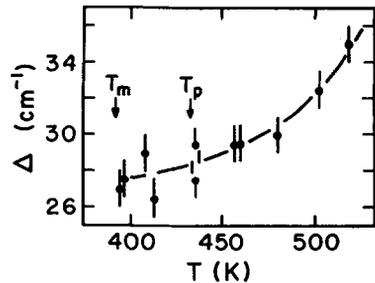


Fig. 4. Temperature dependence of Δ in ℓ -sulfur.

temperature dependence of Δ as deduced from the slopes of the straight lines in Fig. 3. The melting point, T_m , and the polymerization temperature, $T_p = 432$ K, are shown as a reference in Fig. 4.

3. Discussion.— Since one-third of the S_8 molecules of β -sulfur are twofold disordered at $T > 198$ K,²⁾ the broad intermolecular Raman band of β -sulfur centered at 37 cm^{-1} , similar to Fig. 1(b), was attributed to the disorder-induced one-phonon scattering due to the breakdown of the k-selection rule.³⁾ The intermolecular Raman spectrum of the sulfur solidified from liquid (Fig. 1 (d)) is similar to the spectrum of α -sulfur rather than that of β -sulfur obtained through the $\alpha \rightarrow \beta$ transition (Fig. 1(b)). This fact seems to suggest that the degree of disorder is lower in the β -sulfur obtained by the solidification than in the sulfur procured through the $\alpha \rightarrow \beta$ transition.

The position of the hump (40 cm^{-1}) in the Raman spectra of the liquid agrees well with the Stokes shift of the disorder-induced Raman band of the solid. The observation of this hump indicates that order in liquid sulfur exists over the range of a few molecules at $T \leq 440$ K.

As shown in Fig. 3, β -sulfur shows an exponential Raman spectrum in contrast to many kinds of molecular liquids, which show non-exponential spectra approximated by $\omega^{12/7} \times \exp(-\hbar\omega/\Delta)$,⁴⁾ for instance. The exponential spectra have been observed in atomic liquids.^{4,5)} According to the theory of collision-induced Raman scattering in liquids,⁴⁾ the exponential spectra suggest that the molecular frame distortion does not play an important role for the collision-induced polarizability anisotropy compared with the contribution from the electronic overlap effect.

The theories available for the interpretation of high frequency Raman scattering in liquids predict that the value of Δ in Eq. (1) is expected to vary as $\Delta \propto \sqrt{T}$ ⁵⁾ or $\sqrt{T}/[1 - (2/\pi)\arctan \sqrt{2\varepsilon/T}]$,⁴⁾ where ε is the energy constant for the Lennard-Jones potential. Figure 4, however, shows that Δ varies more rapidly than \sqrt{T} , especially above T_p . Gee⁶⁾ has reported that the weight fraction of S_8 -ring in the liquid decreases above T_p while the fraction of S_n -polymer increases abruptly, and the fraction of polymer reaches 50 % at about 510 K. The extraordinary increase in Δ above T_p , therefore, may be attributed to the appearance of polymeric chains.

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