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ON THE TEMPERATURE DEPENDENCE OF POSSIBLE S_8 INFRARED BANDS IN PLANETARY ATMOSPHERES

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ABSTRACT

Measurements of the temperature dependence between 77 and 333K of the infrared spectrum of cyclic octatomic sulfur suggest that the 23 μm Jovian feature very tentatively identified by Houck et al. (1975) is not due to S_8; and that the temperature dependence of the frequency of the 835 cm^{-1} band of S_8 may be a useful temperature marker in planetary studies.

Because of the high cosmic abundance of sulfur, it should be present in elemental or combined form in many solar system environments. Cyclic octatomic sulfur, S_8, is produced in high yield on ultraviolet irradiation in a variety of reducing atmospheres, and has been proposed as a constituent in the clouds of Jupiter and other objects in the outer solar system (Khare and Sagan, 1975). In addition, polymeric sulfur (linear or cyclic) may possibly be present in the clouds of Venus (Hapke, 1975) and on the surface of Io (Wamsteker et al., 1974; Fanale et al., 1974). The strongest permitted infrared transition of S_8 at wavelengths short of 50 microns is in the vicinity of 469 cm^{-1} -- a frequency in fair agreement with that of the strongest unidentified feature in the Jovian infrared spectrum (Houck et al., 1975). While there is perhaps as much as a 10 cm^{-1} uncertainty in the frequency of the Jovian band, it is displaced from the room temperature frequency of the corresponding S_8 band by about 20 cm^{-1}. While Houck et al. have expressed considerable caution about the reality of their 23 μm feature, it still seems worth-while to investigate the temperature dependence of nearby S_8 features. The temperature dependence of infrared vibrational features of several other constituents of potential interest for planetary astronomy have been measured (Smythe, 1975; Fink and Larson, 1975; Kieffer and Smythe, 1974; Pollack and Sagan, 1968) and are of potential utility in determining the temperatures of planetary and satellite surfaces and cloud layers. This possibility provides another motivation for measurements of the temperature dependence of the various infrared features of S_8.

A few mg of Mallinckrodt sublimed sulfur was mixed with about

250 mg of CsI powder and a 13 mm diameter pellet was prepared according to the method described in our earlier paper (Khare and Sagan, 1975). The pellet was implanted in a hole in a copper block and affixed with a copper collar and an indium metal O-ring. A copper-constantan thermocouple was placed in thermal contact with the copper block and less than 1 mm from the pellet. The entire block was firmly attached, using a flat indium gasket to a standard infrared research Dewar (Hoffman Laboratories, Newark, New Jersey) equipped with CsI windows. Temperatures were measured with the mentioned thermocouple as well as with another thermocouple imbedded on the cooling block of the Dewar itself. Boiling water and liquid nitrogen were employed in separate experiments to achieve temperatures higher than and significantly lower than room temperture; and, in the latter case, to reach temperatures which are crudely comparable to those of the region of the Jovian atmosphere observed near 23 μm. Because of the energy provided by the infrared spectrometer's infrared source and because of thermal conduction, equilibrium temperatures reached by the CsI pellet, as measured by both thermocouples, were in the two experiments 333°K and 77°K respectively. The highest temperature is < 333°K because the initially boiling water is cooled by heating the dewar during transit. Temperatures at the beginning and the end of each scan were constant within 1 K°.

Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared grating double beam spectrometer, purged with dry air, in the 200 to 4000 cm^{-1} region. The spectra were calibrated in wavelength using an indene film (IUPAC, 1961) and are believed to be accurate to $\pm$ 1 cm^{-1}.

Over this temperature range, the 469 cm^{-1} band maintained a constant frequency within the errors of measurement. Changes were observed in the frequency of the relatively weak feature whose room temperature band center is near 835 cm^{-1}. This feature has a broad absorption maximum which makes it difficult to specify an exact band center. At 333°K the absorption maximum lies between 834 and 845 cm^{-1}; at 77°K, it lies between 852 and 855 cm^{-1}. Other S_8 features at 243 cm^{-1}, 335 cm^{-1}, and 1208 cm^{-1} seem likewise to be temocrature-independent within a few cm^{-1}, a result consistent with previous work (Scott, et al, 1964; Chantry, et al., 1964; Meyer, 1965; Anderson and Loh, 1969). The temperature variation of the 835 cm^{-1} feature is consistent with the quantitative results reported by Neff and Walnut (1961). This absorption band is a combination band rather than a lattice fundamental (Neff and Walnut, 1961). An impression of the overall appearance of the infrared spectra at these two temperatures, as well as at room temperature, is provided in Figure 1.

We conclude that the 23 μm feature of Houck et al. (1975), if real, cannot be attributed to cyclic octatomic sulfur; but that other features of S_8, such as the band with a room temperature central frequency of 835 cm^{-1}, may prove to be useful temperature calibrators if S_8 is unambiguously discovered in planetary or satellite spectra.

While there remains no strong observationsal evidence for polymeric sulfur on Jupiter, for the reasons we have already given (Khare and Sagan, 1975) we still hold that it is a likely constituent of the Jovian clouds.

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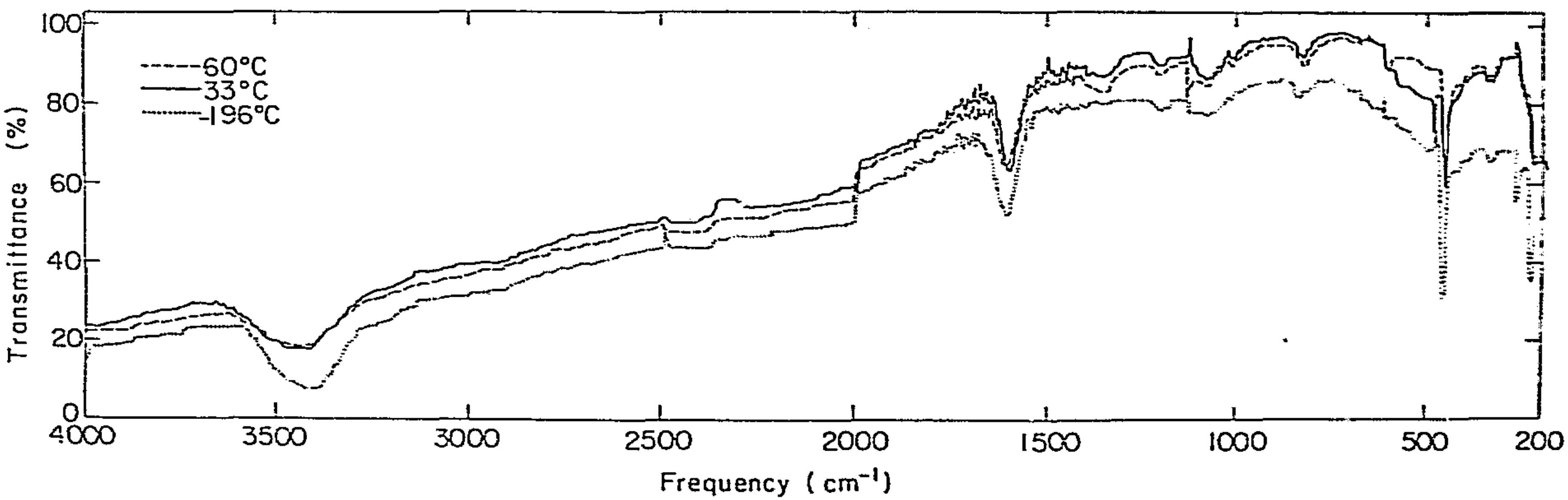
Figure Caption

Figure 1: The transmission spectrum of CsI pellets of S_8 as a function of temperature. The features at 1611 cm^{-1} and at 3450 cm^{-1} are due to water impurities in CsI. The negative peak at 2330 cm^{-1} is due to absorption by atmospheric CO_2 in the sample compartment in the reference beam. The discontinuities near 2300, 2000, 1150, 630, 500 and 295 cm^{-1} are instrumental artifacts due to changes in filters or gratings and should be disregarded.



60°C
33°C
-196°C
Transmittance (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
200
Frequency (cm⁻¹)