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Cyclic Octatomic Sulfur: A Possible Infrared and Visible Chromophore in the Clouds of Jupiter

Abstract. *A brown polymeric material, produced under simulated Jovian conditions, is composed primarily of cyclic octatomic sulfur, although a range of complex organic compounds is also present. The polymeric sulfur, produced from the ultraviolet photolysis of hydrogen sulfide, exhibits its strongest band at 465 reciprocal centimeters, in fair agreement with the frequency of the unidentified Jovian absorber recently announced by Houck* et al. *Polymeric octatomic sulfur may be an important constituent of the Jovian clouds.*

Near-ultraviolet (near-UV) light is known to be an effective agent for the photoproduction of a range of organic molecules from simulated primitive Earth and contemporary Jovian environments (*1, 2*). In the course of such experiments, a complex powdery polymeric material is produced, which, we have suggested (*2*), may be related to the molecular chromophores responsible for the coloration in the clouds of Jupiter. In this report we discuss the infrared spectrum of this powder and its comparison with recent high-altitude infrared spectra of Jupiter.

In a typical experiment, a spherical reaction vessel with a capacity of 12.7 liters is filled with 3350 cm³ of CH_4, 3437 cm³ of NH_3, and 2862 cm³ of H_2S, and the gases are irradiated with the resonance emission lines of mercury from a 450-watt high-pressure quartz lamp (Hanovia) radiating 5.8 watts at 2537 Å. The gases, along with the photolytic products, are recycled by a greaseless solenoid pump (Watson) out from and back into the reaction vessel. (Both CH_4 and NH_3 have been observed spectroscopically in the Jovian atmosphere, and, in an excess of H_2, H_2S is expected to be present.) As the photolysis continues, the interior walls of the reaction vessel accumulate an orange-brown precipitate. After 12 hours and 40 minutes of photolysis, 3521 cm³ of C_2H_6 (now known to be a minor constituent of the Jovian atmosphere) and an additional 850 cm³ of H_2S are introduced. After 29 hours of further photolysis, a seal is magnetically broken, permitting the pump to circulate gases and reaction products over an NH_4OH bath (corresponding to the proposed lower clouds of Jupiter). After another 6 days and 19 hours, 1150 cm³ of H_2S are introduced. The experiment is terminated after an additional 8 days and 22 hours. The visual appearance of the brownish powder did not change after the first few hours of photolysis. The NH_4OH bath, which was not exposed to UV radiation, also acquired a distinct brownish coloration after the reaction products acquired access to it. Additional H_2S was introduced because this molecule is the primary photon acceptor in such experiments; its photolysis produces hot hydrogen atoms superthermal by several electron volts, which initiate subsequent steps of the reactions. Solar near-UV photons are calculated to reach atmospheric levels on Jupiter at which H_2S photolysis will proceed. In such experiments a wide variety of organic molecules are produced, including upon hydrolysis more than 40 amino acids, among them cystine (*1–3*).

In our earlier experiments, the polymer was separated by paper chromatography into two components, one described as "brown" and the other as "yellow." The yellow material is a complex mixture of organic compounds with negligible elemental sulfur, as determined, for example, by mass spectrometry. The brown material must contain large quantities of sulfur and its compounds. Clear mass spectrometric evidence of polymeric sulfur from S_1 to S_8 was secured for an evaporated aliquot of the aqueous bath. We have now examined the properties of the full polymeric powder, not subjected to either chromatographic separation or organic chemical extraction techniques. After hydrolysis of the full polymer with 6*N* HCl an atomic analysis (*4*) of the residue gives the following abundances (in percent by weight): hydrogen, 0.15; carbon, 1.44; oxygen, 1.89; nitrogen, 0.42; and sulfur, 95.99. The residue is clearly primarily sulfur.

A few milligrams of our raw precipitate were scraped from the wall of the reaction vessel and mixed with about 250 mg of CsI powder in a stainless steel vial with a stainless steel ball pestle. Grinding was accomplished in 2 minutes with an electric mixer. The mixed powder appeared brownish. It was then transferred to a die assembly which was pumped for 10 minutes to remove water vapor. A pressure of 1700 atm was then applied for 10 minutes, and the press repeated twice. Figure 1 shows the in-

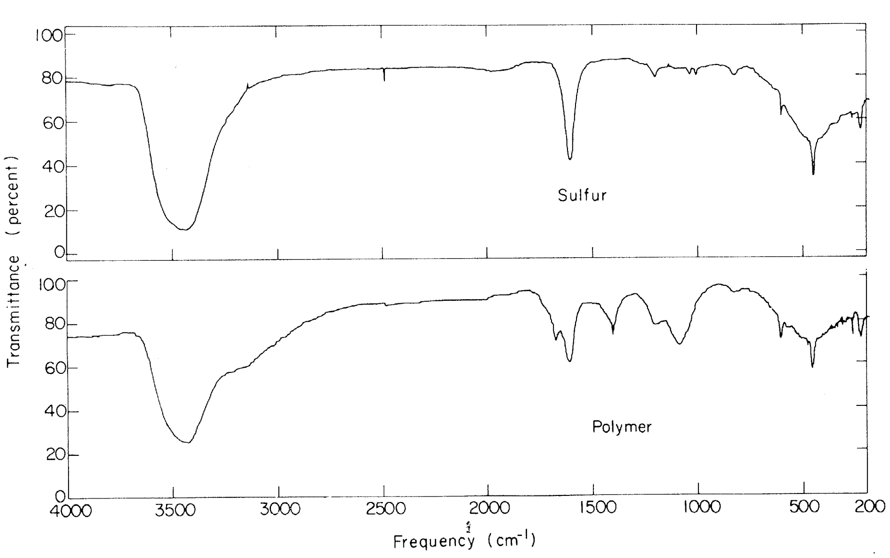

Fig. 1. The infrared spectra of the brown polymeric material (bottom) and sulfur (top). The additional absorption features in the experimental product are due to a variety of organic compounds.

frared spectrum of this CsI pellet, run in double-beam mode against an identically prepared pellet of pure CsI on a grating spectrophotometer (Perkin-Elmer model 621). Also shown is the comparable double-beam spectrum of a pair of CsI pellets, one a control and the other containing a few milligrams of sublimed sulfur (Mallinckrodt). The agreement is excellent. The bands at 3440 and 1613 cm^{-1} in both spectra are due to bound water. The strong features near 465 and 243 cm^{-1} are characteristic of elemental sulfur in the cyclo-S_8 configuration (*5*). Our sample was also examined by laser Raman spectroscopy (Spex model 1401; 2-watt argon irradiation at 5145 Å; 100 mw at the sample; 0.3-cm^{-1} resolution) and exhibits Raman bands at 151, 185, 217, 246, 434, and 470 cm^{-1}, all corresponding (*5*) to S_8.

We conclude that the infrared spectrum of our powder is dominated by cyclic octatomic sulfur (with water contaminants), and that the organic molecules that we know are present have an abundance that is an order of magnitude less than that of sulfur. The spectra of Fig. 1 suggest that the S_8 ring vibrational features at 465 and 243 cm^{-1} be searched for in the infrared spectra of Jupiter and other objects in the outer solar system. The only such spectra that we know of are those obtained by Houck *et al.* at aircraft altitudes and described in the preceding report (*6*). In addition to the expected $J = 0$ and $J = 1$ rotational transitions of H_2, these spectra apparently reveal an unexpected absorption feature centered near 23 μm. A comparison of the spectrum of this Jovian feature with the spectrum of the CsI pellet containing our brown precipitate, both obtained with the same flight spectrometer, is exhibited in Fig. 2. The spectrum of the precipitate has been displaced 1 μm to longer wavelengths in the comparison. The temperature sensitivity of the 465-cm^{-1} S_8 feature has apparently not been studied, but variations as much as 10 cm^{-1} in the frequency of maximum absorption with temperature excursions over plausible Jovian regimes are known for other bands of S_8 [for example, see (*7*)]. In addition, the absolute wavelength calibration of the spectrometer used in the comparison is uncertain to about 10 cm^{-1} (*8*).

The strongest infrared absorption feature present in powders produced under simulated Jovian conditions roughly matches the most prominent unidentified infrared feature in the spectrum of Jupiter; accordingly we suggest that both are due to the same material, cyclic octatomic sulfur. However, because of the tentative nature of the announcement of the Jovian feature (*6*), its reality must be considered with caution. The question can be settled with higher-resolution spectroscopy of the apparent 23-μm feature, or by searches for the other strong infrared transitions of S_8, those at 150 cm^{-1} and at 200 to 250 cm^{-1} (*5*), if they are not obscured by Jovian NH_3 and H_2. That elemental sulfur might be produced on Jupiter by solar UV photolysis of H_2S was proposed in 1937 by Wildt (*9*). In recent speculation that the optical frequency chromophores on Jupiter might be compounds of sulfur (*10, 11*), attention has concentrated on compounds of sulfur and NH_3 and not on elemental sulfur, although this possibility has been mentioned by Lewis and Prinn (*11*). The chromatographic fraction of our sample which is sulfur-free is nevertheless strongly absorbing in visible light, and we continue to hold that organic molecules may be the optical frequency chromophores on Jupiter. However, it is clearly prudent to consider polymeric sulfur as an additional prime candidate.

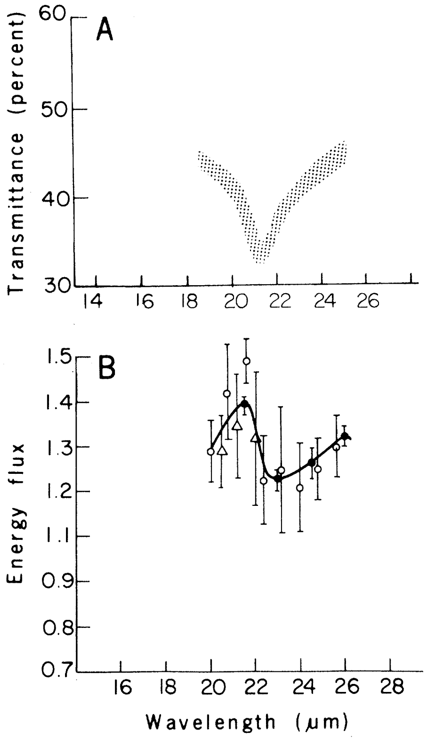

Fig. 2. The infrared transmission of a CsI pellet containing the brown polymeric material (A) as compared with the infrared spectrum of the Jovian feature at 22 to 24 μm (B), both taken with the same flight spectrometer. The two spectra are displaced from each other by 1 μm. Experimental errors in (B) are indicated by error bars; experimental errors in (A) are indicated by the width of the curve.

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Sun-Tracking Solar Furnaces in High Arctic Flowers: Significance for Pollination and Insects

Abstract. *Heliotropic flowers* (Dryas integrifolia, Papaver radicatum) *act, in sunshine, as solar reflectors, their corollas focusing heat on the sporophylls. Considerable intrafloral temperatures are generated. Winds above 3.8 meters per second and cloud abolish the effect. Insects that bask in the flowers also gain heat. The phenomena are important in maximizing the small heat budget.*

In the arctic, any biotic mechanism for maximizing use of the small heat budget is advantageous. Heliotropism is such a mechanism in plants and is defined by Kevan (*1*) as turning to and with the sun—that is, sun-tracking. It is a manifestation of positive phototropism in which turning proceeds at a rate of 15° of arc per hour.

The flowers of two common high arctic plants (which occur widely in arctic and alpine regions) around Hazen Camp, Lake Hazen, Ellesmere Island, Northwest Territories, Canada (about 82°N), were found to be heliotropic under optimal conditions—*Papaver radicatum* Rottb. (Papaveraceae) for a possible maximum of 24 hours and *Dryas integrifolia* M. Vahl. (Rosaceae) for a possible maximum of about 6 to 8 hours centered about 11.00 hours solar time (Fig. 1). The possibility that this phenomenon