

## Raman Spectra of Liquid Sulfur Around the Polymerization Transition

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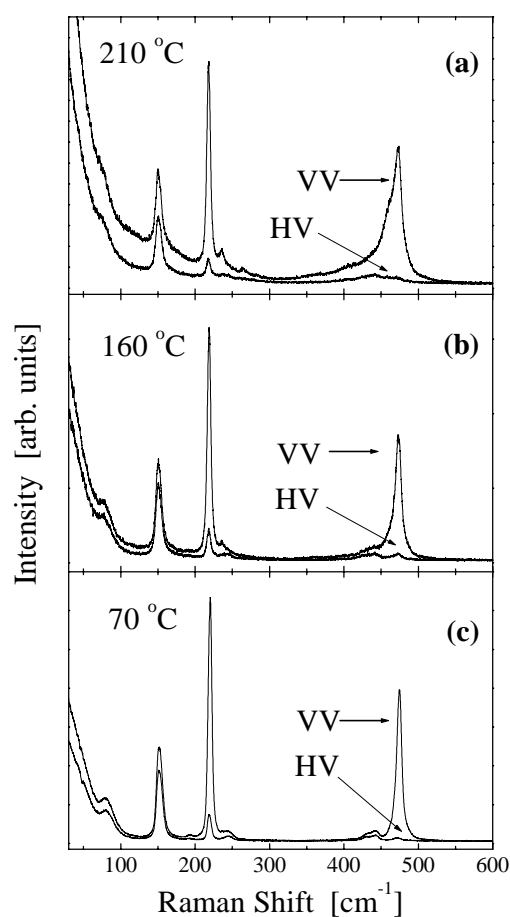
Elemental Sulfur is one of the most representative and simplest examples of inorganic systems undergoing an equilibrium polymerization transition. Solid Sulfur melts at  $T_m \approx 120$  °C forming a light yellow liquid, consisting primarily of  $S_8$  rings. Near  $T_p \approx 160$  °C liquid Sulfur polymerizes exhibiting a sudden dramatic increase of its viscosity [1]. Much below  $T_p$  the liquid is mainly made of  $S_8$  rings, while approaching the transition the liquid becomes gradually a mixture of  $S_8$  rings and long  $S_n$  chains. The degree of polymerization becomes almost maximum at  $T_p$ .

Sulfur of purity 99.999% was flame sealed in evacuated quartz ampoules. Right-angle Stokes Raman spectra were recorded with a double monochromator with a resolution of  $\sim 1$   $cm^{-1}$ . The exciting source was a  $Kr^+$  ion laser operating at 647.1 nm far away from the absorption tail of the reddish liquid at very high temperatures. Both polarized (VV) and depolarized (HV) spectra have been registered. The temperature was controlled with an accuracy of  $\pm 0.5$  K. Although crystalline sulfur melts at about 120 °C, it is possible by slowly supercooling to avoid crystallization and to maintain the metastable liquid up to 70 °C.

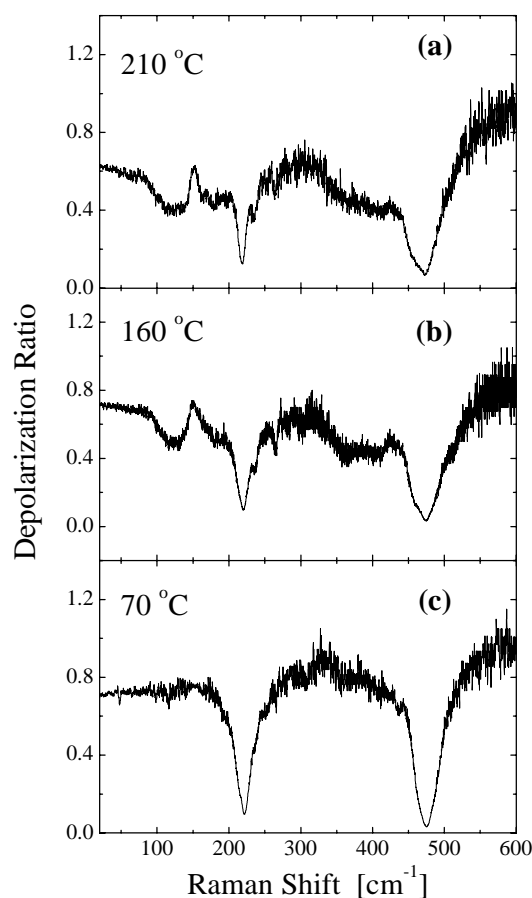
Figure 1 shows representative polarized and depolarized Raman spectra at three characteristic temperatures, namely at the lowest supercooled point (c), near the polymerization transition (b), and at the highest temperature studied in the present work (a). The spectra are dominated by the intense vibrational lines located at 150, 219, and 473  $cm^{-1}$  characteristic of the  $S_8$  ring. The 473  $cm^{-1}$  band is assigned to the symmetric bond-stretching mode, the 219  $cm^{-1}$  band to the symmetric bond-bending mode, and the 150  $cm^{-1}$  to the antisymmetric bond-bending mode of the  $S_8$  ring [2]. These peaks seem to survive in the whole temperature range measured. This fact does not contradict the polymerization scheme according to which  $S_8$  rings break up and form quasi one-dimensional chains; they are present in the spectra due to the much higher magnitude of the corresponding element in the Raman polarizability tensor (strong cross section). On the other hand, new weaker peaks start to appear presumably due to the formation of  $S_n$  molecular fragments. Since the intensity of the polymer-like segments is weaker compared to that of the  $S_8$  rings we have employed the depolarization ratio as a rather sensitive indicator to follow the subtle changes that the spectra develop with increasing temperature. As is seen in Fig. 2, the depolarization ratio exhibits significant qualitative changes upon heating, revealing detailed changes in the existing vibrational modes and the appearance of new ones.

### References

- [1] B. Mayer, Chem. Rev. **76**, 367 (1976).
- [2] D. W. Scott, et al. J. Mol. Spectrosc. **32**, 13 (1969).



**Figure 1.** Representative polarized (VV) and depolarized right-angle Stokes Raman spectra for liquid sulfur. (a) High temperature melt. (b) Liquid at the polymerization transition  $T_p \approx 160$  °C. (c) Supercooled liquid ( $T_m \approx 120$  °C)



**Figure 2.** Depolarization ratios of liquid sulfur corresponding to the spectra shown in Fig. 1.