

Vaporization of Ices Containing S₂—Implications for Comets

M. H. MOORE,¹ B. DONN,* AND R. L. HUDSON†

*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 S₂ 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 S₂ be stored in ices during warming, and (2) is S₂ released during vaporization of its water ice matrix?

We have recorded the ultraviolet spectrum of S₂ in argon and krypton matrices and water ice in which the ratio of matrix or molecular ice to S₂ was the order of 500 : 1. The intensity of S₂ absorptions decreased in argon during warming. In water the weak S₂ signal was detected from 12 to 140°K during short annealing periods, but was not detected after annealing at 140°K for 17 hr. S₃ and S₄ were also detected in some ices along with seven unidentified absorption features centered near 6250 Å.

S₂ was not detected with a mass spectrometer during vaporization of Ar : S₂, Kr : S₂, Kr : ³⁴S₂, or H₂O : ³⁴S₂ (each ~500 : 1) mixtures. Our experiments support the idea that the S₂ : H₂O 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 S₂ 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 S₂ in Comet IRAS-Araki-Alcock, 1983d, a long period comet ($P = 1000$ years). S₂ 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. S₂ was detected in all spectra although its production rate varied much more than that of other species (Feldman *et al.* 1984). S₂ 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 S₂ 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 S₂ in a cometary nucleus and review arguments against the direct accretion of S₂ from the gas phase. In general it seems unlikely that S₂ 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 S₂. The interstellar abundance of S is less than 10% that of carbon, therefore the amount of S₂ 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 5×10^{-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 S₂ disappeared rapidly from argon matrices during annealing to 31°K (near $\frac{1}{3} T_m$). Meyer *et al.* (1972) showed S₂ diffused in krypton matrices annealed at 30°K (near $\frac{1}{4} T_m$) to form S₄. These experiments shed some doubt on whether it is possible to release S₂ 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 S₂. The LIF signal of S₂ was found to remain constant as the photolyzed ice was warmed to near 120°K ($\frac{2}{5} T_m$). 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 S₂ due to evaporation with the water molecules. These studies show that S₂ 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 S₂ 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 S₂. To do this we constructed a system to mass-spectrometrically detect S₂ in the vapors released during sublimation of ices known (from ultraviolet spectroscopy) to contain S₂ 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 S₂. The gases used were argon (Matheson, prep. grade), krypton (Matheson, research grade), and H₂O (deionized, degassed, $R > 10^{+7}$ ohm). ³²S sublimed sulfur was obtained from Mallenckrodt Chemical Works; ³⁴S was 93.6 atom% enriched from Monsanto Research Corp. Mound Laboratory. Because both ³²S₂⁺ and ³²SO₂⁺ (a possible oxidation product) have $m/e = 64$, ³⁴S was used in some experiments which allowed discrimination in the mass spectrometer scan between ³²S₂⁺ and ³⁴SO₂⁺ (68 and 66, respectively).

S₂ 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 S₂ (see, for example, Brewer *et al.* 1965). The complex vapors effusing from this oven (S₈; S₇; S₆; 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 S₂. 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 S₂ could result from fragmentation of larger sulfur molecules (S₃, S₄, S₅,

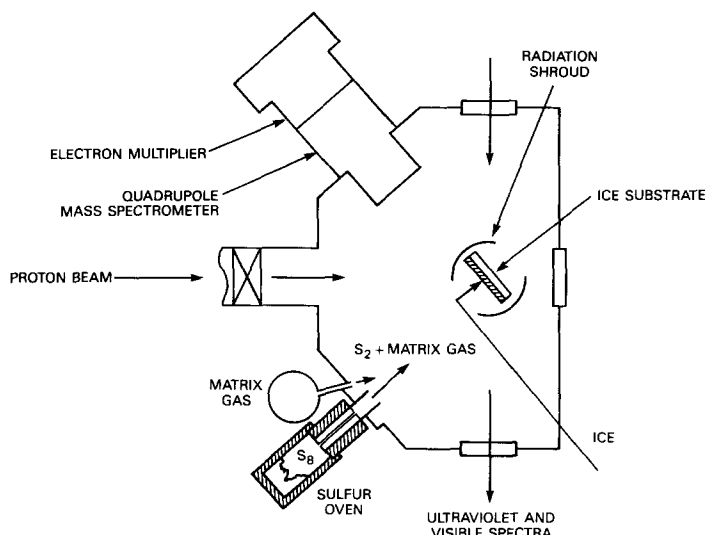


FIG. 1. In this multiport chamber, a variety of measurements can be performed on gases condensed on substrates cooled to temperatures as low as 12°K. Here the substrate is shown facing the sulfur oven. S₂ from the oven and a beam of gas are co-deposited to form matrix-isolated S₂. The ultraviolet transmission 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 S₃, S₄, S₅. Typical M : R ratios of 500 : 1² (matrix gas : radical) were required to form a reasonable quality S₂ band spectrum in the ultraviolet. When the M : R ratio was lower, strong S₄ and S_x (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 S₂. The relative S₂ concentration in the gas phase, measured by the QMS, was representative of the rela-

tive S₂ concentration in the condensed phase. This is supported by noting that under some conditions of deposit, other molecules (e.g., SO₂ and H₂S) with nearly equal signal intensities to S₂ were detected during deposit. These molecules were condensed (along with S₂) and were detected during vaporization of the ice (S₂ 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. S₂ was seen in absorption near 2800 Å (Brewer *et al.* 1965) along with some S₃ and S₄ which have transitions near 4100 and 5200 Å, respectively (Meyer *et al.* 1972). S₂ spectra were identified in mixtures of Ar : S₂, Kr : S₂, and H₂O : S₂.

² 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.

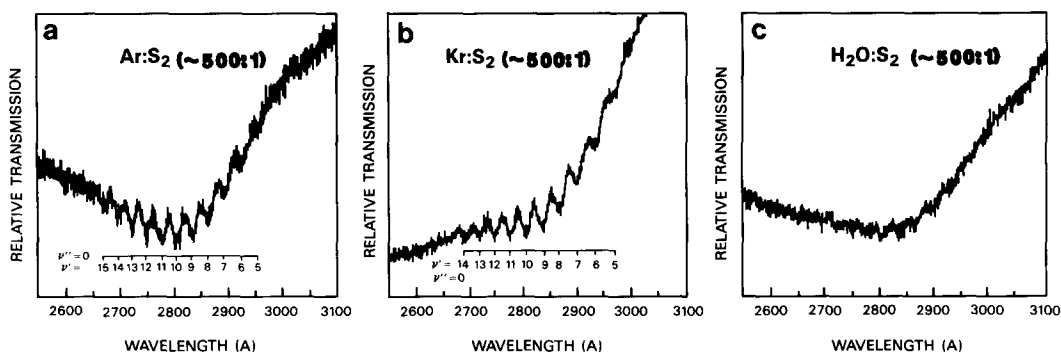


FIG. 2. The redrawn ultraviolet absorption spectra of matrix-isolated S₂ in argon (a), krypton (b), and water (c) at temperatures near 12°K. All absorption bands are attributed to the $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$ system of S₂. Transition assignments are listed in Table I.

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 S₂

Ultraviolet spectra of thin ice films of S₂ 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 S₂ and appear to be superimposed on a broad feature suggested by Brewer *et al.* (1965) to result from unresolved S₂ bands. Following Brewer *et al.* (1965), transition assignments are listed in Table I for S₂ in argon and krypton matrices. We extended these assignments to the weak vibrational structure in water ice. S₂ signatures in water were very weak possibly because of substantial S₂-H₂O intermolecular interaction. Nevertheless the spectrum was sufficient to prove the S₂ was present in the ice.

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

S₂ are shown in Figs. 3a, 3b, and 3c, respectively. S₂ was identified in all mass spectra of the gas in the vacuum chamber. The spectrum in Fig. 3b shows no detectable ³⁴SO₂⁺ (*m/e* = 66), only ³⁴S₂⁺ (*m/e* = 68). Other deposit spectra (not shown) recorded

TABLE I
ABSORPTION SPECTRUM OF S₂

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

^a Average of three experiments.

^b One experiment.

^c Accuracy ± 10 Å due to weak and broad features in water ice.

^d Tentative assignment.

^e Average of two experiments.

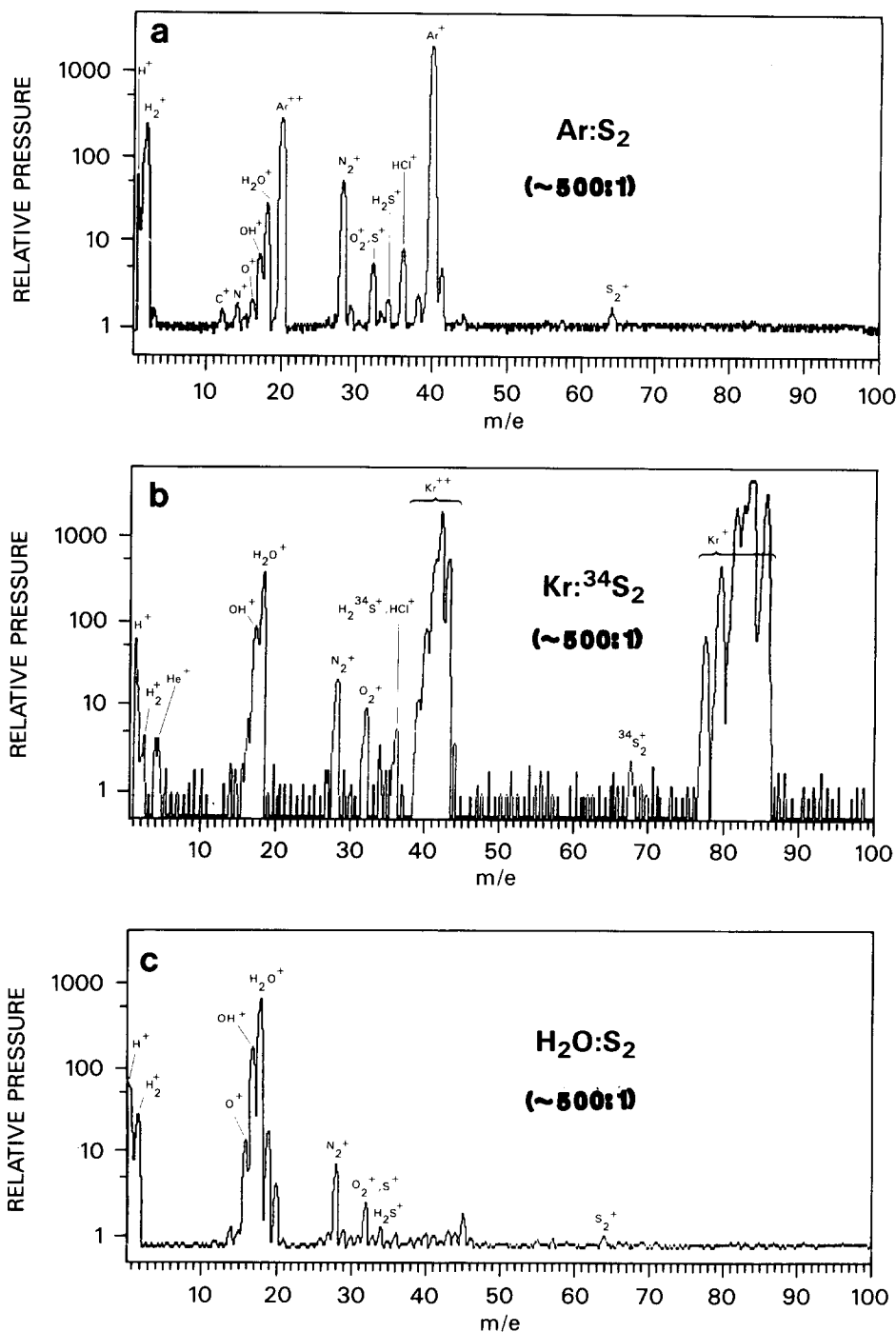


FIG. 3. Mass scans from 1 to 100 of residual gases in the vacuum system during condensation of Ar:S₂ (a), Kr:³⁴S₂ (b), and H₂O:S₂ (c). Other gas peaks represent contaminants in the system. Total pressure during deposits was near 5×10^{-6} Torr. These spectra were recorded with the electron multiplier off. Baselines for (a) and (c) were smoothed using an electronic QMS feature not used for the spectrum in (b).

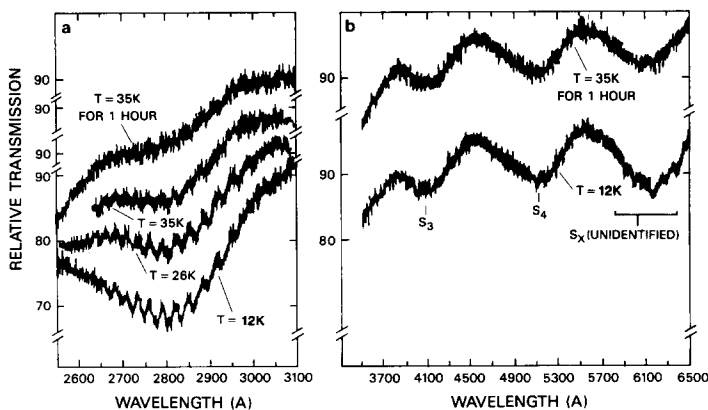


FIG. 4. The redrawn ultraviolet absorption spectra of Ar: S₂ (~500:1) showing effects of temperature on the strength of the S₂ (a) and the S₃, S₄, and S_x (unidentified) visible absorption features (b). S₂ absorptions weakened and eventually disappeared when the argon was removed through vaporization after 1 hr at 35°K. S₃ and S₄ remained stable. Some of the S_x structure weakened when the temperature reached 35°K.

to $m/e = 200$ showed no detectable S₃, S₄, S₅, or ³²S₆. These spectra support the position that (1) S₂ was the dominant species from the oven, and (2) S₂ was not the result of fractionation of larger sulfur molecules by the QMS ionizer.

b. Effect of Temperature on Icy Mixtures Containing S₂

Our initial studies of the effects of temperature on S₂ in ices were on Ar:S₂ (~500:1) since the S₂ absorption features in inert matrices were more intense than in water. Figure 4a is the ultraviolet spectrum of an Ar:S₂ (500:1) matrix deposited at 12°K along with changes observed during annealing. In this experiment the conditions for the deposit of S₂ were optimized. Relatively small signatures identified with larger sulfur molecules (S₃, S₄, and S_x—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 S₂ bands appear decreased (50%). This decrease was not attributable to vaporization. It was calculated that less than 1% of a 3- μ m-thick argon matrix would be lost due to vaporization at 26°K over a period of 15 min. This envelope

and S₂ 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 S₄ was prepared by annealing S₂ trapped in a krypton matrix at 31°K for 10 min or more. They also found that annealing S₂ in krypton matrices at 20°K always formed bands around 6250 Å. Although the relative absorption coefficients of S₂, S₄, and S_x are not known, Fig. 4b does not show a detectable increase in strength of S₄ or S_x with annealing.

Figure 5 shows spectra obtained when our experiments were not optimized for S₂ production ($M:R < 500:1$). Under these conditions some S₂ is trapped (Fig. 5a) but other S₂ reacts to form new molecules. Strong S₄ and S_x absorptions are shown in Fig. 5b. A vibrational band spectrum for S_x at 12°K was formed containing seven distinct features with an average spacing of 302 cm⁻¹. Meyer *et al.* (1972) found a similar but weaker spectrum after annealing S₂ in a krypton matrix. Meyer and Stroyer-Hansen (1972) gave an average spacing of 380 cm⁻¹ for the 6250-Å features and speculated on their associations with S₆ or S₈

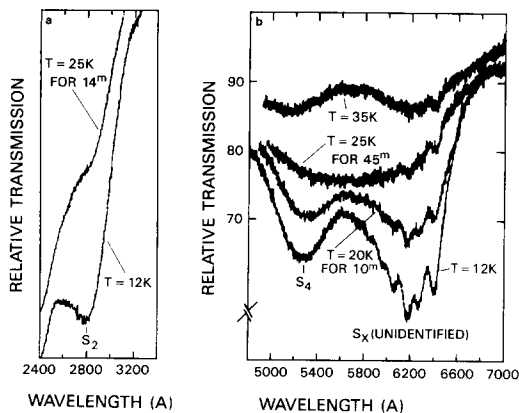


FIG. 5. Redrawn ultraviolet absorption spectra of Ar: S_2 ($<500:1$) (a) and the relatively strong visible absorption features identified as S_4 and S_x (b) deposited at $T = 12^\circ\text{K}$. The S_2 envelope is very temperature sensitive. S_4 and S_x absorptions weakened with increased temperature. S_x appears to be a vibrational transition with an average spacing of 302 cm^{-1} . Table II lists absorption maxima observed for S_3 (see Fig. 4b), S_4 , and S_x .

chains. Grim and Greenberg (1987) also detected weak features in the 5350- to 6750- \AA region in photolyzed $\text{H}_2\text{O}:\text{H}_2\text{S}$, 1:1. Table II lists the absorption maxima for the S_3 , S_4 and S_x vibrational bands observed in our experiments.

Figure 5a shows that the S_2 envelope significantly decreases when the matrix is warmed to 25°K . Both S_4 and S_x 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_4 . They estimated a lifetime of 57.7 hr for S_4 at 171°K . A feature identified with S_4 at 5275 \AA at 10°K shifts to near 5200 \AA 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_2 , S_3 , S_4 , and S_x 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- \AA region.

Spectra of $\text{H}_2\text{O}:\text{S}_2$ ($\sim 500:1$) ice are shown in Fig. 6 as a function of temperature. The original spectra (not redrawn spectra) are shown because the S_2 absorptions were very weak. The S_2 spectrum was identified at 12°K each time after the ice was annealed for 15 min to 35 ($\sim \frac{1}{5} T_m$), 75 ($\frac{1}{4} T_m$), 110 ($\sim \frac{2}{5} T_m$), and 140°K ($\frac{1}{2} T_m$). These results are consistent with the LIF detection of S_2 in ices to temperatures near 140°K reported by Grim and Greenberg (1987). S_2 could not be identified in the re-cooled ice after annealing at 140°K for 17 hr. Since the intensity of the original S_2 features were small, identification of a reduced number of S_2 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; $\sim 0.1\ \mu\text{m}$ of water was lost (less than 10% the estimated sample thickness). This experiment shows that S_2 can

TABLE II

ABSORPTION MAXIMA (\AA) OF S_3 , S_4 , AND S_x (UNIDENTIFIED) BANDS IN ARGON MATRICES AT 12°K

S_3^a	4150 ^b
S_4^a	5200 ^c
S_x^d	5750(vw) ^e
	5850(vw) ^e
	5960(w) ^b
	6060 ^f
	6180 ^f
	6280 ^f
	6410 ^f

^a Data for S_3 had $\pm 170\ \text{\AA}$ scatter, for S_4 $\pm 70\ \text{\AA}$ scatter.

^b Average of three experiments.

^c Average of five experiments.

^d Data for S_x was within $\pm 14\ \text{\AA}$ scatter.

^e One experiment.

^f Average of four experiments.

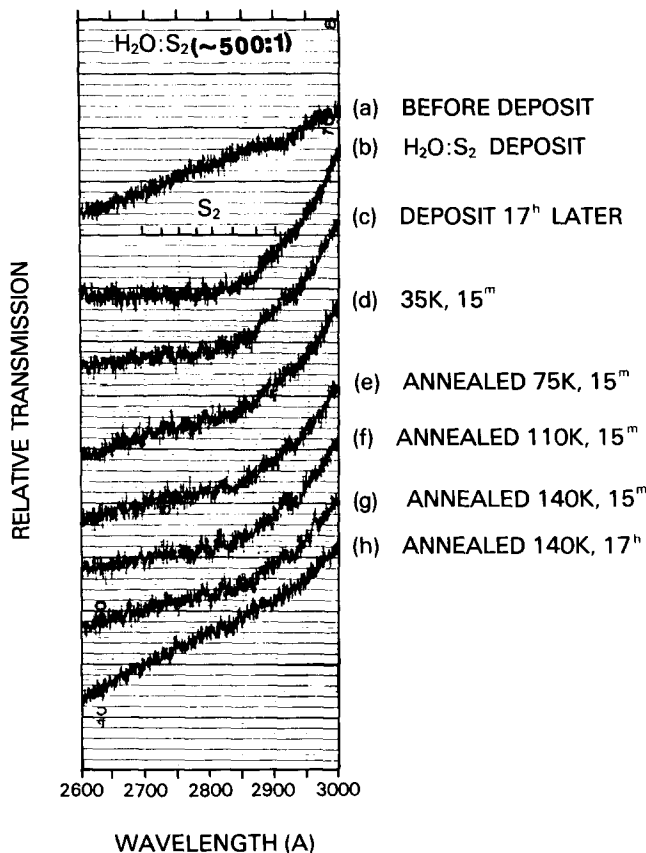


FIG. 6. Ultraviolet absorption spectra of H₂O:S₂ (~500:1) show the effects of temperature. Curve (a) is the "background" spectrum of the sapphire substrate before deposit. S₂ features are marked above spectrum (b) and are detected in spectra (b) through (g). Spectrum (b) immediately after deposit of H₂O:S₂, (c) after storage at 12°K for 17 hr, (d) at 35°K after storage at 35°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 S₂ pattern).

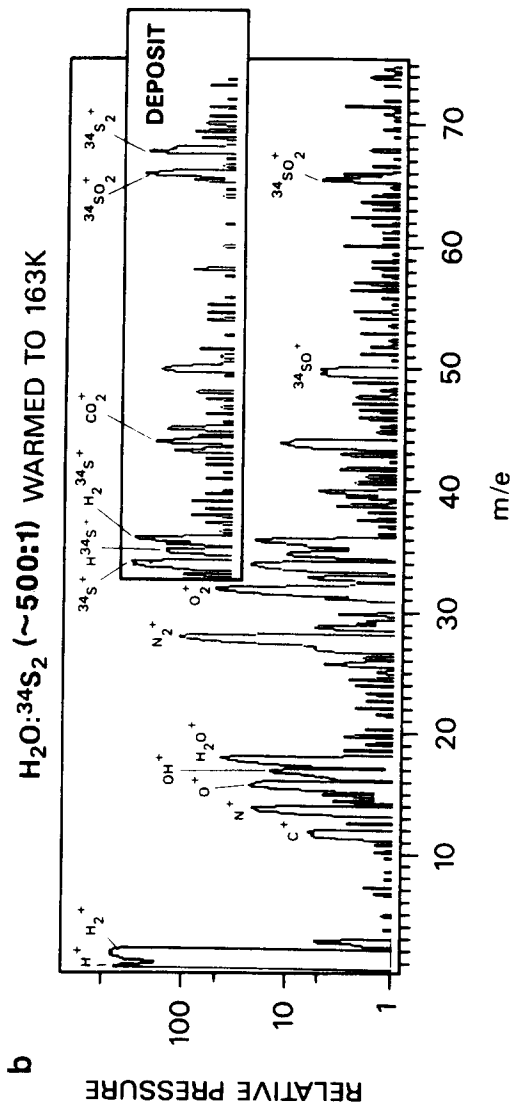
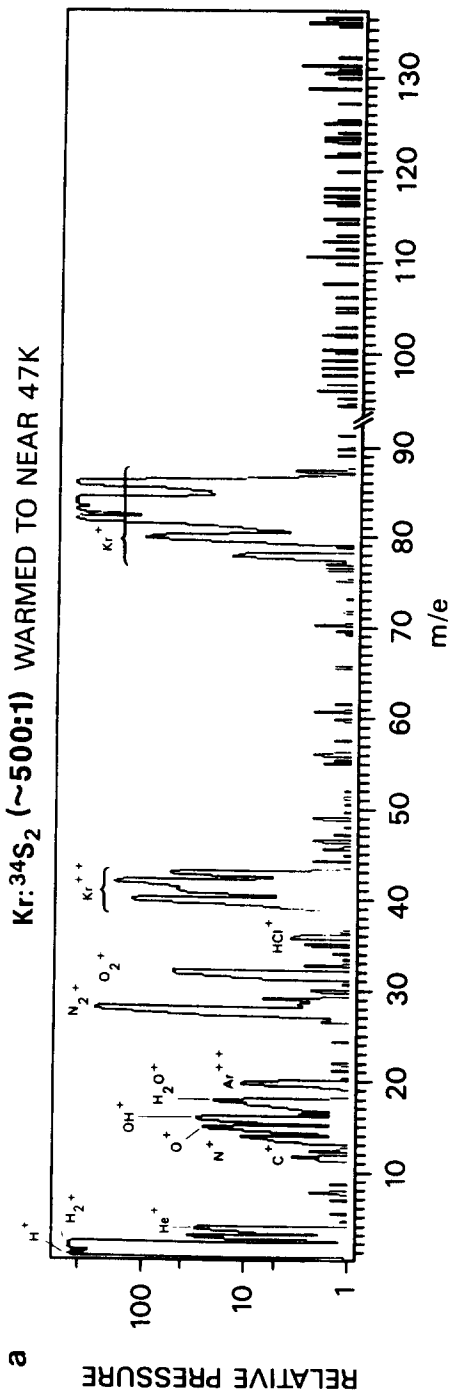
survive in water-dominated ices (*M*:*R*, 500:1) for at least 15 min to temperatures as high as 140°K. For storage times the order of hours at 140°K, the amount of S₂ appears to decrease significantly. Grim and Greenberg (1987) did not study the LIF signal of S₂ during long storage times.

A weak, broad feature attributed to S₄ was detected at 5220 Å in H₂O:S₂ (~500:1) ice after deposit at 12°K. The intensity of S₄ increased 25% after annealing to 110°K for 15 min. S₄ 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 S₂

QMS data recorded during vaporization of krypton matrix and water ice containing S₂ 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 10⁻⁶ to 10⁻⁵ Torr, near 47°K for krypton and 163°K for water.

Figure 7a shows that no ³⁴S₂⁺ (*m/e* = 68) signals were detected during vaporization



of Kr:³⁴S₂ (~500:1). This experimental result was reproduced several times. It was possible to detect S₂ at a partial pressure as low as 5×10^{-11} Torr which was nearly an order of magnitude lower than the strength of the usual S₂ signals during deposit ($2-3 \times 10^{-10}$ Torr). Although 5×10^{-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 S₂ 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 S₃ or S₄ was released from the ice.

Figure 7b is the QMS spectra during warming an H₂O:³⁴S₂ ice. The insert spectrum, recorded during deposit, shows that ³⁴S₂ along with reaction products ³⁴SO₂ and H₂³⁴S were deposited. ³⁴SO₂⁺, ³⁴SO⁺, H₂³⁴S⁺, and H³⁴S⁺ were detected during vaporization of the water ice but no ³⁴S₂⁺ 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 SO₂ from Krypton Matrices

We observed species vaporizing from Kr:SO₂ matrices ($M:R = 100:1$ and $2:1$) to determine when SO₂ was released. This ice mixture was chosen because SO₂ had the same molecular weight as S₂ and was less volatile than krypton. In all experiments our preliminary results supported the idea that detectable SO₂ 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 SO₂. Signals for SO₂ were detected near 100°K, a temperature at which its gas vapor pressure was approximately 10^{-8} Torr.

DISCUSSION

We have identified weak ultraviolet S₂ 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. S₂ absorptions were not detected after the ice was kept at 140°K for 17 hr, suggesting that some fraction of the S₂ had diffused in the ice and reacted with other species. Diffusion of S₂ 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 S₂. (a) A composite of two mass scans (covering $m/e = 1$ to 137) of vaporizing Kr:³⁴S₂ near 47°K (vapor pressure of krypton near 10^{-5} Torr). No ³⁴S₂ is detected. (b) A mass scan from 1 to 75 of vaporizing H₂O:³⁴S₂ near 163°K (vapor pressure of water near 10^{-6} Torr). The insert spectrum was taken during deposit and shows nearly equal signals of ³⁴S₂ and reaction products ³⁴SO₂ and H₂³⁴S. ³⁴SO₂ and H₂³⁴S are detected during vaporization but S₂ 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.³ 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 ($T < 140^\circ\text{K}$)⁴ 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

³ 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.

⁴ 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 $\frac{1}{2} T_m$).

which decreases in intensity with annealing. S_4 was relatively unaffected by irradiation.³ 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 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.³ 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.⁵ However, not a hint of S_2 was detected during slow warm-ups designed to optimize the signal-to-noise ratio.⁶ 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 2×10^{-4} and 1.4×10^{-3} , which is consistent with the observed ratio of S_2/OH of 5×10^{-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.

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

⁶ 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 S₂ would not release S₂ into the coma. Our experiments support the idea that S₂ 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 S₂ 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 S₂ as an extended cloud a few hundred kilometers above nucleus. There is, however, a potentially serious dilemma with the hypothesis that S₂ 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 S₂. The dilemma is that in the process of producing a significant concentration of S₂, other molecules in the mantle would also be processed. For example, sulfur atoms can react with oxygen to form SO or SO₂. Grim and Greenberg (1987) report the formation of both S₂ and SO in photolyzed icy mixtures. This raises the problem that if S₂ is trapped in an irradiated mantle and is the source of S₂ in the coma, then SO or SO₂ 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, S₂ may remain on the core as our experiments suggest. (2) Mantle processing may reduce its volatility, preventing sufficient rapid release of S₂ 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 S₂ observation.

It may also be possible to remove S₂ non-thermally from the nucleus through jets or

other explosive mechanisms. Another possibility is sputtering of S₂ by kiloelectron volt ion bombardment. Chrisey *et al.* (1987) found that 65% of the total yield from sulfur targets corresponded to S₂. S₂ was also sputtered effectively from H₂S and CS₂ 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 S₂ observed in Comet 1983d. Yields of sputtered S₂ probably also diminish when H₂S is mixed with H₂O (as in cometary ices) since competitive pathways for reactions are present. These experiments on icy mixtures have not been done.

The problem of S₂ but not SO₂ 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 S₂ 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 S₂ observations: What is the source of S₂ 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 S₂ problem.

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