

Vaporization of Ices Containing S<sub>2</sub>—Implications for CometsM. H. MOORE,<sup>1</sup> B. DONN,<sup>\*</sup> AND R. L. HUDSON<sup>†</sup>*University of Maryland, College Park, Maryland 29782; \*NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771; and †Eckerd College, St. Petersburg, Florida 33733*

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The detection of S<sub>2</sub> in Comet IRAS-Araki-Alcock 1983d and the suggestion that it was a parent molecule has raised many interesting astrochemical questions concerning its origin and eventual release into the coma. Experimentally, we have examined the following two questions: (1) Can S<sub>2</sub> be stored in ices during warming, and (2) is S<sub>2</sub> released during vaporization of its water ice matrix?

We have recorded the ultraviolet spectrum of S<sub>2</sub> in argon and krypton matrices and water ice in which the ratio of matrix or molecular ice to S<sub>2</sub> was the order of 500:1. The intensity of S<sub>2</sub> absorptions decreased in argon during warming. In water the weak S<sub>2</sub> signal was detected from 12 to 140°K during short annealing periods, but was not detected after annealing at 140°K for 17 hr. S<sub>3</sub> and S<sub>4</sub> were also detected in some ices along with seven unidentified absorption features centered near 6250 Å.

S<sub>2</sub> was not detected with a mass spectrometer during vaporization of Ar:S<sub>2</sub>, Kr:S<sub>2</sub>, Kr:<sup>34</sup>S<sub>2</sub>, or H<sub>2</sub>O:<sup>34</sup>S<sub>2</sub> (each ~500:1) mixtures. Our experiments support the idea that the S<sub>2</sub>:H<sub>2</sub>O ratio in the solid phase may not be a predictor of the gas phase ratio. After warming, a room temperature residue was always formed. Sulfur was detected in that residue. We conclude that similar vaporization from a cometary nucleus would not release the bulk of any S<sub>2</sub> trapped in the ice and that an alternate mechanism for releasing this diradical is required. © 1988 Academic Press, Inc.

## INTRODUCTION

A'Hearn *et al.* (1983) reported the detection of the diradical S<sub>2</sub> in Comet IRAS-Araki-Alcock, 1983d, a long period comet ( $P = 1000$  years). S<sub>2</sub> was detected in the inner coma and the authors argue that its spatial distribution was consistent with its being a parent molecule residing in the nucleus as opposed to being a radical formed by molecular dissociation in the coma. It was this comet's small geocentric distance which provided the favorable conditions necessary to detect species confined so close to the nuclear region. S<sub>2</sub> was detected in all spectra although its production rate varied much more than that of other species (Feldman *et al.* 1984). S<sub>2</sub> was detected both

before and after the sharp outburst in cometary brightness which was well correlated with a sharp increase in solar wind speed. These authors concluded, however, that the bulk of S<sub>2</sub> measured was probably not associated with the outburst except that during the burst its emission features were easier to detect due to its short time scale compared to that of other species.

A'Hearn and Feldman (1984) discuss possible sources of S<sub>2</sub> in a cometary nucleus and review arguments against the direct accretion of S<sub>2</sub> from the gas phase. In general it seems unlikely that S<sub>2</sub> could form in the gas phase and condense with other materials to form comets since many calculations (see, for example, Mitchell 1984) support the idea that most S atoms would form species other than S<sub>2</sub>. The interstellar abundance of S is less than 10% that of carbon, therefore the amount of S<sub>2</sub> formed

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relative to molecules containing carbon should be very small. A'Hearn *et al.* (1983) calculated a  $S_2/OH$  relative production rate of  $5 \times 10^{-4}$  which was comparable to the relative production rate of  $CS/OH$ . The high abundance of  $S_2$  in IRAS-Araki-Alcock is not easily understood.

An alternate formation mechanism examined by A'Hearn and Feldman (1984) is the radiation synthesis of  $S_2$  from sulfurous molecules. The synthesis of new species in ices has been demonstrated in various laboratory experiments. Irradiation studies using ices of astrophysical interest include proton irradiation (e.g., Moore *et al.* 1983, Strazzulla *et al.* 1984, Calcagno *et al.* 1985), ion erosion and modification (e.g. Lanzerotti *et al.* 1984, Johnson *et al.* 1984), and photolysis (e.g., Sagan and Khare 1979, Greenberg 1982). A'Hearn *et al.* (1984) concluded that cosmic ray or solar wind radiation synthesis in cometary ices would not work. Ultraviolet irradiation of grain mantles prior to accumulation into the nucleus was also suggested as a possible mechanism for producing a relatively large  $S_2$  concentration throughout the nucleus. Recently Grim and Greenberg (1987) reported  $S_2$  synthesis as the result of photolysis of  $H_2S$  in ices composed of molecules such as Ar,  $H_2O$ , CO, and  $CH_4$ . In view of the detection of  $S_2$  in Comet IRAS-Araki-Alcock, and the proposal that it was a parent molecule, we undertook experiments to study the behavior of  $S_2$  in icy mixtures.

Several laboratory studies have shown that  $S_2$  can be formed and stored in rare gas matrices. Using electrical discharge or photolysis of matrix-isolated molecules such as  $CS_2$  ( $T < 15^\circ K$ ), S atoms are formed in the matrix. During warming these ground state S atoms diffuse in the matrix and combine with each other forming  $S_2$ . Fournier *et al.* (1977) and Lee and Pimental (1979) studied  $S_2$  formed in matrix-isolated OCS and  $CS_2$ . Smardzewski (1978) studied  $S_2$  emission in ultraviolet photolyzed matrix-isolated  $H_2S$ .

Because cometary ices and mantles of interstellar grains contain water it is of astro-

chemical interest to study  $S_2$  in water-dominated icy mixtures. Grim and Greenberg (1987) have reported the detection of SH,  $S_2$ , CS, SO, and  $SO_2$  in various UV-photolyzed icy mixtures. The  $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$  system of  $S_2$  was identified using laser-induced fluorescence, LIF, in mixtures such as Ar: $H_2O$ :CO: $CH_4$ : $H_2S$  (300:1:1:1:1) and  $H_2O$ : $H_2S$  (10:1).  $S_2$  abundances relative to  $H_2S$  of about 0.012 were calculated for Ar: $H_2S$  and 0.008 for Ar: $H_2O$ :CO: $CH_4$ : $H_2S$  mixtures. A formation technique for  $S_2$  tried in our laboratory was the proton radiation analog to a photolysis experiment ( $S_2$  formed when matrix isolated, photolyzed  $CS_2$  was warmed). In this experiment we irradiated Ar: $CS_2$  (100:1) at  $T = 12^\circ K$  with 1-MeV protons. We tried to observe the formation of  $S_2$  by detecting its chemiluminescence while warming but were plagued with the intense phosphorescence of  $SO_2$  whose spectrum overlapped any  $S_2$  emissions (several photolysis experiments with the same matrix composition gave similar results). Infrared absorption features of  $SO_2$  were also identified in the proton-irradiated matrix ( $S_2$  has no dipole moment and is not detectable using infrared spectroscopy). We felt that more rigorous experimental techniques could have eliminated water contamination, but decided this method of detecting  $S_2$  was too marginal to pursue. We also concluded that if similar processes occurred in icy mantles, then  $SO_2$  would form along with any  $S_2$  that may form. This conclusion led us to check the IUE observations of Comet 1983d for evidence of  $SO_2$  emissions but none were detected (M. A. A'Hearn, private communication). Neither  $SO_2$  nor SO has been detected in any cometary spectra.

The next question of astrochemical interest which arises is what effect does time, radiation, and temperature have on the storage of  $S_2$  in, or release from, cometary type ices. Several laboratory studies of  $S_2$  in inert matrices support the idea that  $S_2$  diffuses in the ice when the temperature is raised to  $\frac{1}{4}$  or  $\frac{1}{3}$   $T_m$  ( $T_m$  is the melting point of

the matrix). For example, Hopkins and Brown (1975) showed that the Raman signal of S<sub>2</sub> disappeared rapidly from argon matrices during annealing to 31°K (near  $\frac{1}{3} T_m$ ). Meyer *et al.* (1972) showed S<sub>2</sub> diffused in krypton matrices annealed at 30°K (near  $\frac{1}{4} T_m$ ) to form S<sub>4</sub>. These experiments shed some doubt on whether it is possible to release S<sub>2</sub> through vaporization of a cometary ice without its reacting with another molecule. Grim and Greenberg (1987) also studied the warming of several photolyzed water ices containing S<sub>2</sub>. The LIF signal of S<sub>2</sub> was found to remain constant as the photolyzed ice was warmed to near 120°K ( $\frac{2}{3} T_m$ ). The emission signal actually increased above 120°K coincident with the amorphous to crystalline phase transition of ice. After 160°K the LIF signal decreased, which was interpreted as the loss of S<sub>2</sub> due to evaporation with the water molecules. These studies show that S<sub>2</sub> can be stored in photolyzed water ice mixtures (at least for short time periods) to temperatures near  $\sim\frac{1}{2} T_m$  perhaps due to effective intermolecular bonding.

The crucial question which remains is whether a species such as S<sub>2</sub> can be released during the vaporization of its volatile matrix. No experimental studies have investigated this type of ice mixture. In fact, the opposite has been studied. In a recent paper, Bar-Nun *et al.* (1985) discuss the release of a more volatile molecule from a less volatile ice. They show that volatile molecules are released in three or four distinct temperature ranges, each resulting from a different trapping mechanism. The major goal of our research was to investigate the vaporization of ices containing S<sub>2</sub>. To do this we constructed a system to mass-spectrometrically detect S<sub>2</sub> in the vapors released during sublimation of ices known (from ultraviolet spectroscopy) to contain S<sub>2</sub> at low temperatures.

#### EXPERIMENTAL

A standard Air Products cryostat was used to cool a substrate onto which our ex-

perimental ices were deposited at temperatures as low as 12°K (for details see Moore 1981). A six-sided chamber (Fig. 1) was designed to provide a variety of *in situ* capabilities by rotating the cold substrate to face various sides.

The multiport chamber and cryostat are permanently interfaced with a Van de Graaff accelerator which can be used to irradiate ices with 1-MeV protons, although in this paper the main emphasis is on the vaporization of icy films. All ices were formed by co-depositing a gas along with S<sub>2</sub>. The gases used were argon (Matheson, prep. grade), krypton (Matheson, research grade), and H<sub>2</sub>O (deionized, degassed,  $R > 10^{+7}$  ohm). <sup>32</sup>S sublimed sulfur was obtained from Mallenckrodt Chemical Works; <sup>34</sup>S was 93.6 atom% enriched from Monsanto Research Corp. Mound Laboratory. Because both <sup>32</sup>S<sub>2</sub><sup>+</sup> and <sup>32</sup>SO<sub>2</sub><sup>+</sup> (a possible oxidation product) have  $m/e = 64$ , <sup>34</sup>S was used in some experiments which allowed discrimination in the mass spectrometer scan between <sup>32</sup>S<sub>2</sub><sup>+</sup> and <sup>34</sup>SO<sub>2</sub><sup>+</sup> (68 and 66, respectively).

S<sub>2</sub> was produced using a double furnace in which sulfur powder was heated in a vacuum to around 373°K (a temperature sufficient to melt the sulfur and raise the pressure in the oven to near 0.005 Torr). This is a standard pyrolysis technique for the formation of S<sub>2</sub> (see, for example, Brewer *et al.* 1965). The complex vapors effusing from this oven (S<sub>8</sub>; S<sub>7</sub>; S<sub>6</sub>; etc.) were passed through a  $\frac{1}{2}$ -mm capillary tube heated to 1020°K. At 1020°K and pressures below 1 Torr the equilibrium is shifted to simpler sulfur species (Berkowitz *et al.* 1962); nearly 95% of the vapor is S<sub>2</sub>. These diradicals were mixed with a beam of gas and deposited onto the cold substrate.

Located at 90° to the sulfur oven was a Dycor quadrupole mass spectrometer (QMS). During deposition of the ice the QMS analyzed the composition of the gas in the vacuum system. It is well documented that S<sub>2</sub> could result from fragmentation of larger sulfur molecules (S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>,

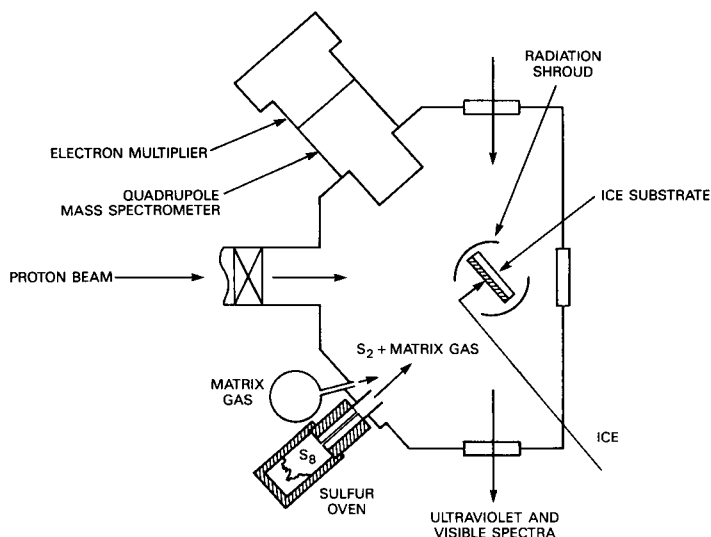


FIG. 1. In this multiport chamber, a variety of measurements can be performed on gases condensed on substrates cooled to temperatures as low as 12°K. Here the substrate is shown facing the sulfur oven. S<sub>2</sub> from the oven and a beam of gas are co-deposited to form matrix-isolated S<sub>2</sub>. The ultraviolet transmission spectrum can be measured, the ice can be irradiated with protons, or the icy sample can be rotated to face the quadrupole mass spectrometer during vaporization.

etc.) by the 75-eV electron impact ionizer of our QMS (Berkowitz and Marquart 1963, Chrisey *et al.* 1988); however, we did not detect signals of S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>. Typical M : R ratios of 500 : 1<sup>2</sup> (matrix gas : radical) were required to form a reasonable quality S<sub>2</sub> band spectrum in the ultraviolet. When the M : R ratio was lower, strong S<sub>4</sub> and S<sub>x</sub> (unidentified) absorptions were present in the spectra. These larger sulfur molecules were probably forming in the ice. This is possible because of local warming which could occur from the heat dissipated during condensation of hot, reactive S<sub>2</sub>. The relative S<sub>2</sub> concentration in the gas phase, measured by the QMS, was representative of the rela-

tive S<sub>2</sub> concentration in the condensed phase. This is supported by noting that under some conditions of deposit, other molecules (e.g., SO<sub>2</sub> and H<sub>2</sub>S) with nearly equal signal intensities to S<sub>2</sub> were detected during deposit. These molecules were condensed (along with S<sub>2</sub>) and were detected during vaporization of the ice (S<sub>2</sub> was not detected). The intensity of the  $m/e = 36, 66,$  and  $68$  signals in Fig. 7b demonstrate this. Typical deposition times of 1–2 hr resulted in ice films estimated to be several micrometers in thickness. These estimates were based on comparisons with several preliminary experiments in which interference fringes were used to calculate ice thickness.

Ultraviolet spectra of ice films on sapphire substrates were recorded using a Cary 14 spectrophotometer. S<sub>2</sub> was seen in absorption near 2800 Å (Brewer *et al.* 1965) along with some S<sub>3</sub> and S<sub>4</sub> which have transitions near 4100 and 5200 Å, respectively (Meyer *et al.* 1972). S<sub>2</sub> spectra were identified in mixtures of Ar:S<sub>2</sub>, Kr:S<sub>2</sub>, and H<sub>2</sub>O:S<sub>2</sub>.

<sup>2</sup> The intensity of each species in the gas phase was determined by including single and double ionized signals with fractionation and isotopic peaks. M : R ratios measured during deposits were near ~1000 : 1. Relative partial pressure ratios, estimated by applying numerous corrections to account for ionizer sensitivity, quadrupole transmission factors, etc., reduced the M : R intensity ratio a factor of about 2. All concentrations are therefore listed as ~500 : 1.

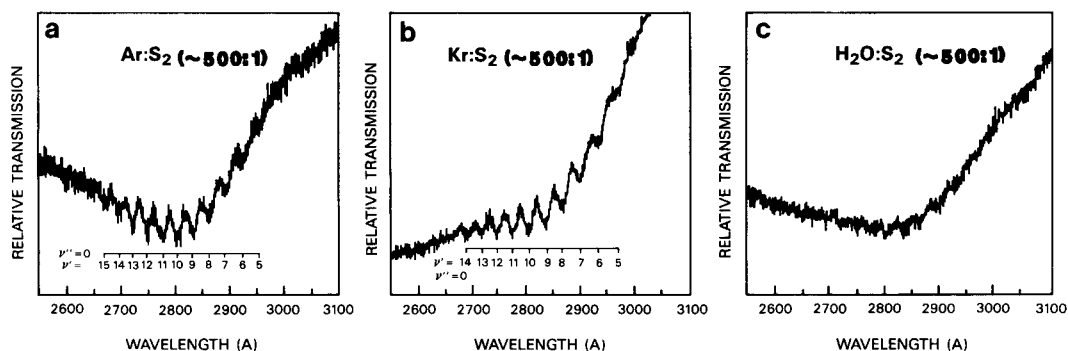


FIG. 2. The redrawn ultraviolet absorption spectra of matrix-isolated S<sub>2</sub> in argon (a), krypton (b), and water (c) at temperatures near 12°K. All absorption bands are attributed to the  $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$  system of S<sub>2</sub>. Transition assignments are listed in Table I.

To study the sublimation of these icy films, the substrate was changed to a 2.5-cm-diameter gold-coated aluminum disk attached to the tail of the cryostat with an appropriate thermal link. The metal disk had a heater epoxied to its back so that only local heating occurred. Using this technique it was possible to cool the metal disk to 17°K for deposition and to warm it to 167°K without raising the temperature of the tail of the cryostat above 45°K.

## RESULTS

### a. Deposition of Icy Films Containing S<sub>2</sub>

Ultraviolet spectra of thin ice films of S<sub>2</sub> in argon and krypton matrices and in water ice deposited near 12°K are shown in Figs. 2a, 2b, and 2c. All absorption bands are attributed to the  $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$  system of S<sub>2</sub> and appear to be superimposed on a broad feature suggested by Brewer *et al.* (1965) to result from unresolved S<sub>2</sub> bands. Following Brewer *et al.* (1965), transition assignments are listed in Table I for S<sub>2</sub> in argon and krypton matrices. We extended these assignments to the weak vibrational structure in water ice. S<sub>2</sub> signatures in water were very weak possibly because of substantial S<sub>2</sub>-H<sub>2</sub>O intermolecular interaction. Nevertheless the spectrum was sufficient to prove the S<sub>2</sub> was present in the ice.

Typical QMS spectra recorded during deposition of argon, krypton, or water with

S<sub>2</sub> are shown in Figs. 3a, 3b, and 3c, respectively. S<sub>2</sub> was identified in all mass spectra of the gas in the vacuum chamber. The spectrum in Fig. 3b shows no detectable <sup>34</sup>SO<sub>2</sub><sup>+</sup> (*m/e* = 66), only <sup>34</sup>S<sub>2</sub><sup>+</sup> (*m/e* = 68). Other deposit spectra (not shown) recorded

TABLE I  
ABSORPTION SPECTRUM OF S<sub>2</sub>

$\nu'' = 0, \nu'$	Absorption maxima (Å) $\pm 3$ Å		
	Ar matrix <sup>a</sup>	Kr matrix <sup>b</sup>	H <sub>2</sub> O ice <sup>a,c,d</sup>
4	3000(vw) <sup>b</sup>		3013 <sup>b</sup>
5	2958(w)	2970(vw)	2975 <sup>b</sup>
6	2927	2932	2930
7	2894	2900	2899
8	2863	2865	2867
9	2833	2835	2833
10	2805	2805	2799
11	2777	2775	2775 <sup>e</sup>
12	2749	2747	2749
13	2723	2720	2716
14	2697	2690	2680 <sup>e</sup>
15	2671		
16	2646 <sup>e</sup>		
17	2622 <sup>b</sup>		

<sup>a</sup> Average of three experiments.

<sup>b</sup> One experiment.

<sup>c</sup> Accuracy  $\pm 10$  Å due to weak and broad features in water ice.

<sup>d</sup> Tentative assignment.

<sup>e</sup> Average of two experiments.

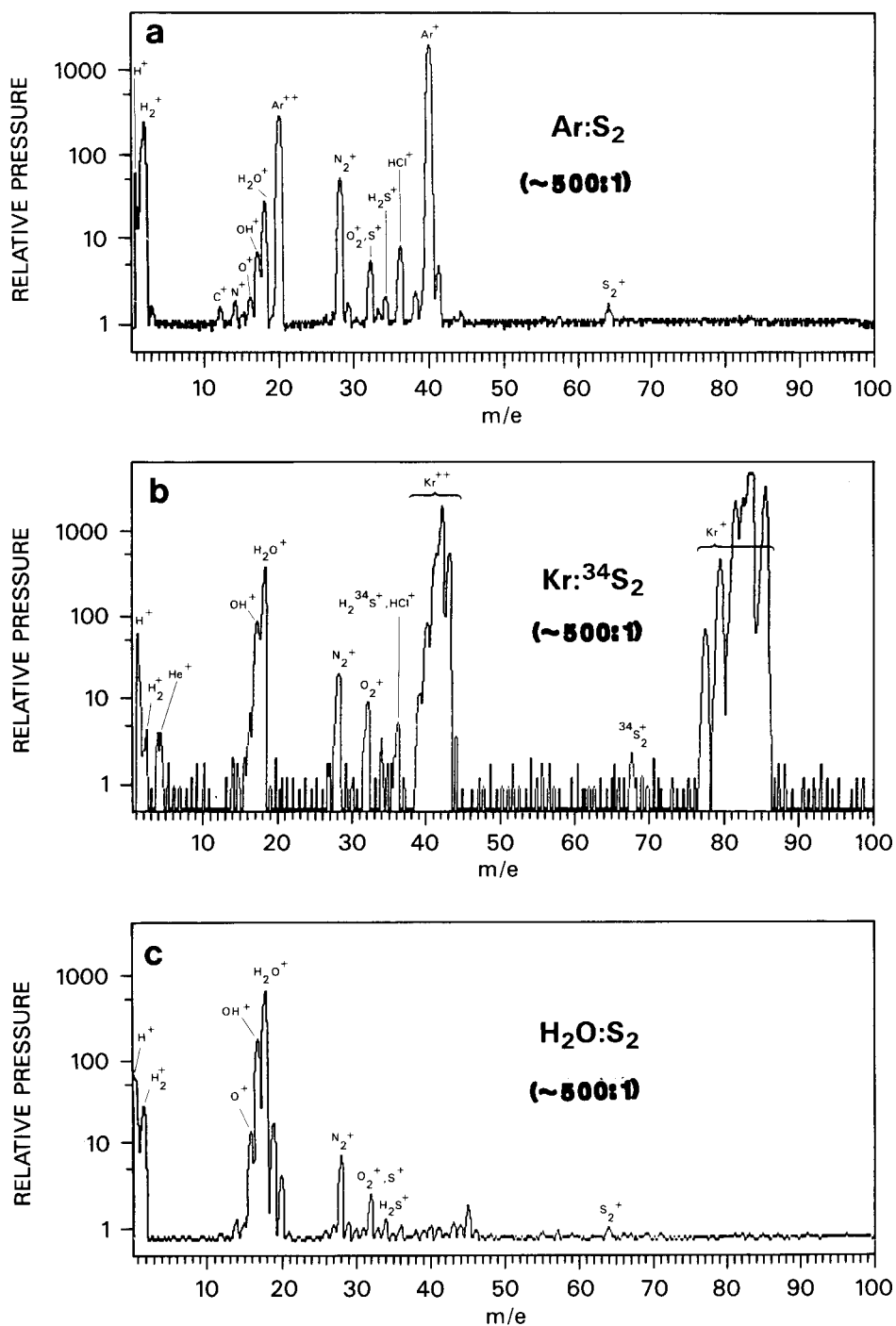


FIG. 3. Mass scans from 1 to 100 of residual gases in the vacuum system during condensation of Ar: S<sub>2</sub> (a), Kr: <sup>34</sup>S<sub>2</sub> (b), and H<sub>2</sub>O: S<sub>2</sub> (c). Other gas peaks represent contaminants in the system. Total pressure during deposits was near  $5 \times 10^{-6}$  Torr. These spectra were recorded with the electron multiplier off. Baselines for (a) and (c) were smoothed using an electronic QMS feature not used for the spectrum in (b).

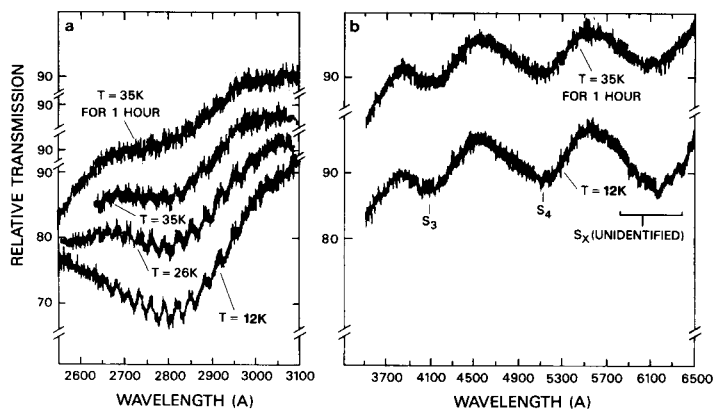


FIG. 4. The redrawn ultraviolet absorption spectra of Ar:S<sub>2</sub> (~500:1) showing effects of temperature on the strength of the S<sub>2</sub> (a) and the S<sub>3</sub>, S<sub>4</sub>, and S<sub>x</sub> (unidentified) visible absorption features (b). S<sub>2</sub> absorptions weakened and eventually disappeared when the argon was removed through vaporization after 1 hr at 35°K. S<sub>3</sub> and S<sub>4</sub> remained stable. Some of the S<sub>x</sub> structure weakened when the temperature reached 35°K.

to  $m/e = 200$  showed no detectable S<sub>3</sub>, S<sub>4</sub>, S<sub>5</sub>, or <sup>32</sup>S<sub>6</sub>. These spectra support the position that (1) S<sub>2</sub> was the dominant species from the oven, and (2) S<sub>2</sub> was not the result of fractionation of larger sulfur molecules by the QMS ionizer.

#### b. Effect of Temperature on Icy Mixtures Containing S<sub>2</sub>

Our initial studies of the effects of temperature on S<sub>2</sub> in ices were on Ar:S<sub>2</sub> (~500:1) since the S<sub>2</sub> absorption features in inert matrices were more intense than in water. Figure 4a is the ultraviolet spectrum of an Ar:S<sub>2</sub> (500:1) matrix deposited at 12°K along with changes observed during annealing. In this experiment the conditions for the deposit of S<sub>2</sub> were optimized. Relatively small signatures identified with larger sulfur molecules (S<sub>3</sub>, S<sub>4</sub>, and S<sub>x</sub>—unidentified bands around 6250 Å) are shown in Fig. 4b. When the ice was annealed to 26°K ( $\frac{1}{3} T_m$ —melting point of argon is 84°K) the envelope on which the S<sub>2</sub> bands appear decreased (50%). This decrease was not attributable to vaporization. It was calculated that less than 1% of a 3- $\mu$ m-thick argon matrix would be lost due to vaporization at 26°K over a period of 15 min. This envelope

and S<sub>2</sub> absorption bands further weakened when the temperature was raised to 35°K ( $\frac{2}{3} T_m$ ) and disappeared after 1 hr at 35°K during which time the argon matrix was removed due to vaporization. Meyer *et al.* (1972) reported that S<sub>4</sub> was prepared by annealing S<sub>2</sub> trapped in a krypton matrix at 31°K for 10 min or more. They also found that annealing S<sub>2</sub> in krypton matrices at 20°K always formed bands around 6250 Å. Although the relative absorption coefficients of S<sub>2</sub>, S<sub>4</sub>, and S<sub>x</sub> are not known, Fig. 4b does not show a detectable increase in strength of S<sub>4</sub> or S<sub>x</sub> with annealing.

Figure 5 shows spectra obtained when our experiments were not optimized for S<sub>2</sub> production ( $M:R < 500:1$ ). Under these conditions some S<sub>2</sub> is trapped (Fig. 5a) but other S<sub>2</sub> reacts to form new molecules. Strong S<sub>4</sub> and S<sub>x</sub> absorptions are shown in Fig. 5b. A vibrational band spectrum for S<sub>x</sub> at 12°K was formed containing seven distinct features with an average spacing of 302 cm<sup>-1</sup>. Meyer *et al.* (1972) found a similar but weaker spectrum after annealing S<sub>2</sub> in a krypton matrix. Meyer and Stroyer-Hansen (1972) gave an average spacing of 380 cm<sup>-1</sup> for the 6250-Å features and speculated on their associations with S<sub>6</sub> or S<sub>8</sub>

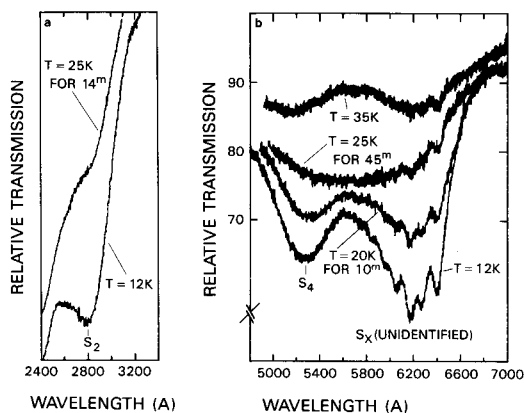


FIG. 5. Redrawn ultraviolet absorption spectra of Ar: S<sub>2</sub> (<500:1) (a) and the relatively strong visible absorption features identified as S<sub>4</sub> and S<sub>x</sub> (b) deposited at T = 12°K. The S<sub>2</sub> envelope is very temperature sensitive. S<sub>4</sub> and S<sub>x</sub> absorptions weakened with increased temperature. S<sub>x</sub> appears to be a vibrational transition with an average spacing of 302 cm<sup>-1</sup>. Table II lists absorption maxima observed for S<sub>3</sub> (see Fig. 4b), S<sub>4</sub>, and S<sub>x</sub>.

chains. Grim and Greenberg (1987) also detected weak features in the 5350- to 6750-Å region in photolyzed H<sub>2</sub>O: H<sub>2</sub>S, 1:1. Table II lists the absorption maxima for the S<sub>3</sub>, S<sub>4</sub> and S<sub>x</sub> vibrational bands observed in our experiments.

Figure 5a shows that the S<sub>2</sub> envelope significantly decreases when the matrix is warmed to 25°K. Both S<sub>4</sub> and S<sub>x</sub> bands are temperature sensitive and decrease during annealing, although there is some evidence that both are still present at 35°K (Fig. 5b). Meyer and Stroyer-Hansen (1972) found a similar temperature effect on infrared absorption bands they attributed to S<sub>4</sub>. They estimated a lifetime of 57.7 hr for S<sub>4</sub> at 171°K. A feature identified with S<sub>4</sub> at 5275 Å at 10°K shifts to near 5200 Å during warming to 35°K. At 300°K all absorption features in our experiments disappeared into a smooth absorption which increased into the ultraviolet and which could be removed by cleaning. All annealing experiments were consistent with the conclusion that S<sub>2</sub>, S<sub>3</sub>, S<sub>4</sub>, and S<sub>x</sub> molecules were either (a) released from the ice during vaporiza-

tion or (b) converted to different sulfur molecules which did not have strong absorption features in the 2600- to 6500-Å region.

Spectra of H<sub>2</sub>O: S<sub>2</sub> (~500:1) ice are shown in Fig. 6 as a function of temperature. The original spectra (not redrawn spectra) are shown because the S<sub>2</sub> absorptions were very weak. The S<sub>2</sub> spectrum was identified at 12°K each time after the ice was annealed for 15 min to 35 (~ $\frac{1}{5}$  T<sub>m</sub>), 75 ( $\frac{1}{4}$  T<sub>m</sub>), 110 (~ $\frac{2}{5}$  T<sub>m</sub>), and 140°K ( $\frac{1}{2}$  T<sub>m</sub>). These results are consistent with the LIF detection of S<sub>2</sub> in ices to temperatures near 140°K reported by Grim and Greenberg (1987). S<sub>2</sub> could not be identified in the re-cooled ice after annealing at 140°K for 17 hr. Since the intensity of the original S<sub>2</sub> features were small, identification of a reduced number of S<sub>2</sub> absorbers would not be possible using these ultraviolet spectral techniques. We calculated that a significant fraction of the water ice had not been removed by evaporation during the 17-hr warming period; ~0.1 μm of water was lost (less than 10% the estimated sample thickness). This experiment shows that S<sub>2</sub> can

TABLE II

ABSORPTION MAXIMA (Å) OF S<sub>3</sub>, S<sub>4</sub>, AND S<sub>x</sub> (UNIDENTIFIED) BANDS IN ARGON MATRICES AT 12°K

S <sub>3</sub> <sup>a</sup>	4150 <sup>b</sup>
S <sub>4</sub> <sup>a</sup>	5200 <sup>c</sup>
S <sub>x</sub> <sup>d</sup>	5750(vw) <sup>e</sup>
	5850(vw) <sup>e</sup>
	5960(w) <sup>b</sup>
	6060 <sup>f</sup>
	6180 <sup>f</sup>
	6280 <sup>f</sup>
	6410 <sup>f</sup>

<sup>a</sup> Data for S<sub>3</sub> had ±170 Å scatter, for S<sub>4</sub> ±70 Å scatter.

<sup>b</sup> Average of three experiments.

<sup>c</sup> Average of five experiments.

<sup>d</sup> Data for S<sub>x</sub> was within ±14 Å scatter.

<sup>e</sup> One experiment.

<sup>f</sup> Average of four experiments.



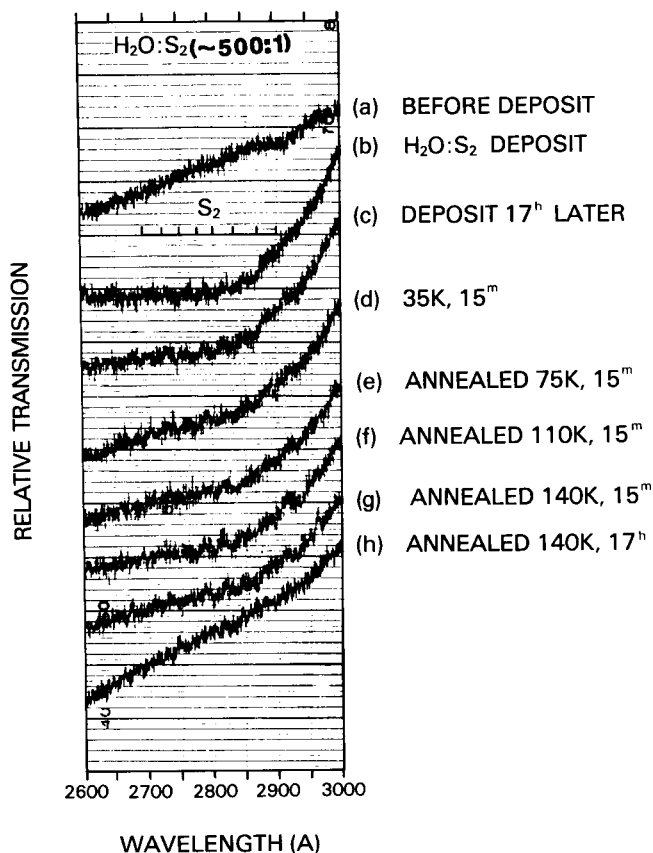


FIG. 6. Ultraviolet absorption spectra of H<sub>2</sub>O:S<sub>2</sub> (~500:1) show the effects of temperature. Curve (a) is the "background" spectrum of the sapphire substrate before deposit. S<sub>2</sub> features are marked above spectrum (b) and are detected in spectra (b) through (g). Spectrum (b) immediately after deposit of H<sub>2</sub>O:S<sub>2</sub>, (c) after storage at 12°K for 17 hr, (d) at 35°K after storage at 12°K for 15 min, (e) at 12°K after annealing to 75°K for 15 min, (f) at 12°K after annealing to 110°K for 15 min, (g) at 12°K after annealing to 140°K for 15 min, (h) at 12°K after annealing to 140°K for 17 hr (no longer shows the S<sub>2</sub> pattern).

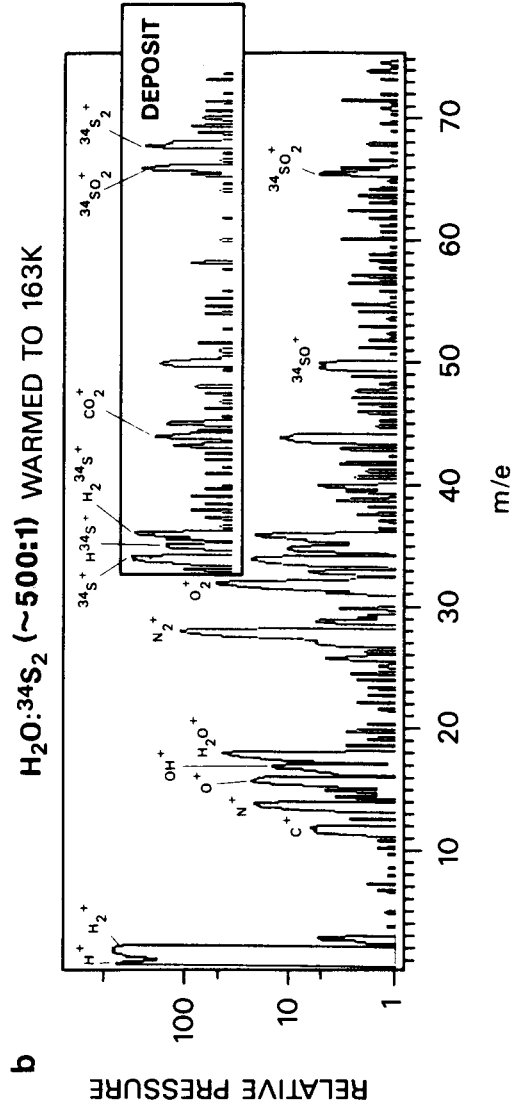
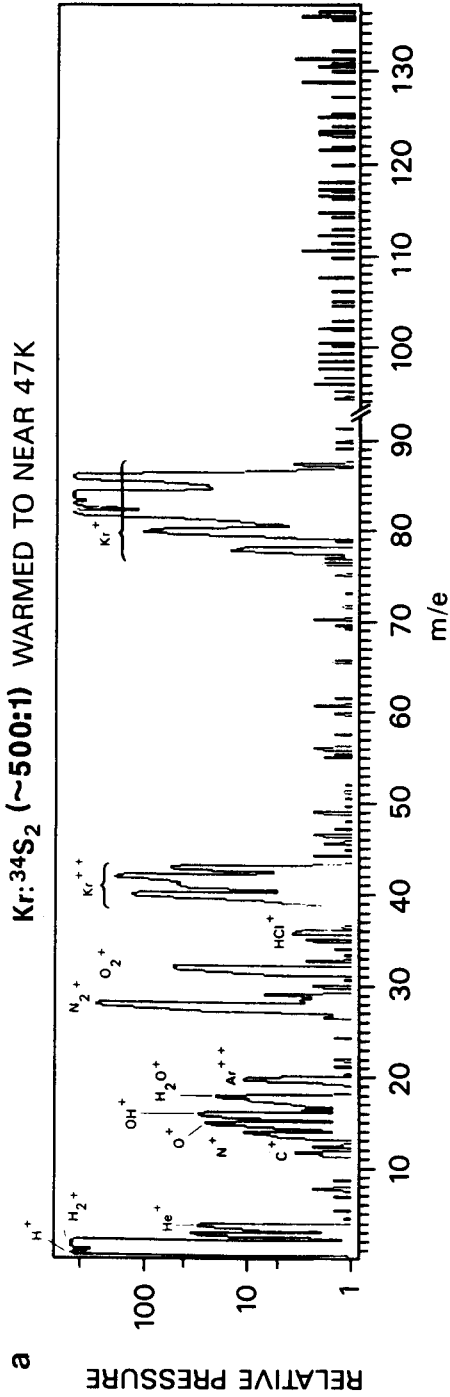
survive in water-dominated ices (*M*:*R*, 500:1) for at least 15 min to temperatures as high as 140°K. For storage times the order of hours at 140°K, the amount of S<sub>2</sub> appears to decrease significantly. Grim and Greenberg (1987) did not study the LIF signal of S<sub>2</sub> during long storage times.

A weak, broad feature attributed to S<sub>4</sub> was detected at 5220 Å in H<sub>2</sub>O:S<sub>2</sub> (~500:1) ice after deposit at 12°K. The intensity of S<sub>4</sub> increased 25% after annealing to 110°K for 15 min. S<sub>4</sub> was still detected after the ice was annealed for 17 hr at 140°K although its intensity had decreased 60%.

### c. Vaporization of Icy Mixtures Containing S<sub>2</sub>

QMS data recorded during vaporization of krypton matrix and water ice containing S<sub>2</sub> are shown in Fig. 7. Spectra were recorded at many temperatures during warming from 12°K. Mass spectra in Fig. 7 are typical of gases released when the vapor pressure of the condensate was 10<sup>-6</sup> to 10<sup>-5</sup> Torr, near 47°K for krypton and 163°K for water.

Figure 7a shows that no <sup>34</sup>S<sub>2</sub><sup>+</sup> (*m/e* = 68) signals were detected during vaporization



of Kr: <sup>34</sup>S<sub>2</sub> (~500:1). This experimental result was reproduced several times. It was possible to detect S<sub>2</sub> at a partial pressure as low as  $5 \times 10^{-11}$  Torr which was nearly an order of magnitude lower than the strength of the usual S<sub>2</sub> signals during deposit ( $2-3 \times 10^{-10}$  Torr). Although  $5 \times 10^{-11}$  Torr represented the intensity of the background noise during most scans, development of weaker signals was detectable since these exhibited a width of  $m/e = 1$ . During slow warmups, no S<sub>2</sub> was detected even when an increased gain of over 1000 provided by the electron multiplier was used. Increased gain also increased the noise, but greater sensitivity was possible especially when the rate of scanning was decreased. Another QMS display choice was to tabulate peak intensities of several preselected masses during vaporization. In this mode the signal to noise ratio could be maximized. Figure 7a is a composite of two mass scan ranges covering a total  $m/e$  range from 1 to 137. It shows that no S<sub>3</sub> or S<sub>4</sub> was released from the ice.

Figure 7b is the QMS spectra during warming an H<sub>2</sub>O: <sup>34</sup>S<sub>2</sub> ice. The insert spectrum, recorded during deposit, shows that <sup>34</sup>S<sub>2</sub> along with reaction products <sup>34</sup>SO<sub>2</sub> and H<sub>2</sub><sup>34</sup>S were deposited. <sup>34</sup>SO<sub>2</sub><sup>+</sup>, <sup>34</sup>SO<sup>+</sup>, H<sub>2</sub><sup>34</sup>S<sup>+</sup>, and H<sup>34</sup>S<sup>+</sup> were detected during vaporization of the water ice but no <sup>34</sup>S<sub>2</sub><sup>+</sup> was measured even though all of the molecules had nearly equal signal intensities during deposit.

#### d. Analysis of Room Temperature Residues

Examination of icy substrates warmed to room temperature revealed the presence of a hazy residue which had an absorption spectrum smoothly increasing into the

ultraviolet. A strong signal due to sulfur atoms in a residue was detected using scanning Auger analysis techniques (the molecular form of sulfur was not determinable). An upper limit for the thickness of the residue of several hundred angstroms is known from analysis of the detected Auger electron signals.

#### e. Vaporization of SO<sub>2</sub> from Krypton Matrices

We observed species vaporizing from Kr: SO<sub>2</sub> matrices ( $M:R = 100:1$  and  $2:1$ ) to determine when SO<sub>2</sub> was released. This ice mixture was chosen because SO<sub>2</sub> had the same molecular weight as S<sub>2</sub> and was less volatile than krypton. In all experiments our preliminary results supported the idea that detectable SO<sub>2</sub> was not released during vaporization of the more volatile matrix. Instead it remained on the substrate until warmed to a temperature nearly consistent with the vaporization of bulk SO<sub>2</sub>. Signals for SO<sub>2</sub> were detected near 100°K, a temperature at which its gas vapor pressure was approximately  $10^{-8}$  Torr.

#### DISCUSSION

We have identified weak ultraviolet S<sub>2</sub> absorption features in a low temperature amorphous water ice ( $M:R \sim 500:1$ ). These weak features were identified even after the ice was annealed to 140°K ( $\frac{2}{3} T_m$ ) for 15 min. S<sub>2</sub> absorptions were not detected after the ice was kept at 140°K for 17 hr, suggesting that some fraction of the S<sub>2</sub> had diffused in the ice and reacted with other species. Diffusion of S<sub>2</sub> near 140°K could also be enhanced by the phase change from amorphous to crystalline water ice that occurs at about that temperature. Due to the weakness of the ultraviolet absorp-

FIG. 7. Recorded mass scans of gases above vaporizing ice containing S<sub>2</sub>. (a) A composite of two mass scans (covering  $m/e = 1$  to 137) of vaporizing Kr: <sup>34</sup>S<sub>2</sub> near 47°K (vapor pressure of krypton near  $10^{-5}$  Torr). No <sup>34</sup>S<sub>2</sub> is detected. (b) A mass scan from 1 to 75 of vaporizing H<sub>2</sub>O: <sup>34</sup>S<sub>2</sub> near 163°K (vapor pressure of water near  $10^{-6}$  Torr). The insert spectrum was taken during deposit and shows nearly equal signals of <sup>34</sup>S<sub>2</sub> and reaction products <sup>34</sup>SO<sub>2</sub> and H<sub>2</sub><sup>34</sup>S. <sup>34</sup>SO<sub>2</sub> and H<sub>2</sub><sup>34</sup>S are detected during vaporization but S<sub>2</sub> is not.

tions in water, it was not possible to measure the lifetime of  $S_2$  at these higher temperatures which are more typical of parts of the cometary nucleus near perihelion. More intense  $S_2$  absorptions were measured in similarly formed inert matrices which were chosen, for convenience, for several studies even though cometary ices do not contain a dominant fraction of inert gases. The intensity of  $S_2$  absorption lines diminished when Ar :  $S_2$  (500 : 1) matrices were warmed to  $\frac{1}{4} T_m$ , suggesting that diffusion in the matrix occurred. Although we cannot say what reactions occurred, we did not detect any increase in the  $S_4$  absorption feature from the reaction  $S_2 + S_2 \rightarrow S_4$  during annealing. Dimerization of  $S_2$  triggered by annealing was discussed by Meyer and Strojer-Hansen (1972), who also mentioned that it was triggered by illumination with a tungsten-iodine lamp. The intensity of  $S_2$  absorption bands in argon decrease also after irradiation with protons.<sup>3</sup> These experiments suggest that it may be possible to store low concentrations (<0.2%) of  $S_2$  in cometary type water-dominated ices at temperatures low enough to prevent diffusion ( $T < 140^\circ\text{K}$ )<sup>4</sup> in dark, low radiation environments.

$S_3$ ,  $S_4$ , and  $S_x$  (unidentified) were prominent features in our spectra after deposits in which the  $M : R$  ratio was lower than 500 : 1.  $S_3$  was identified with a band at 4130 Å. Meyer *et al.* (1972) reported an extinction coefficient for  $S_3$  an order of magnitude larger than  $S_4$ . Therefore, the observed intensity of  $S_3$  suggests  $S_4$  is nearly twice as abundant. This supports the idea that reactions during deposit favor dimerization of  $S_2$ .  $S_4$  appeared as a broad band at 5185 Å

which decreases in intensity with annealing.  $S_4$  was relatively unaffected by irradiation.<sup>3</sup> The  $S_x$  features appear to be vibrational bands with seven absorptions at 5745, 5845, 5960, 6062, 6182, 6280, and 6413 Å with an average spacing of 302  $\text{cm}^{-1}$ . These absorptions decreased in intensity as the temperature of the argon matrix was increased to 35°K.  $S_x$  features decreased after proton irradiation.<sup>3</sup> Similar weak  $S_x$  features have been reported by Meyer and Strojer-Hansen (1972) to decrease under tungsten-iodine lamp illumination.  $S_3$ ,  $S_4$ , and  $S_x$  allotropes are rare and unstable but are vividly colored.  $S_x$  has been considered as a possible candidate for some of the coloring on Amalthea (Gradie *et al.* 1980). All of these allotropes exhibit some degree of temperature and radiation instability.

Vaporization studies of Ar :  $S_2$  (~500 : 1), Kr :  $S_2$  (~500 : 1), Kr :  $^{34}\text{S}_2$  (~500 : 1),  $\text{H}_2\text{O} : S_2$  (~500 : 1), and  $\text{H}_2\text{O} : ^{34}\text{S}_2$  (~500 : 1) icy mixtures have demonstrated that during vaporization  $S_2$  was not detected in the gases released. It is possible that a small percentage (<10–20%) of the  $S_2$  deposited in our experimental ice could have been released during rapid vaporization and not been detected by our QMS.<sup>5</sup> However, not a hint of  $S_2$  was detected during slow warm-ups designed to optimize the signal-to-noise ratio.<sup>6</sup> We estimate that an  $S_2$  signal whose intensity was 10 to 20% that of the original deposited signal could be detected. By scaling their experimental results to the S/O cosmic abundance, Grim and Greenberg (1987) predict the  $S_2/\text{H}_2\text{O}$  ratio in interstellar grains is between  $2 \times 10^{-4}$  and  $1.4 \times 10^{-3}$ , which is consistent with the observed ratio of  $S_2/\text{OH}$  of  $5 \times 10^{-4}$  in Comet IRAS-Araki-Alcock 1983d. Our experiments suggest that no definite predictions can be made of the gas phase  $S_2/\text{H}_2\text{O}$  ratio based on the  $S_2/\text{H}_2\text{O}$  ratio in the solid phase.

<sup>3</sup> Ultraviolet spectra of Ar :  $S_2$  (~500 : 1) at 12°K showed a decrease in the strength of the  $S_2$ ,  $S_4$  and  $S_x$  bands after 1-MeV proton irradiation to an estimated dose of 0.3 eV/molecule.

<sup>4</sup> Pimental (1960) gives a "rule of thumb" for diffusion: it becomes rapid for temperatures near  $\frac{1}{2} T_m$ . Since astronomical time scales can be very long, Delsemme and Miller (1971) suggested using  $\frac{1}{4} T_m$ . Therefore, in a cometary nucleus you would expect diffusion of radicals above 70 or 140°K (i.e.,  $\frac{1}{4}$  or  $\frac{1}{2} T_m$ ).

<sup>5</sup> During rapid vaporization the system pressure often rose above  $10^{-5}$  Torr, a pressure too high for efficient operation of the QMS.

<sup>6</sup> A differentially pumped QMS system has been constructed. This will improve the S/N ratio at least an order of magnitude.

We conclude that thermal vaporization of cometary ices containing S<sub>2</sub> would not release S<sub>2</sub> into the coma. Our experiments support the idea that S<sub>2</sub> would react within the warming cometary ice either with another diradical or with oxygen or oxygen-containing species to form either amorphous sulfur or a sulfurous molecule which would remain behind on the nucleus.

We can imagine several alternative mechanisms for releasing S<sub>2</sub> into the coma. Following the ideas of Delsemme and Miller (1971), it may be possible to carry this diradical off the nucleus in sub-micron-size ice grains which rapidly vaporize leaving S<sub>2</sub> as an extended cloud a few hundred kilometers above nucleus. There is, however, a potentially serious dilemma with the hypothesis that S<sub>2</sub> is released from small volatile grains. Greenberg (1982) has proposed a model of a comet nucleus that contains a large fraction of many small interstellar grains with nonvolatile cores and irradiated mantles containing S<sub>2</sub>. The dilemma is that in the process of producing a significant concentration of S<sub>2</sub>, other molecules in the mantle would also be processed. For example, sulfur atoms can react with oxygen to form SO or SO<sub>2</sub>. Grim and Greenberg (1987) report the formation of both S<sub>2</sub> and SO in photolyzed icy mixtures. This raises the problem that if S<sub>2</sub> is trapped in an irradiated mantle and is the source of S<sub>2</sub> in the coma, then SO or SO<sub>2</sub> should also be present. However, neither of these has been detected. Two other problems which arise are: (1) During evaporation of volatile species from a mantle, S<sub>2</sub> may remain on the core as our experiments suggest. (2) Mantle processing may reduce its volatility, preventing sufficient rapid release of S<sub>2</sub> to explain the presence of this sulfur species in the cometary coma close to the nucleus. These prospects need to be carefully examined before the small grain hypothesis is accepted as a mechanism which explains the cometary S<sub>2</sub> observation.

It may also be possible to remove S<sub>2</sub> non-thermally from the nucleus through jets or

other explosive mechanisms. Another possibility is sputtering of S<sub>2</sub> by kiloelectron volt ion bombardment. Chrissey *et al.* (1987) found that 65% of the total yield from sulfur targets corresponded to S<sub>2</sub>. S<sub>2</sub> was also sputtered effectively from H<sub>2</sub>S and CS<sub>2</sub> icy targets (Boring *et al.* 1986), although Feldman *et al.* (1984) and Boring *et al.* (1986) both concluded that current modeling using only solar wind bombardment was insufficient to account for the production rate of S<sub>2</sub> observed in Comet 1983d. Yields of sputtered S<sub>2</sub> probably also diminish when H<sub>2</sub>S is mixed with H<sub>2</sub>O (as in cometary ices) since competitive pathways for reactions are present. These experiments on icy mixtures have not been done.

The problem of S<sub>2</sub> but not SO<sub>2</sub> or SO being produced in grain mantles by ultraviolet irradiation applies equally to energetic particle irradiation or sputtering of ice mixtures. This difficulty does not arise if S<sub>2</sub> is derived from a very short-lived parent molecule although there is no indication at present of what that molecule might be.

There thus remain two major problems in explaining the cometary S<sub>2</sub> observations: What is the source of S<sub>2</sub> and how is it released from the nucleus. More extensive experiments on irradiation and sputtering of simulated cometary ice mixtures and on release of molecules from the final product are needed. In common with all laboratory experiments, including those of Grim and Greenberg (1987), we have studied very thin macroscopic icy films. We are aware that results from these bulk ices may not be directly applicable to low density cometary ices or sub-micron particles. Future experiments need to develop techniques for studying properties of low density ices and small icy grains. Results from these experiments could make a substantial contribution toward resolving the cometary S<sub>2</sub> problem.

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