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Structure and vibrational modes of sulfur around the λ -transition and the glass-transition

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Abstract

In this paper we present a detailed temperature-dependence of Raman spectroscopic study of the vibrational modes of elemental sulfur around its polymerization transition or λ -point (T_λ) in order to elucidate the structural transformations. The considerable supercooling that liquid sulfur exhibits makes it possible to extend the light scattering study to ~ 50 °C below melting point as well as to glassify sulfur by fast quenching the high temperature melt. Despite the apparent simplicity of sulfur, the determination of its structure has proved considerably puzzling. The results are discussed within the context of existing structural models for liquid sulfur.

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1. Introduction

The study of elemental sulfur has been a challenge for many investigators due to its unique variety of stable molecules which can be formed in the solid, the liquid, and the gaseous state resulting in singular chemical and physical properties. The chemical conversion of these allotropic forms occurs at moderate temperature [1,2]. At room temperature elemental sulfur is found in the stable crystalline orthorhombic modification (α - S_8) where the structure is based on the packing of crown-like S_8 -rings. Ortho-

rhombic α -sulfur converts into monoclinic β -sulfur at 95.3 °C and melts at ~ 115 °C forming a pale-yellow liquid of relatively low viscosity whose structure consists mainly of S_8 rings as has been supported by spectroscopic data [3,4]. Liquid sulfur preserves this structure up to the polymerization transition point, $T_\lambda \approx 159$ °C, where it becomes gradually a mixture of S_8 rings and long polymer S_n chains [1,2]. This polymerization results in a dramatic viscosity increase (of about five orders of magnitude [5]) which further decreases with increasing temperature, exhibiting a λ -type transition, thus showing a completely different behavior compared to other liquids [1]. Fast quenching of molten sulfur in liquid nitrogen results in a glass whose glass transition temperature falls within -40 to -20 °C depending on the thermal history [6].

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The structure of liquid sulfur has been the subject of neutron [7,8] and X-ray [9] diffraction studies, as well as some Raman [3,4] scattering investigations. Sound propagation and attenuation have repeatedly been studied indicating characteristic changes at least for the former around T_λ [10]. Despite the large amount of experimental data and the plethora of theoretical models it is a consensus that the structural changes around T_λ are not yet fully understood.

2. Experimental

Appropriate amounts of sulfur (Alfa, 99.9995%) were doubly distilled and then loaded and flame-sealed under vacuum (0.06 Torr) in carefully cleaned cylindrical quartz ampoules. In order to avoid moisture, the treatment took place in an inert gas (Ar) filled glove-bag. The samples were kept at $\sim 240^\circ\text{C}$ for 24 h and then quenched at liquid nitrogen temperature to produce the glass. The obtained glass was pale-yellow, transparent and free of any cracks. Glass formation was not observed when the liquid was quenched from temperatures below T_λ .

Right-angle Raman spectra were recorded with a 0.85 m double monochromator (Spex 1403). The excitation source was a Kr^+ laser operating at $\lambda_0 = 647.1\text{ nm}$ with an output power of about 20–30 mW on the sample. The instrumental resolution was fixed at 1 cm^{-1} for temperatures ranging from -180 to 240°C and 2 cm^{-1} for the temperature interval 240 – 270°C . The temperature was controlled with an accuracy of $\pm 0.5\text{ K}$. Both the polarized (VV) and depolarized (HV) scattering geometries were employed, while a Hg lamp was used to calibrate the frequency scale. Corrections for polarization were made with the aid of liquid CCl_4 . Low temperature spectra were recorded with the aid of a specially designed home made Raman LN_2 optic cell with a resistive heating to achieve temperatures between LN_2 and room temperature.

3. Results

Fig. 1 shows the Raman spectra of the two sulfur crystalline polymorphs. At $T_{\text{tr}} = 95.3^\circ\text{C}$

orthorhombic α -sulfur converts into monoclinic β -sulfur [1]. The spectral changes are more obvious in the lower part of the spectrum (below 80 cm^{-1}) where the initially resolved multiplet of libration and translation peaks – characteristic of the crystal lattice – merge into a featureless spectral envelope above T_{tr} .

Representative Raman spectra of liquid sulfur over the temperature interval 70 – 210°C are shown in Fig. 2. In order to follow in detail the subtle, low-intensity spectral changes, which are caused by certain structural rearrangements around the transition at T_λ , we use in this figure a semi-log representation. The already existing modes at $T < T_\lambda$ do not experience significant changes when crossing the λ -transition. On the other hand, new modes begin to rise in the frequency region below ca. 150 cm^{-1} , as well as in the spectral range 250 – 500 cm^{-1} . The main vibrational peaks of the S_8 ring molecule persist over the whole temperature range, namely the strong peaks at 472 cm^{-1} (ν_1 : S–S stretching vibration), the $\sim 220\text{ cm}^{-1}$ (ν_2 : S–S–S bending vibration) and the $\sim 150\text{ cm}^{-1}$ (ν_8 : S–S–S bending vibration). The relatively weak Raman bands at $\sim 440\text{ cm}^{-1}$ (ν_{10}), $\sim 239\text{ cm}^{-1}$ (ν_4) and $\sim 85\text{ cm}^{-1}$ (ν_9) remain also in the spectrum of the liquid

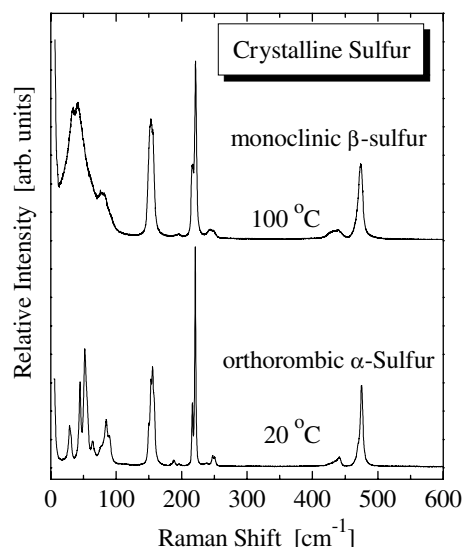


Fig. 1. Right-angle Stokes-side Raman spectra of the two crystalline polymorphs α - and β -sulfur. Transition temperature: $T_{\text{tr}} \approx 95.3^\circ\text{C}$; excitation line: $\lambda_0 = 647.1\text{ nm}$.

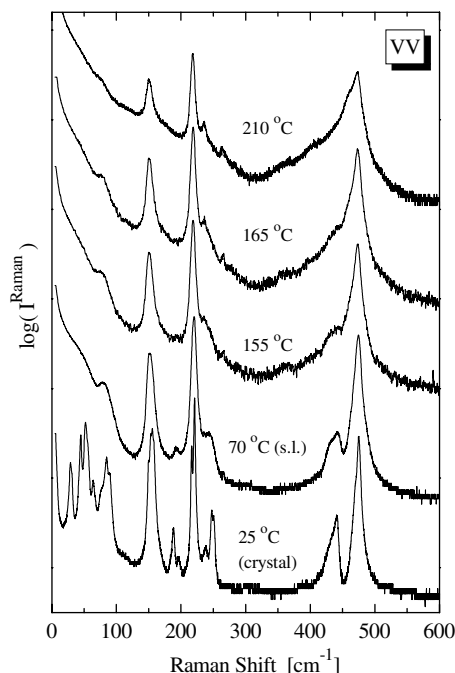


Fig. 2. Representative polarized (VV) Stokes-side Raman spectra of supercooled liquid (s.l.) and molten sulfur shown in a semi-logarithmic representation. The spectrum of α -sulfur is also shown at bottom for comparison.

with the ν_4 becoming even sharper above the transition point T_λ .

4. Discussion

It is well known that the population of the vibrational energy levels involved in the scattering process is amenable to temperature variations. Therefore, in order to disentangle the spectral changes caused either by temperature or by alterations of local species equilibria (modifications in structure) one has to employ the so-called reduction procedures. Because phonons obey Bose-like statistical description, their mean number at a particular temperature is given by $n(\nu, T) = [\exp(\hbar\nu/k_B T) - 1]^{-1}$ where \hbar and k_B are the Planck's and Boltzmann's constants, respectively. Therefore, the Stokes-side reduced Raman intensity (I^{red}) is related to the experimentally measured one (I^{exp}) through the equation

$$I^{\text{red}}(\nu) = (\nu_0 - \nu)^{-4} \nu [n(\nu, T) + 1]^{-1} I^{\text{exp}}(\nu), \quad (1)$$

where the term in the fourth power is the usual correction for the wavelength dependence of the scattered intensity; ν is the frequency in cm^{-1} , and ν_0 denotes the wavenumber of the incident radiation.

Fig. 3 shows the semi-log representation of the reduced isotropic (R^{ISO}) spectra. The isotropic (ISO) spectra have been calculated with the aid of polarized and depolarized spectra through the relation, $I^{\text{ISO}} = I^{\text{VV}} - 4/3 I^{\text{HV}}$ and allows one to discern purely vibrational features.¹ As is made out from Fig. 3 extra isotropic modes appear in the region 100–180 cm^{-1} . However, it is even more evident the onset of new broad vibrational modes at $\sim 360 \text{ cm}^{-1}$ and $\sim 410 \text{ cm}^{-1}$ in the spectrum of 165 °C. These latter modes gain intensity and broaden further with increasing temperature as can be seen from the spectrum at 210 °C. Even more drastic intensity changes around T_λ experience the relatively sharp peaks located at 461 and 472 cm^{-1} . Their relative intensity exhibits strong temperature dependence with increasing temperature. In particular the vibrational mode located at 461 cm^{-1} gains intensity at the expense of the 472 cm^{-1} line. As it has been anticipated [3] long S_n chains are characterized by a strong vibrational line at $\sim 456 \text{ cm}^{-1}$ which is very close to the 461 cm^{-1} line. It should be noted here that the 410 cm^{-1} vibrational mode mentioned above is also very close to the 416 cm^{-1} line [3] of the S_n chains. A detailed analysis [11] followed by a deconvolution procedure in the region 430–530 cm^{-1} has revealed that the ratio I^{461}/I^{472} changes (increases) as a function of temperature abruptly when getting across T_λ .

Representative Raman spectra for glassy sulfur, which has been quenched from 240 °C to liquid nitrogen, are shown in Fig. 4. The spectra have been recorded by gradually increasing the tem-

¹ The noisy pattern around 150 cm^{-1} is a computational product arising from the fact that the ν_8 vibrational mode is totally depolarized (depolarization ratio: 3/4) which results to a zero intensity isotropic spectrum. The logarithmic representation has also contributed to the magnification of this noisy pattern.

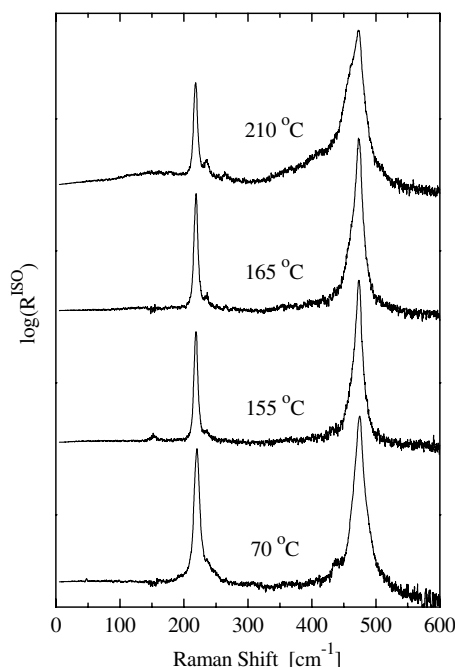


Fig. 3. Semi-logarithmic representation of the reduced-isotropic (R^{ISO}) Raman spectra of liquid sulfur shown in Fig. 2.

perature. In the temperature range between -180 and 0 °C, changes in the relative intensities of the stronger peaks of sulfur occur. In particular, the intensity of the 472 cm^{-1} band decreases relative to the 220 cm^{-1} band as temperature increases from -180 to 0 °C. Another interesting finding is that the temperature dependence of the intensity ratio of the 461 and 472 cm^{-1} lines in the glassy state has the opposite trend compared to that in the melt. Specifically, the ratio I^{461}/I^{472} decreases as temperatures rises. This is consistent with the interpretation given above, according to which the 461 cm^{-1} line is associated with the vibrational modes of the S_n chains. Indeed, when quenching the melt from high temperature a large fraction (~ 0.56 in weight as measured in [12]) of S_n chains which exists in equilibrium with S_8 rings (as well as other molecular units) is captured into a metastable solid configuration. As the temperature increases, the S_n chains anneal and convert to more stable structures; as a result the intensity of the 461 cm^{-1} line characteristic of these chains decreases monotonically with temperature.

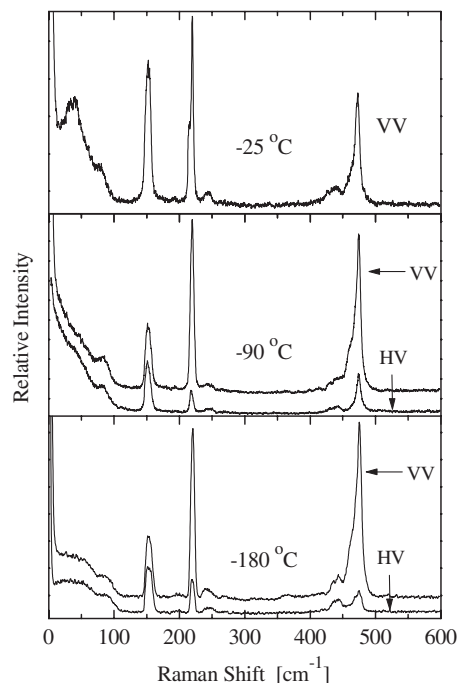


Fig. 4. Representative polarized (VV) and depolarized (HV) Stokes-side Raman spectra of glassy sulfur.

The low-frequency part of the Raman spectrum is dominated by two spectral features ubiquitously present in the case of non-crystalline phases, namely the Boson peak and the quasi-elastic line. The presence of translation/libration low-frequency bands does not allow for an easy inspection of the Boson peak which is expected below 15 cm^{-1} as is evident from the lower panel of Fig. 4. Since the Boson peak intensity follows the Bose thermal population factor of first order scattering, it is expected to be very weak at -180 °C. The temperature increase to -90 °C strengthens its intensity although it still cannot be completely resolved since it is located at very low frequency. A further increase of the temperature reveals a well-resolved dip at low frequencies close and above the glass transition temperature which presumably originates from the complete absence (overdamping at such high temperatures) of the modes that give rise to the Boson peak. This may be due to its softening in frequency and/or due to the fact that the structural entities responsible for the Boson peaks' presence cease to exist. Such structural

entities could be presumably the S_n chains. The exact spectral behavior of the quasi-elastic line and its interrelation to the Boson peak [13,14] feature could not unequivocally clarified from the present study.

5. Conclusions

The main conclusions from this study are: (i) α - and β -sulfur differ mainly in the low-frequency region where the initially resolved multiplet of libration and translation peaks merge into a featureless spectral envelope across the $\alpha \rightarrow \beta$ transition. (ii) New peaks in the reduced isotropic spectra have been identified with increasing temperature. Their frequencies compare favorably with older experimental data on polymeric sulfur. Further support was provided here by checking their temperature dependence in the melt and in the glassy phase. (iii) The unexpected temperature dependence of the scattered intensity at frequencies below ca. 40 cm^{-1} , which exhibits a dip above the glass transition temperature indicates the presence of the Boson peak although it is not

clearly resolved due to the complications of the low-frequency Raman spectrum of glassy sulfur.

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