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THE COLOR OF LIQUID SULFUR

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Communication to the Editor, Journal of the American Chemical Society, Physical Chemistry Section

The Color of Liquid Sulfur

Sir:

At the melting point, liquid sulfur is yellow; at the boiling point it is dark red. The color change, which is demonstrated in every freshman class, is due to an apparently monotonous shift of the absorption edge towards the red and due to an increase of the visible absorption (Figure 1). While the accompanying viscosity change is well known and well understood[1,2], the color change has drawn little scientific attention.

Only three spectral studies have been reported[3-5], and the latest view[5] is that the shift of the absorption edge is caused by thermal population of ground state vibrational modes of S_8.

We have studied the absorption spectrum of liquid sulfur in the temperature range between the melting point and 700°C. The temperature dependent shift of the red absorption edge is about 23.6 cm^{-1} per degree.[6] This shift is 10 times larger than the shift of the red absorption edge of S_8 in solution in the temperature range between 76°K and 25°C.[6] The shift in the liquid is too large to be due to thermal population alone. Furthermore, the temperature dependent shift is only reversible if the liquid is very slowly cooled. Rapid quenching of the liquid to room temperature does not yield the absorption of S_8, as shown in Figure 2a, but it yields the spectrum in Figure 2b. The shoulder at 3600 Å is due to quenched, metastable polymeric sulfur.[6] The formation, concentration and composition of polymers in liquid sulfur are well established.[1,2] The spectrum of polymeric sulfur explains the apparently large shift in the spectrum of the liquid between the melting point and 300°C and the sudden increase of the shift at 160°C.

However, above 300°C, where the concentration of polymers decreases, the color of the liquid continues to darken. If boiling sulfur is quenched in liquid nitrogen, we obtain a red glass with the spectrum shown in Figure 2c. At about -80°C the red films convert into yellow polymeric sulfur. The quenching experiments prove that the spectrum of hot liquid sulfur is not due to thermal broadening of S_8 absorption alone, but due to superposition of the spectrum of S_8 with that of polymeric sulfur and that of the red species which absorb at 4000 Å and 5100 Å.

In order to identify the red species, we compared the spectrum of the liquid with that of the vapor at 17 torr and 450°C, Figure 2d. The structured absorption at 4000 Å and the continuum at 5100 Å were first reported in 1910,[7] and later[8,9] assigned to either S_3 or S_4. This assignment has been confirmed by a study of the intensity of this system as a function of vapor pressure and temperature , and by comparison with the mass spectroscopic data[10,11] on the vapor composition. We have now recorded spectra with ^{34}S, and determined that the electronic origin of the 4000 Å system lies at 4235 Å. If one allows for a solvent shift and considers the temperature difference, the Franck-Condon curve and the electronic origin agree very well with that of the absorption of frozen liquid sulfur.

In order to determine whether the absorption, and therefore the red color, was really due to S_3 or S_4, we decided to prepare small sulfur species in a low temperature matrix. Sulfur vapor is not a suitable source for the synthesis of S_3 or S_4, because it always also contains other species.[10,11] Instead we used the photolysis of S_3Cl_2 in an organic glass and in rare gas matrices. S_3Cl_2 was prepared from SCl_2 and liquid H_2S.[12] In this synthesis only chlorosulfanes with an odd number of sulfur atoms are formed, and S_4Cl_2 is absent. 99% pure S_3Cl_2 can be obtained by vacuum distillation. A 10^{-4} molar solution of S_3Cl_2 in 1:2 isopentane-cyclohexane at 77°K, with the spectrum shown in Figure 2g, was photolyzed with a high pressure mercury arc. The spectrum of the photolysis products is shown in Figure 2e. Figure 2f shows the photolysis products of S_3Cl_2 in a krypton matrix at 20°K. The experimental techniques used in the preparation and handling of low temperature samples was similar to that described elsewhere.[13] The spectrum has a vibrational spacing, a Franck-Condon curve and an origin as expected for the cold gas species responsible for the absorption of sulfur vapor in Figure 2d. This indicates that the gas species absorbing at 4000 Å is the same as that produced by photolysis of S_3Cl_2, and is S_3, thiozone. The mechanism of the photolysis of S_3Cl_2 yielding thiozone seems to be analogous to that of the photolysis of S_2Cl_2,[14] which yields S_2, and very little S_2Cl. Whether the continuous absorption at 5100 Å, which also occurs in frozen liquid, is due to S_3 or S_4 has not yet been determined.

The similarity among the matrix spectrum, the vapor spectrum at 450°C and that of quenched red sulfur indicates that hot liquid sulfur contains S_3. S_3 and S_4 have similar thermal properties and always occur together.[10,11] Thus, hot liquid sulfur contains S_3 and S_4.

We conclude that the color change upon heating of sulfur is due to formation of S_3 and S_4. The optical density at 4000 Å and 5100 Å indicates that at the boiling point sulfur contains from 1 to 3% S_3 and S_4.

Detailed data and analysis will be presented later.

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Figure Captions

Figure 1:	Shift of red absorption edge of liquid sulfur.
Figure 2:	a) Absorption of S_8 in methanol at 25°C. b) Absorption of polymeric sulfur in glycerin at room temperature. c) Absorption of boiling sulfur quenched in liquid nitrogen. d) Absorption of sulfur vapor at 450°C and 20 torr. e) Absorption of S_3Cl_2 photolyzed in a krypton matrix at 20°K. f) Absorption of S_3Cl_2 photolyzed in 1:2 isopentane-cyclohexane glass at 77°K. g) S_3Cl_2 before photolysis.

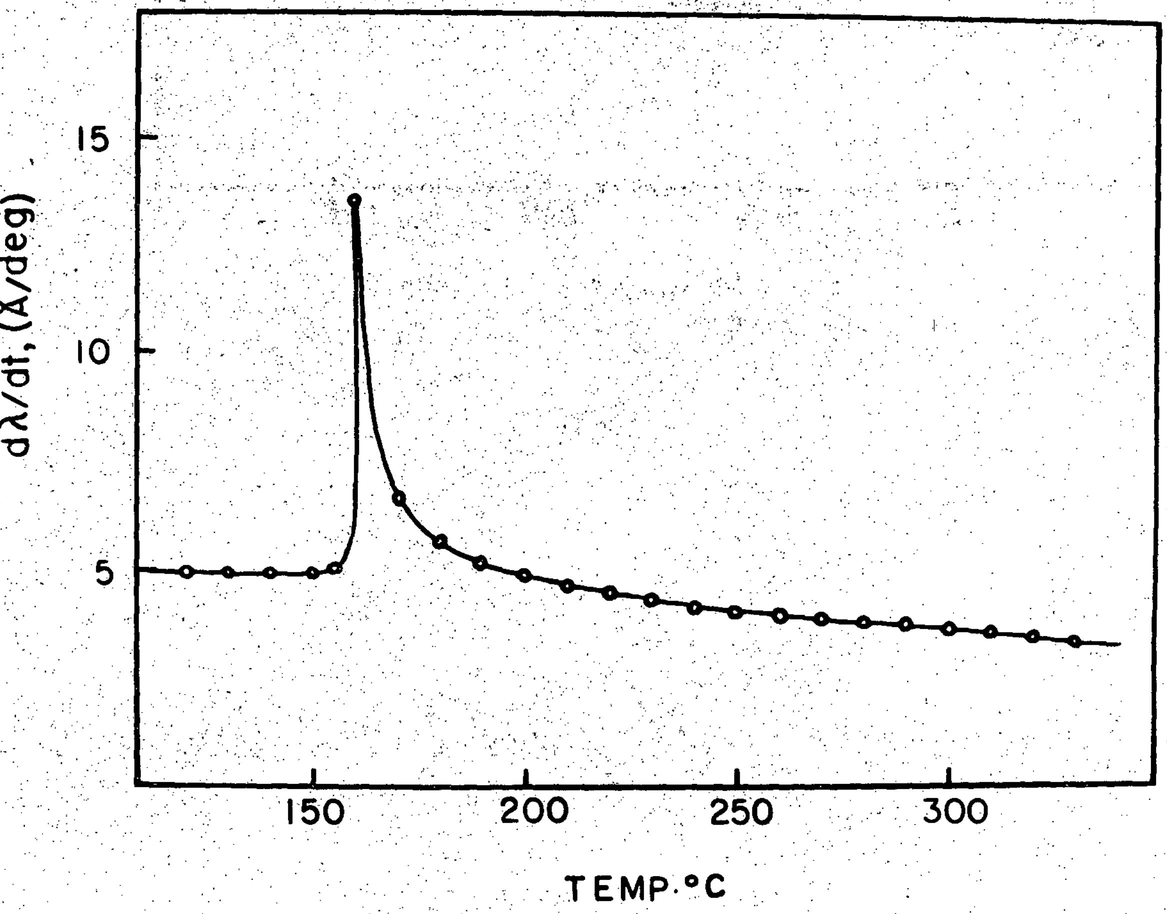

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Fig. 1

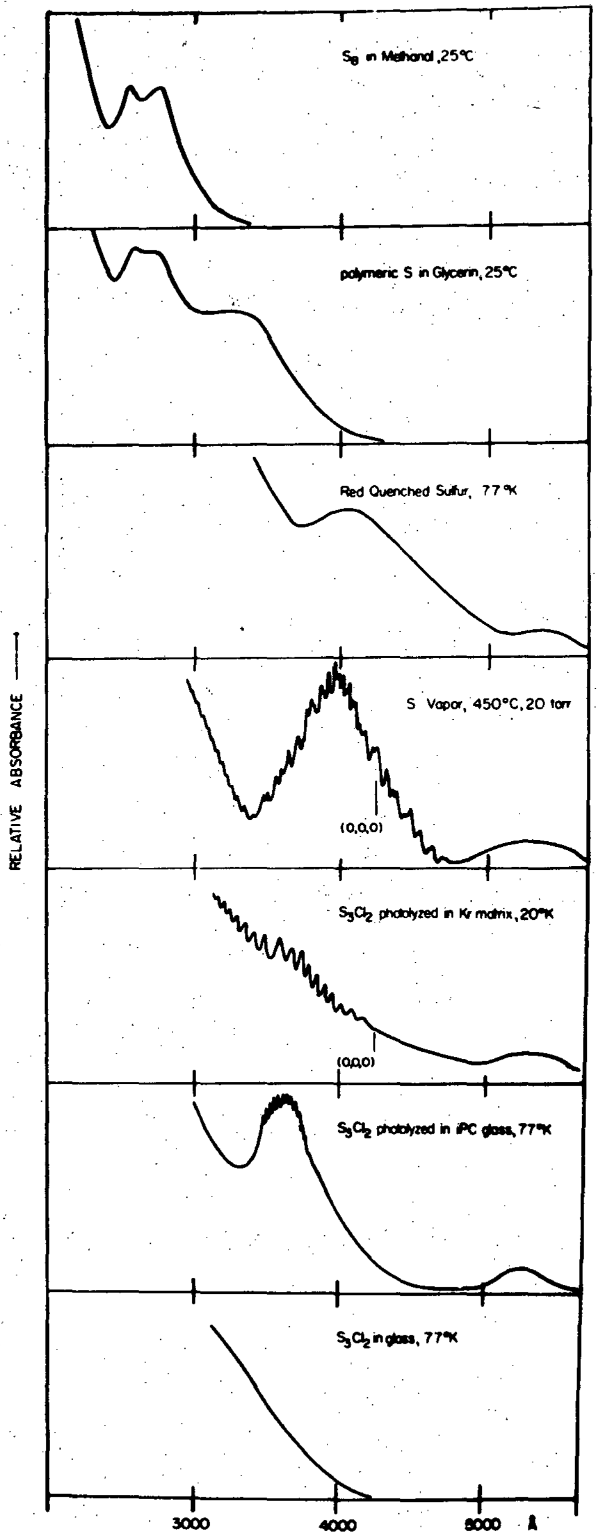

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Fig. 2

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