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Photoprocessing of H_2S in interstellar grain mantles as an explanation for S_2 in comets

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Summary. The observation of S_2 in comet IRAS-Araki-Alcock 1983 VII has raised critical questions regarding whether the precometary formation of this molecule occurred in the gas phase or in the solid interstellar ices. The implications of these results on the origin of comets are interpreted using laboratory analogue experiments on S_2 formation.

We show that ultraviolet photolysis of H_2S embedded in dirty ices composed of molecules such as H_2O, CO and CH_4 converts the H_2S molecules into S_2 and other sulfur bearing species. From these experiments, using the cosmic abundance of sulfur relative to oxygen, we calculate that the $[S_2]/[H_2O]$ ratio in interstellar grains lies between $2\,10^{-4}$ and $1.4\,10^{-3}$, consistent with the observed ratio $[S_2]/[OH] = 5\,10^{-4}$ in IRAS-Araki-Alcock 1983 VII.

We argue that S_2 cannot be simply used as a discriminant for the comet formation temperature, unless one properly takes into account the aggregation time scales. Elevated temperatures for long times within interstellar grains may lead to depletion of S_2 and e.g. CO. Until the diffusion effect is studied in detail, the experiments suggest that for comet formation times of 10^6 yr temperatures *well under* 100 K (perhaps as low as 30–40 K) are indeed required so that comets could have been formed no closer than the Uranus-Neptune region.

Key words: comets – interstellar medium: dust – molecules – spectroscopy – UV radiation

1. Introduction

The very close approach to the earth (0.032 A.U.) of comet IRAS-Araki-Alcock 1983 VII was a rare opportunity to observe the comet with a high spatial resolution. Ultraviolet emission spectra of the coma obtained with the International Ultraviolet Explorer (IUE) satellite showed the presence of S_2 close to the cometary nucleus (A'Hearn et al., 1983). At the same time, spectroscopic and photographic observations with the 182 cm Asiago Telescope suggested the presence of H_2S^+ and HCO in the cometary coma (Cosmovici and Ortolani, 1984, 1985). It must be noted that H_2S has a photo-ionization probability (relative to dissociation into SH and H) of $1.7\,10^{-4}$, which is at least an order of magnitude lower than that of H_2O (0.03; Huebner and Carpenter, 1979), making a positive identification of this species extremely difficult. We shall therefore argue that it is reasonable to assume that H_2S is present in cometary ices.

Although many sulfur molecules have been observed in the interstellar medium (Mann and Williams, 1980), S_2 is not one of these. An upper limit of about 2% of the cosmic abundance of atomic sulfur has been deduced for S_2 in the interstellar gas by radio investigations of dark clouds (Liszt, 1978), while model calculations predict a low fractional abundance for S_2 (Millar, 1982; Mitchell, 1984). On the other hand, its presence in solid state photoprocessed grain mantles may be inferred from the recent observation of H_2S and OCS towards W33 A (Geballe et al., 1985) in combination with sulfur recombination chemiluminescence experiments in low temperature argon matrices (Smardzewski, 1978; Lee and Pimentel, 1979).

As shown in Geballe et al. (1985), starting with a frozen gas mixture of H_2O, CO, CH_4, NH_3 and H_2S, ultraviolet photolysis produces a series of absorptions which closely resembles the features of the infrared spectrum towards W33 A. The band observed at 4.9 micron (2040 cm^{-1}) is identified with the ν_3 vibration of OCS and is shifted slightly (~ 10 cm^{-1}) to lower frequencies upon warmup, an effect which has already been recognized by Verderame and Nixon (1966) upon heating of solid carbonyl sulfide (OCS). The absorption band in W33 A at 3.93 micron (2544 cm^{-1}) is ascribed to the vibrational mode of H_2S and, together with the laboratory experiments, provides convincing evidence that sulfur molecules in grain mantles towards W33 A are photoprocessed producing new molecular species of which S_2 could be a likely one.

The remaining question is what the origin is of the observed S_2 emission in the coma of IRAS-Araki-Alcock 1983 VII. As has been argued in A'Hearn et al. (1983) the observed emission results from resonance fluorescence by solar radiation and the spatial profiles indicate a direct release of the S_2 molecules from the nucleus. Another possible, but excludable, mechanism for the emission in the coma, not discussed by A'Hearn et al., arises from the recombination of two ground state sulfur atoms which has been shown to occur in chemiluminescence experiments within photolyzed low temperature matrices (Smardzewski, 1978; Lee and Pimentel, 1979). The observed relative intensities of the IUE data are not in agreement with the chemiluminescence intensities and, therefore, chemiluminescence of S_2 as a possible origin of the observed S_2 emission can be excluded.

Thus, accepting that S_2 is indeed an initial component of the cometary ice, we examine how it became part of the solid cometary material before or after the comet formation. Recombination of two sulfur atoms in the gas phase, followed by subse-

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Send offprint requests to: R.J.A. Grim quent condensation on the interstellar grains, is unlikely because a two-body recombination reaction is known to have a much too low reaction rate (Mitchell, 1984). The possibility that S_2 is formed on the comet surface during one cycle may also be ruled out for a periodic comet like IRAS-Araki-Alcock 1983 VII: the ultraviolet photon and/or cosmic ray fluxes are too low to replenish the outer layers of the cometary nucleus between two passages (A'Hearn and Feldman, 1985). The only remaining possibility is: not only must S_2 be a parent molecule, but it must also be a constituent *throughout* the interior of the cometary nucleus and, therefore, it must have been present since the comet was formed. Such a condition requires the aggregation of interstellar dust particles carrying photoprocessed ice mantles as suggested in the model of Greenberg (1982a, 1983a). Laboratory experiments in which energetic processing is simulated either by ultraviolet photolysis (Geballe et al., 1985; d'Hendecourt et al., 1986) or proton bombardment (Moore et al., 1983) of dirty ices support the suggestion that S_2 has been formed as a result of the irradiation of sulfur molecules in interstellar grain mantles, which ultimately have aggregated into comets.

Laboratory formation of S_2 by ion bombardment of sulfur or sulfurous compounds at 15 K has been demonstrated recently in mass spectrometry experiments by Boring et al. (1985). Bombardment of a thick sulfur target led to a 40% conversion rate into S_2. When frozen H_2S was bombarded, an upper limit of 20% was estimated. The authors agreed with A'Hearn and Feldman (1985) that S_2 cannot have been produced in the coma by solar wind ions. Moreover, they underlined that S_2 must have been formed in the solid state by ion bombardment either of condensed sulfur compounds or of some sulfurous residue which in time grows a condensed mantle. According to Boring et al. ion bombardment places less constraints on (i) the temperature of the ices in the comet formation region and (ii) the required irradiation flux. Item (i) will be discussed in more detail in Sect. 4.2. Secondly, the energy input by cosmic ray bombardment of the cometary aggregation is generally negligible compared with that of ultraviolet irradiation of interstellar grains during a typical lifetime of 10^9 yr (Greenberg, 1985).

The first aim of this work is to demonstrate that S_2 is produced by ultraviolet photolysis of dirty ices containing H_2S as a parent molecule (Cosmovici and Ortolani, 1984; Geballe et al., 1985). Because the S_2 molecule does not possess any infrared active bands, other techniques (Laser Induced Fluorescence and Ultraviolet Spectroscopy) are needed to detect its presence. Early results on ultraviolet photolysis experiments with H_2S in combination with these techniques have been described in a paper published recently (Grim et al., 1986). The question of the production rate of S_2 will be addressed and the number derived will be compared with the S_2 concentration in IRAS-Araki-Alcock 1983 VII which is estimated from the production rate ($\sim 2\,10^{25}\,\mathrm{s}^{-1}$) to be roughly a factor of $5\,10^{-4}$ the OH production rate (A'Hearn et al., 1983). Moreover, this number is known to vary by an order of magnitude due to temporal and spatial variations of the S_2 fluxes. These variations have been interpreted in terms of a non-homogeneous distribution of the volatiles in the cometary ice (Feldman et al., 1984). From the observed CS production rate in IRAS-Araki-Alcock 1983 VII, which is comparable with that of S_2, and the fact that production rates of CS relative to OH agree within a factor of two for several comets at the same heliocentric distances (Weaver et al., 1981), we infer that S_2 is probably present in all comets in amounts comparable with CS_2, the parent molecule of CS (Jackson et al., 1986). This conclusion supports the generally accepted theory that all comets share a common composition and origin (Weaver et al., 1981).

The next important question is if the S_2 molecule can be used as a probe for establishing the formation temperature of comets as suggested by A'Hearn and Feldman (1985). This suggestion was based on laboratory experiments by Hopkins and Brown (1975) in which the Raman spectra of S_2 in argon indicated S_2 disappearance due to chemical reactions in, or diffusion out of the annealed matrices.

As a test for comet formation temperature, we have studied the diffusivity and reactivity of S_2 with techniques similar to those of Van IJzendoorn et al. (1986b). Controlled diffusion of HCO radicals, studied with Laser Induced Fluorescence, leads to glyoxal formation. From the diffusion coefficients derived, it has been shown that at least 50% of the initial radicals (assumed $\sim 1\%$) survives for $2\,10^6$ yr in a dirty ice with a mean temperature of 15 K (Van IJzendoorn et al., 1986b). In addition to the fluorescence studies we have searched for possible reaction products such as S_3 and S_4, which are known to absorb in the visible (Meyer et al., 1972).

Another approach to test the chemical composition and thermal history of comets is based on condensation and sublimation of volatile molecules (Yamamoto et al., 1983, 1985). In this model, comets are proposed to have been formed in two stages. First, condensation of ice on grains is assumed to have taken place in low temperature regions of interstellar clouds and, subsequently, the aggregation of these particles into a cometary nucleus occurred in the solar nebula, where the higher gas density and temperature also provided a thermal cycling of the cometary ice. The Clapeyron-Clausius relation is used to obtain the condensation and sublimation temperatures of several molecules under interstellar conditions. Combining these values with an assumed chemical composition of the comet, Yamamoto et al. calculated the formation temperature based on the sublimation temperatures *of pure substances* for two different cases, each of them explaining an assumed absence of CO in cometary ices; an assumption which seems to be in contradiction with recent observations (Feldman, 1983; and late Halley results). As we shall demonstrate later in this paper, trapping or clathrate formation invalidates the assumption that a molecule sublimes independently of its environment, thus making inappropriate the temperature ranges calculated on the basis of condensation/sublimation processes.

After H_2, CO is known to be the major component of interstellar molecular clouds and has also been recently detected in the solid ice mantles of preaggregated interstellar grains (Lacy et al., 1984; Whittet et al., 1985). Therefore, CO may also be expected in cometary ices if comets have been coagulated out of interstellar dust particles as suggested by Greenberg (1977, 1982a, 1983a). Furthermore, far ultraviolet observations (Feldman and Brune, 1976) have shown the Fourth Positive system ($A\,^1\Pi \rightarrow X\,^1\Sigma^+$) of CO in the coma of comet West 1975 VI. Although there still exists some disagreement about the origin of the emission, CO is believed to be a parent molecule and not a dissociation product of CO_2 (Feldman, 1983). This again favors an interstellar origin of comets. The large variations in CO production rates relative to OH may be explained by (i) considering different regions (and temperatures) for comet coagulation, or (ii) a result of the combined chemistry of the gas and grains in the interstellar medium (d'Hendecourt et al., 1985).

The relationship of our experiments with the evaporation studies by Bar-Nun et al. (1985) will be discussed in Sect. 4.2, where we address the implications of this study for the formation temperature and origin of comets.

2. Experimental methods

The main points of the experimental set-up and techniques are briefly reviewed here; a complete description can be found in Van IJzendoorn et al. (1985, 1986a). After preparation in a greaseless vacuum glass line, gas mixtures containing H_2S are deposited onto a cold (12 K) sample substrate. The thickness of the samples is evaluated by measuring the interference fringes with a He-Ne laser (Person, 1981) and a calibrated flow capillary. The aluminum substrate is coated with a layer of gold to reduce background fluorescence caused by metal oxides on the surface and is cooled by an Air Products CSA-202A displex closed cycle refrigeration system. A hydrogen flow lamp provides the ultraviolet photon flux necessary for the dissociation of the H_2S molecules. The formation of S_2 molecules is probed either by ultraviolet spectroscopy or by laser induced fluorescence (LIF).

In each experiment absorption spectra have been recorded by a Hamamatsu R212 photomultiplier in combination with (i) the hydrogen discharge lamp or a deuterium lamp for the ultraviolet region (200–400 nm) or (ii) a 250 W quartz halogen lamp for the visible region (380–800 nm). In some experiments the same set-up has been used for recording chemiluminescence spectra during slow warmup of the processed samples.

The fluorescence spectra of the photolyzed samples, normally ranging from 380 to 550 nm, are recorded, after excitation at 308 nm with a pulsed XeCl excimer laser (Lambda Physik EMG 100), by a Spex double monochromator (Model 1672, dispersion 1.8 nm with 600 nm blazed gratings) in combination with a low noise photomultiplier (ITT-FW 130) and a transient digitizer (Gould Biomation Model 4500). In emission and excitation studies the fluorescence signals are averaged over 64 laser shots (~0.5–1.5 mJ typically) using a slit width of about 0.2–0.5 mm and a step size of 0.2 nm for the monochromator. For lifetime studies the signal is averaged over 256 laser shots.

The mixtures used in our experiments can be separated in two groups. First, experiments in which H_2S has been embedded in noble or inert gas matrices (argon and nitrogen) at various ratios. These provide the basis for a positive identification of the S_2 emission systems. In the second group of experiments H_2S was embedded in mixtures of H_2O, CO and CH_4. As a result of the strong ultraviolet absorption by water molecules, the irradiation of these dirty ices had to be simultaneous with deposition.

Due to the reactivity in the gas phase of NH_3 with H_2S, leading to the formation of the NH_4SH crystal (Bézard et al., 1983), NH_3 has not been included in these experiments. A way to avoid this problem would have been to use CH_3NH_2 as an initial molecule for the source of nitrogen.

3. Results

In the laboratory the formation of new species upon ultraviolet photolysis is normally studied by means of infrared, visible or ultraviolet spectroscopy. Since S_2 lacks a dipole moment it cannot be observed in the infrared. On the other hand, S_2 can easily be identified from its ultraviolet absorption into the vibrational levels of the $B\,^3\Sigma_u^-$ or $B''\,^3\Pi_u$ states (Brewer et al., 1965; Brewer and Brabson, 1966). The main difficulties arising from using this technique to probe the formation of S_2 are the low initial H_2S concentrations and the unknown photolysis conversion rate. We therefore also probed the S_2 formation by Laser Induced Fluorescence (LIF), knowing that S_2 molecules strongly fluoresce upon excitation in the near ultraviolet (300–500 nm; Brewer and Brabson, 1966). We shall first describe the experiments using LIF and, following this, the ultraviolet absorption studies. Finally, the temperature behavior of the processed mixtures is presented.

3.1. Emission spectra

The formation of S_2 upon UV irradiation of H_2S is clearly shown in Fig. 1a, where the emission spectrum after 7 hrs photoprocessing is shown. As summarized in Table 1 the peak locations of the strong vibrational progression coincide well with the $B \rightarrow X$ fluorescence of S_2 in argon as observed by Brewer and Brabson (1966). The precise identification of the emitting state is unclear. In several chemiluminescence studies the emitting state has been identified with $B\,^3\Sigma_u^-$ (Brom and Lepak, 1976; Fournier et al., 1977; Smardzewski, 1978). Later investigations (Bondybey and English, 1978; Lee and Pimentel, 1979) have raised questions about this assignment and stated that the emission probably originated from the excited $B''\,^3\Pi_u$ state, which lies a few hundred cm^{-1} lower in energy than the $B\,^3\Sigma_u^-$ state (Swope et al., 1979; Patiño and Barrow, 1982). The $B''\,^3\Pi_u$ state corresponds to two ground state (^3P) sulfur atoms, whereas the $B\,^3\Sigma_u^-$ state correlates with one ground state and one excited (^1D) sulfur atom. The $B\,^3\Sigma_u^-$ state, as has been noted by Bondybey and English (1978), cannot be populated by recombination of two ground state sulfur

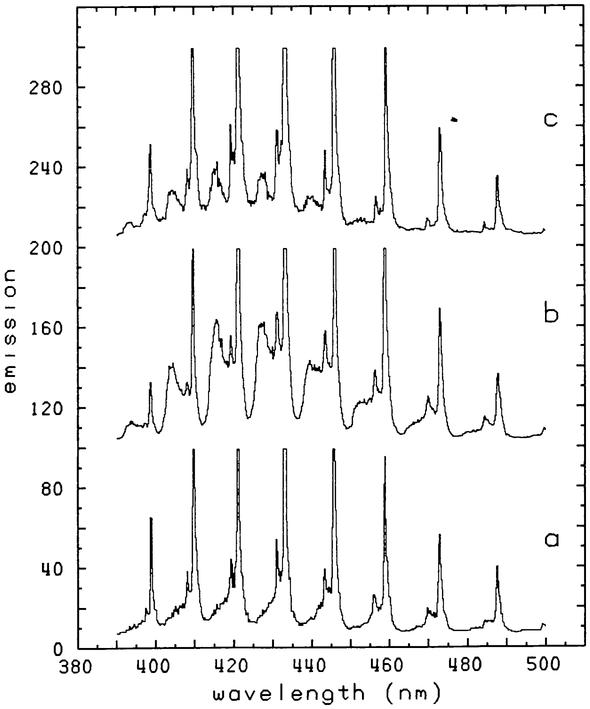

Fig. 1. Observed fluorescence lines of the $B \rightarrow X$ transition of S_2 in photolyzed matrices containing H_2S; $Ar/H_2S = 1000/1$ at 12 K **(a)**, $Ar/H_2S = 100/1$ at 12 K **(b)**, $Ar/H_2O/CO/CH_4/H_2S = 300/1/1/1/1$ after warming to 38 K and recooling to 12 K **(c)**. Emission is in arbitrary units

Table 1. Peak wavelengths of observed emission lines (λ in nm) in a photolyzed $Ar/H_2S = 1000/1$ matrix at 12 K compared with $B \rightarrow X$ fluorescence of S_2 in an argon matrix (Brewer and Brabson 1966). The uncertainty in the wavelength values ($\Delta\lambda$) is ~ 0.2 nm

$Ar/H_2S = 1000/1$		Brewer and Brabson,	
$^{32}S^{32}S$ λ(nm)	$^{32}S^{34}S$ λ(nm)	$^{32}S^{32}S$ λ(nm)	$^{32}S^{34}S$ λ(nm)
	397.4		397.0
398.6		399.0	
	408.2		407.5
409.6		409.9	
	419.2		418.8
420.8		421.4	
	430.8		430.8
433.0		433.5	
	443.2		442.7
445.6		446.1	
	456.0		455.9
458.8		459.3	
	469.6		
472.8		473.3	
	484.2		
487.4		487.9	
	499.0		
502.8		503.7	
	515.8		
519.4		520.5	
	532.8		
537.0			
	547.5		
555.5			
	569.0		
575.0			
595.0			
618.0			

Table 2. A comparison of S_2 fluorescent emission lines in various experiments ($\Delta\lambda \leq 0.5$ nm).

a λ(nm)	b λ(nm)	c λ(nm)	d λ(nm)	e λ(nm)	f λ(nm)
398.6	393.6	393.6			
409.6	404.4	404.4	402	401	403
420.8	415.6	415.8	412	411	413
433.0	427.6	427.6	423	422	424
445.6	439.4	439.8	435	434	436
458.8	454.4	452.8	448	445	448
472.8	467.8	466.2	460	462	462
487.4	481.4		474	476	478
502.8			491	491	

Notes: a) $B''\Pi_u \rightarrow X\,^3\Sigma_g^-$ emission lines of $^{32}S^{32}S$ in a photolyzed $Ar/H_2S = 1000/1$ mixture at 12 K. b) $B \rightarrow X$ fluorescence lines of S_2 complexes in the same matrix at 12 K. c) $B \rightarrow X$ fluorescence lines of S_2 complexes in a photolyzed $Ar/H_2O/CO/CH_4/H_2S = 300/1/1/1/1$ matrix after warming to 38 K and recooling. d) Observed S_2 fluorescence in photolyzed $H_2O/H_2S = 100/1$ at 12 K. e) Same for $H_2O/CO/H_2S = 10/1/1$. f) Same for $H_2O/CO/CH_4/H_2S = 5/2/2/1$

atoms. Moreover, the observed lifetimes of the matrix emissions (Bondybey and English, 1978: $\sim$200 ns; our work: $\sim$160–300 ns for argon and $\sim$800 ns for N_2) are comparable with the lifetime of the $B''\,^3\Pi_u$ state in the gas phase ($\sim$350 ns) and considerably longer than that of the $B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-$ emission ($\sim$35 ns) (Patiño and Barrow, 1982). Although Hamaguchi and Tasumi (1982) also question the assignments we believe the $B''\,^3\Pi_u \rightarrow X\,^3\Sigma_g^-$ emission to be more consistent with our observations.

The other sharp progression observed in Fig. 1a is much weaker, but similar lifetimes are measured for the emission lines indicating again that $B''\,^3\Pi_u$ is the emitting state. The probability of another matrix site has been studied, but isotopic investigations showed that the emission resulted from $^{32}S^{34}S$ in natural isotopic abundance (Bondybey and English, 1978). The $B\,^3\Sigma_u^- \rightarrow X\,^3\Sigma_g^-$ emission in our studies is identified as a weak, broad, high frequency fluorescence satellite on the $B''\,^3\Pi_u \rightarrow X\,^3\Sigma_g^-$ emissions. The observed lifetime for this fluorescence is less than 30 ns, which is comparable to that of the $B\,^3\Sigma_u^-$ state of gaseous S_2 (Patiño and Barrow, 1982). In more concentrated mixtures, $Ar/H_2S = 100/1$ (Fig. 1b) and 30/1, the intensity of the satellite grows and the peak locations of the emission lines are distinguishable (Table 2). The short lifetime (<30 ns) and the broadening of the emission lines indicate strong perturbation of the excited $B''\,^3\Pi_u$ and $B\,^3\Sigma_u^-$ states by nearby H_2S molecules. Due to this perturbation, emission from the $B\,^3\Sigma_u^-$ state is probably enhanced, while that from $B''\,^3\Pi_u$ is weakened. Similar spectra have been recorded upon heating of irradiated Ar/H_2S matrices leading to complex formation of S_2 with H_2S. In irrradiated $Ar/H_2O/H_2S = 1000/10/1$ and $Ar/H_2O/CO/CH_4/H_2S = 300/1/1/1/1$ matrices the complex formation of S_2 could directly be observed without heating (Fig. 1c). Comparing the peak locations of these emission lines with those observed in photolyzed dirty ices (Table 2), we conclude that the environment determines the electronic state from which the S_2 molecules decay.

Figure 2a shows the 380–500 nm spectral emission region of an $H_2O/H_2S = 10/1$ sample after two hours of simultaneous deposition (10 μm hr^{-1}) and irradiation with the hydrogen discharge lamp. For $H_2O/H_2S = 100/1$ and 1/1 similar spectra have been recorded. The intensities of the emission lines in these samples are comparable within a factor of two. Unfortunately the relative numbers of S_2 molecules formed cannot be deduced, because the coupling of S_2 with neighbouring species may vary from experiment to experiment. This is clearly observed in the emission spectrum of a photolyzed $H_2O/CO/CH_4/H_2S = 5/2/2/1$ sample where the $B \rightarrow X$ emission system is hardly recognizable because of weakening and broadening of the emission lines (Fig. 2b).

In the 550–750 nm region of the photolyzed dirty ices other emission lines appear as well (Fig. 3), their strength relative to that of the 423 nm $B \rightarrow X$ emission line of S_2 being approximately 1/20. In argon matrices, emission lines in this region have also been observed. Their intensities relative to the 433 nm S_2 emission line are at least a factor of 10 less ($\sim$1/250) compared with the dirty ice. Because (i) the S_2 emission lines in H_2O/H_2S

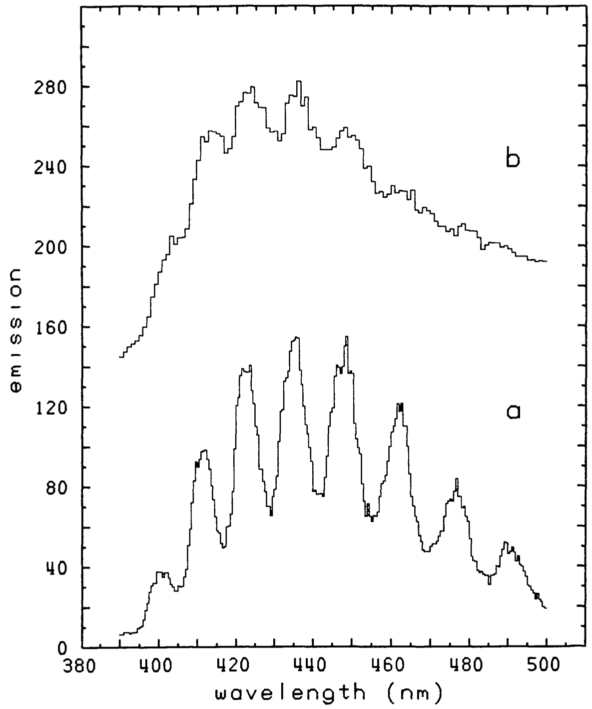

Fig. 2. Same as for figure 1: $H_2O/H_2S = 10/1$ at 12 K **(a)**, $H_2O/CO/CH_4/H_2S = 5/2/2/1$ at 12 K **(b)**

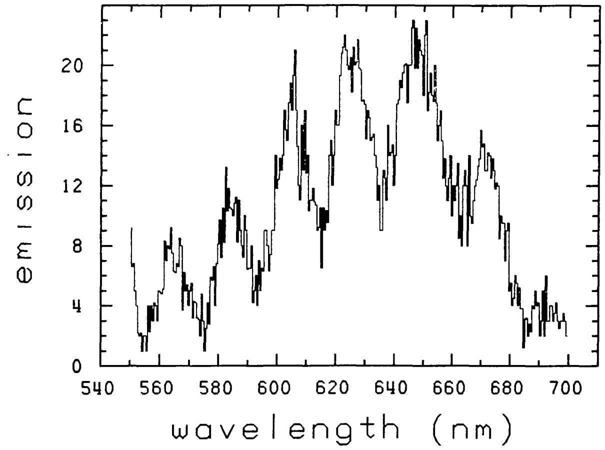

Fig. 3. Observed SO fluorescence in a photolyzed $H_2O/H_2S = 10/1$ dirty ice at 12 K from 550 to 750 nm. Emission is in arbitrary units

Table 3. Observed emission lines in the 550–750 nm region of photolyzed dirty ice samples containing H_2S compared with chemiluminescent bands of SO and S_2 ($\Delta\lambda \leq 0.5$ nm)

a λ(nm)	b λ(nm)	c λ(nm)	d_1 λ(nm)	d_2 λ(nm)	e_1 λ(nm)	e_2 λ(nm)
				538.1		540
545		550.8	550.7		552	
564	557			569.7		571
584	580	584.3	584.1		587	
604	604			603.8		608
624.5	630	621.7	621.6		627	
646	658					
670	689	663.7	663.5		673	
691.5						
720		710.8	711.1			

Notes: a) Observed emission bands in photolyzed H_2O/H_2S samples (average values of 4 experiments). b) $A'\,^3\Delta_u \rightarrow X\,^3\Sigma_g^-$ fluorescent bands of S_2 in solid argon by Lee and Pimentel (1979). c) $c\,^1\Sigma^- \rightarrow a\,^1\Delta$ chemiluminescence bands of SO in solid argon by Lee and Pimentel (1978). d) $c\,^1\Sigma^- \rightarrow a\,^1\Delta$ (first column) and $A'\,^3\Delta \rightarrow X\,^3\Sigma^-$ (second column) chemiluminescence bands of SO in solid argon by Tevault and Smardzewski (1978). e) The same systems as observed in S_2 chemiluminescence experiments by Smardzewski (1978).

samples diminish upon excitation with a BiBuQ dye (lasing at 381 nm) while the others in the 550–750 nm region remain, and (ii) the peak locations of the emissions do not correlate with the observed $c\,^1\Sigma_u^- \rightarrow X\,^3\Sigma_g^-$ (Bondybey and English, 1980) or $A'\,^3\Delta_u \rightarrow X\,^3\Sigma_g^-$ (Lee and Pimentel, 1978) transitions of S_2 (Table 3), we conclude that these emissions originate from species other than S_2. SO_2 as a possible candidate can be ruled out because the strong $a\,^3B_1 \rightarrow X\,^1A_1$ phosphorescence is absent in the 380–500 nm region (Long and Pimentel, 1977). Other possible candidates include SO, HSO and HSOH; however little data are available regarding the emission systems of these molecules. As can be seen from Table 3 the peak locations of the emitting species in our H_2O/H_2S samples resemble those of SO in argon matrices and probably correspond to the $c\,^1\Sigma^- \rightarrow a\,^1\Delta$ and $A'\,^3\Delta \rightarrow X\,^3\Sigma^-$ transitions of this molecule (Tevault and Smardzewski, 1978; Lee and Pimentel, 1979). The differences in the observed peak locations may result from matrix shifts.

3.2. *Ultraviolet absorption spectra*

Due to the low H_2S concentrations used it has been difficult to obtain observational evidence of the $B \leftarrow X$ absorption bands of S_2 in the ultraviolet. Even assuming that 10% of all H_2S molecules in a typical $Ar/H_2S = 100/1$ experiment were converted upon photolysis into S_2, the total number of S_2 molecules would still be at least 30 times less than in a typical absorption experiment of Brewer et al. (1965). For this reason we decided to use rather thick depositions (flowrate 10 μm hr^{-1}) with a simultaneous irradiation of the ultraviolet hydrogen lamp for long periods of time (over 24 hr).

From the measured absorption spectra it is possible to calculate the number of absorbers by using the following expression for the oscillator strength in which all parameters are expressed in S.I.-units:

$$f = \frac{4\varepsilon_0 m_e c}{N e^2} \int_{\nu_1}^{\nu_2} \tau_\nu \, d\nu \tag{1}$$

$\varepsilon_0 = 8.85\,10^{-12}\,\mathrm{C^2\,kg^{-1}\,s^2\,m^{-3}}$

$m_e = 0.911\,10^{-30}\,\mathrm{kg}$

$c = 3\,10^8\,\mathrm{m\,s^{-1}}$

$e = 1.6\,10^{-19}\,\mathrm{C}$

N is the number of absorbers per unit area (in m^{-2}), and $\int_{\nu_1}^{\nu_2} \tau_\nu\,d\nu$ is the total integrated absorbance. This last value can be approx-

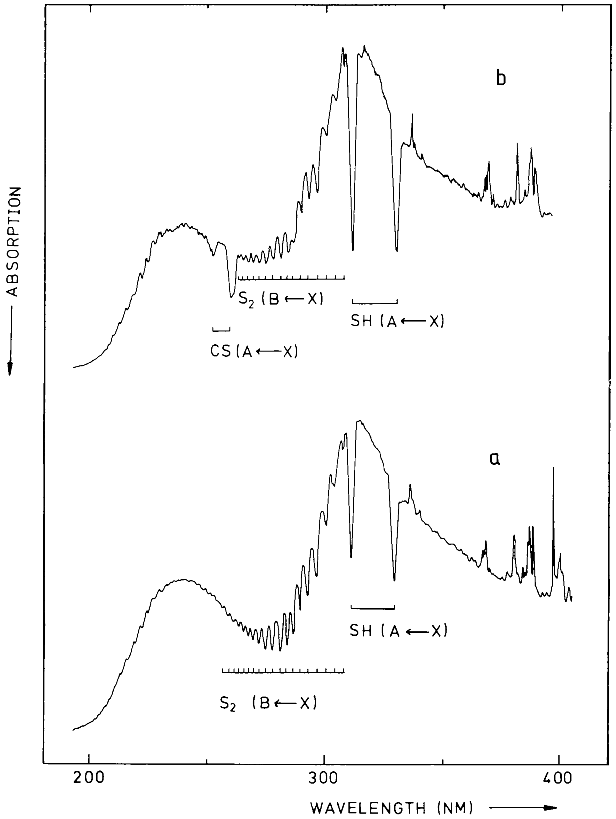

Fig. 4. Ultraviolet absorption spectra at 12 K of photolyzed Ar/H_2S = 300/1 **(a)** and Ar/H_2O/CO/CH_4/H_2S = 300/1/1/1/1 **(b)** obtained with the hydrogen discharge lamp

imated, using Beer's law and a Lorentzian shaped absorption profile, by

$$\int_{\nu_1}^{\nu_2} \tau_\nu \, d\nu \simeq \tau \Delta\nu \tag{2}$$

(Person, 1981), in which τ = the optical depth ($\ln(I/I_0)$) and $\Delta\nu$ = the line width (in s^{-1}) at half maximum. Substituting the constants in Eq. (1) the number of absorbers per unit area is:

$$N(\mathrm{m}^{-2}) = 3.78\,10^5 \tau \Delta\nu f^{-1} \tag{3}$$

Oscillator strengths of some relevant sulfur molecules range from 10^{-2} to 10^{-4}: $S_2(B \leftarrow X)$ 4.5 10^{-3}; SH($A \leftarrow X$) 1.1 10^{-3}; SO($A \leftarrow X$) 1.8 10^{-2} and CS($A \leftarrow X$) 4 10^{-3} (Hsu, 1981). Because the spectra were recorded in reflection at 45°, Eq. (3) should be divided by $2\sqrt{2}$ and multiplied by the surface area of the block ($4\,10^{-4}\,\mathrm{m}^{-2}$) to obtain the number of absorbers in the sample:

$$N(\mathrm{tot}) = 54 \tau \Delta\nu f^{-1} \tag{4}$$

From the uncertainty in establishing the correct baseline we estimate the error in the optical depth to be roughly 10%. The largest uncertainty, however, comes from measuring the widths of the absorption lines (up to 40%), so that we assume the calculated values are correct up to about 40%.

Figure 4a shows a typical absorption spectrum, which is calibrated using the Hα (656.3 nm) and the Hδ (410.2 nm) emission lines of the hydrogen lamp, after 8 hr of *simultaneous deposition and irradiation* of an Ar/H_2S = 300/1 matrix. The lines observed at 330.0 and 311.6 nm are due to absorption of SH radicals from the $X\,^2\Pi$ ground state into the $v' = 0$ and $v' = 1$ vibrational levels of the excited $A\,^2\Sigma^+$ state (Aquista and Schoen, 1970). The absorption progression observed from 260 to 300 nm is assigned to the $B \leftarrow X$ transition of the S_2 molecule in argon (Brewer et al., 1965). During the entire experiment we observe a continuous growth of the absorbing species, which is expected from the simultaneous deposition and irradiation (Fig. 5a).

In Table 4a we summarize the total number of absorbers created after 8 hr ultraviolet photoprocessing of the Ar/H_2S = 300/1 mixture. The ratios of the absorbing species relative to H_2S are given in the final column. Slightly different values are obtained when the same mixture is irradiated *after* rather than *during* deposition. The numbers are given for 2 and 6.5 hr UV photolysis respectively (Table 4b). As shown in Fig. 5b a sharp

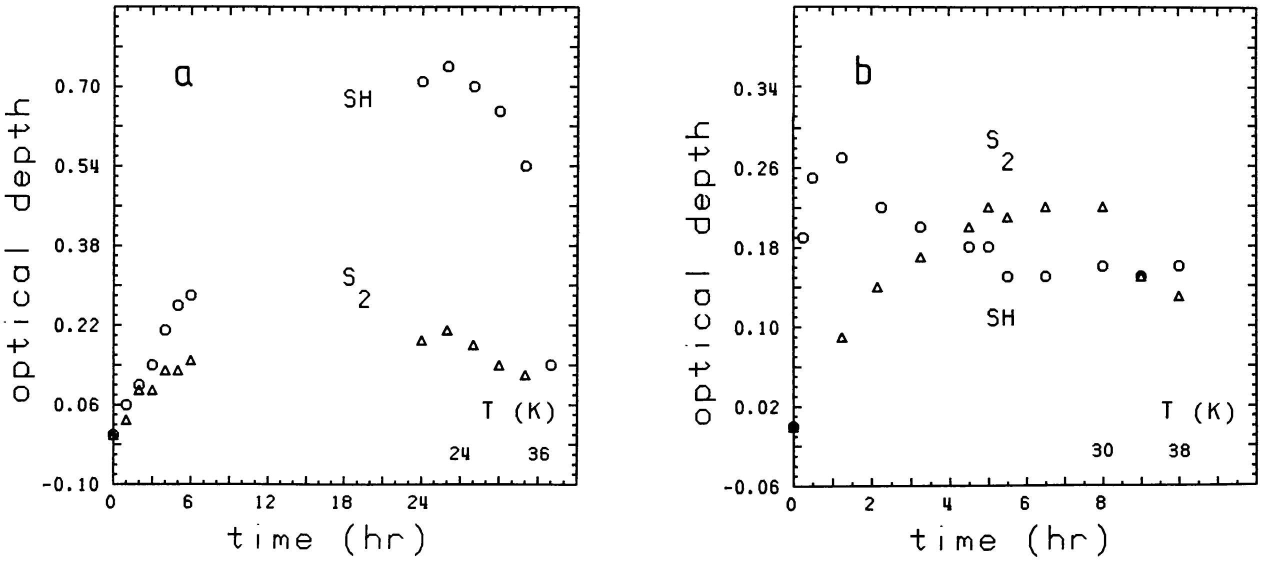

Fig. 5a and b. Optical depths of S_2 at λ = 281 nm (triangles) and SH at λ = 312 nm (circles) upon photolysis and heating of Ar/H_2S = 300/1 matrices; irradiation simultaneous with deposition **(a)** and after deposition **(b)**

Table 4. The production of relevant molecules in some typical experiments. The relative numbers in the final column have been calculated using Eq. 3 in combination with the known deposition rates of the mixtures. The possible errors are ±40%.

Experiment	X	λ (nm)	f	τ	$\Delta\nu$ (s^{-1})	[X]	[X]/[H_2S]
a) $Ar/H_2S = 300/1$[a]	HS	330	1.1×10^{-3}	0.49	9.4×10^{12}	2.2×10^{17}	0.10
	S_2	282	4.5×10^{-3}	0.35	7.1×10^{12}	3.4×10^{16}	0.015
		293	4.5×10^{-3}	0.24	6.2×10^{12}	2.0×10^{16}	0.009
b) $Ar/H_2S = 300/1$[b]	HS	330	1.1×10^{-3}	0.38[c]	9.0×10^{12}	1.7×10^{17}	0.21[c]
				0.18[d]		8.0×10^{16}	0.10[d]
	S_2	293	4.5×10^{-3}	0.20[c]	6.5×10^{12}	1.8×10^{16}	0.02[c]
				0.29[d]		2.6×10^{16}	0.03[d]
c) $Ar/H_2O/CO/CH_4/H_2S = 300/1/1/1/1$[a]							
	HS	312	1.1×10^{-3}	0.69	7.2×10^{12}	2.4×10^{17}	0.14
	CS	261	7.3×10^{-3}	0.47	1.6×10^{13}	5.6×10^{16}	0.04
	SO	261	1.8×10^{-2}	0.47	1.6×10^{13}	2.3×10^{16}	0.013
	S_2	293	4.5×10^{-3}	0.20	4.8×10^{12}	1.3×10^{16}	0.008

[a] UV simultaneously with deposition
[b] UV after deposition
[c] After 2 hr UV
[d] After 6.5 hr UV

increase of the SH absorption is observed during the first two hours. When the H_2S reservoir becomes depleted, photodissociation of SH radicals with 329 nm photons leads to decreasing absorptions. The S_2 absorptions, however, continue to grow until saturation is reached.

Figure 4b shows the ultraviolet absorption spectrum of a 7.25 hr simultaneously deposited and photolyzed $Ar/H_2O/CO/CH_4/H_2S = 300/1/1/1/1$ matrix at 12 K. Again strong absorption lines due to SH are observed at 312 and 331 nm. The $B \leftarrow X$ vibrational progression of S_2 is somewhat weaker relative to the Ar/H_2S experiment. Two additional features appear at 254 and 261 nm and result from $A\,^1\Pi \leftarrow X\,^1\Sigma^+$ absorption of CS and/or $A\,^3\Pi_{0,1,2} \leftarrow X\,^2\Sigma^-$ absorption of SO (Hsu, 1981). Just as in the $Ar/H_2S = 300/1$ matrix a vibrational progression ranging from 200 to 230 nm is observed. As a result of the weakness of the lines on the shoulder of the continuum a positive identification cannot be made. We therefore tentatively ascribe these lines to the $e\,^1\Pi_g \leftarrow X\,^3\Sigma_g^-$ or $B'\,^2\Pi_{g,2} \leftarrow X\,^3\Sigma_g^-$ transitions of S_2 (Rosen, 1970).

In Table 4c it is shown that the [SH]/[H_2S] ratio is higher than in the $Ar/H_2S = 300/1$ experiment (0.14 compared with 0.10), while the [S_2]/[H_2S] ratio has a somewhat lower value (0.008 compared with 0.012). This is explained by an increase of possible deactivation reaction channels for photolytic sulfur atoms. As can be noted from the tabulated data a fair number of CS radicals are produced upon UV photoprocessing. In the next section we shall discuss these numbers and their implications in more detail.

UV absorption spectra of CS or S_2 in dirty ices could not be obtained because of the strong background absorption of the dirty ice (mainly water) components themselves.

3.3. Visible absorption spectra

Visible absorption spectra (380–800 nm) have been recorded in almost every experiment. However, only radicals with low lying electronic states show absorptions in this region. For instance, when CO is an initial component of the photolyzed sample, the $^2A''\Pi \leftarrow X\,^2A'$ vibrational progression of the HCO radical (Van IJzendoorn et al., 1983) can be identified.

In photolyzed H_2O/H_2S samples the following results have been obtained. In a 100/1 matrix no absorptions are observed. For a 10/1 ratio a broad absorption band appears ranging from 550 to 650 nm and in a 1/1 ratio this band shows some structure resulting from weak ($\tau < 0.005$) absorptions (Table 5). Possible

Table 5. The unidentified absorption bands ($\Delta\lambda \sim 2$ nm) in the 500–700 nm region of a photolyzed $H_2O/H_2S = 1/1$ dirty ice (a) compared with transitions of some possible candidates: HSO ($^2A' \leftarrow {}^2A''$) (Schurath et al., 1977) (b) and unidentified bands in annealed Kr/S_2 matrices (Meyer et al., 1972) (c)

a λ (nm)	b λ (nm)	c λ (nm)
535	523	
551	542	
566	563	
578		
583	584	
591		590
600		601
611	610	611
618		
627		623
635	637	632
648		646
657		655
666	665	664
675		

photolysis products and carriers of the absorption bands are SO, HSO or HSOH. HSOH can be formed when a photolytic oxygen atom inserts into an H_2S molecule and is prevented from dissociation by the cage effect (Smardzewski and Lin, 1977). It is a saturated molecule and will not have any low lying electronic states which give rise to absorptions in the visible. The SO radical has low electronic states but are too high in wavelength (1600 nm for $a\,^1\Delta_g \leftarrow X\,^3\Sigma_g^-$ and 955 nm for $b\,^1\Sigma_g^+ \leftarrow X\,^3\Sigma_g^-$; Swope et al., 1979; Theodorakopoulos et al., 1981) to account for the observed spectrum.

Consequently the HSO radical remains as being the most likely candidate for the absorption profile(s). Unfortunately, no spectral absorption data for this species are available in the literature to make a positive identification. Nevertheless, on the basis of studies by Schurath et al. (1977), we can tentatively identify some of the observed absorption lines with chemiluminescence bands of HSO in gaseous $O/H_2O/O_3$ systems (Table 5). The HSO radical is formed by the same mechanism in which HSOH is formed: i.e. insertion of O in an H_2S molecule, but now the intermediate dissociates into HSO and a hydrogen atom (Smardzewski and Lin, 1977). A second reaction channel is the reaction of an SH radical with OH or O. If we assume an oscillator strength for the $^2A' \leftarrow {}^2A''$ transition of HSO of $1.8\,10^{-4}$ (Sannigrahi et al., 1977) we calculate with Eq. (4) ($\tau = 0.006$, $\Delta v = 8.4\,10^{12}\,\mathrm{s}^{-1}$) a total of $1.7\,10^{16}$ HSO radicals. This number, combined with the total amount of H_2S molecules deposited ($8.8\,10^{19}$), gives an $[\mathrm{HSO}]/[\mathrm{H_2S}]$ ratio of $2.0\,10^{-4}$, which is at least a factor of 25 smaller than the $[\mathrm{S_2}]/[\mathrm{H_2S}]$ ratio derived for the Ar/H_2S photolysis experiments. As can be seen from Table 5, many lines remain unidentified.

Special attention has been given to a possible identification of the molecules S_3 and S_4, which are believed to be formed when samples containing S_2 are annealed (Meyer et al., 1972). The importance of the use of these molecules as indicators of S_2 disappearance will be discussed in the following sections. Although both molecules show strong absorptions, S_3 at 410 nm ($\varepsilon = 1\,10^6\,\mathrm{l\,mole^{-1}\,cm}$) and S_4 at 530 nm ($\varepsilon = 1\,10^5\,\mathrm{l\,mole^{-1}\,cm}$) (Meyer et al., 1972), neither of them has been detected in our experiments.

3.4 *Temperature dependence*

The diffusivity and reactivity of S_2 has been studied in several experiments. The motivation for this particular study was initiated by the suggestion of A'Hearn and Feldman (1985) that S_2 can be used as a probe for the determination of the formation temperature of comets. This suggestion was based on experiments performed by Hopkins and Brown (1975) who observed the Raman band of S_2 in argon at 718 cm^{-1} after sulfur-oxygen-inert gas discharges. The S_2 band disappeared rapidly after annealing to 31 K, indicating that it is a very reactive species. In fact, in earlier studies the disappearance of S_2 molecules after annealing of low temperature matrices was inferred from the appearance of an absorption at 530 nm due to S_4 formation (Meyer et al., 1972; Meyer and Shoyer-Hansen, 1972).

The conclusion drawn from both studies is that S_2 molecules upon heating tend to disappear out of the matrices as a result of polymerization reactions. Barnes et al. (1974) studied the UV photolysis of hydrogen sulfide and the behavior of its products in low temperature matrices and arrived at similar conclusions. After warming to higher temperatures (~40 K) they observed strong infrared absorptions due to the formation of hydrogen persulfide (H_2S_2) and higher polymers. Formation of S_2 or S_4 was not observed directly, but was deduced from the resulting chemiluminescence in the violet region. Polymerization left a residue on their window.

In our experiments we have tested the above mentioned possibilities with samples using short deposition times (a few minutes) and high flow rates ($>200\,\mu\mathrm{m\,hr^{-1}}$) in order to minimize air impurities. During the UV irradiation (~6 hr) of the samples absorption spectra have been recorded at 30–75 min intervals. As a next step the photoprocessed matrices were heated to a fixed temperature for ~30 min until the observed chemiluminescence completely faded out, indicating that all molecules and radicals with activation energies for diffusion less than the corresponding activation energy for that particular temperature have been released from their traps (Van IJzendoorn et al., 1986b). In some experiments we have also recorded the corresponding chemiluminescence spectra. After recooling to 12 K, absorption spectra were again obtained.

In Fig. 5b the growth of S_2 and SH upon photolysis and warmup is monitored for an $Ar/H_2S = 300/1$ matrix. The behavior of the SH and S_2 absorptions upon photolysis has been discussed before. Upon warmup to 30 K for approximately 40 minutes both the SH and S_2 absorption lines decrease by ~30%. Even if all S_2 were to combine to form S_4, we would not be able to observe the S_4 absorption band at 530 nm because of the low S_2 concentration ($[\mathrm{S_2}]/[\mathrm{Ar}] < 10^{-4}$) in our sample. The concentrations used by Meyer et al. (1972) were at least a factor 50 higher than ours ($[\mathrm{S_2}]/[\mathrm{Kr}] > 5\,10^{-3}$).

The possibility that both the SH and S_2 have evaporated simultaneously with argon may be checked by calculating the argon evaporation rate at different temperatures. If a gas is frozen at a temperature T_B an equilibrium exists between the gas molecules that stick on the cold surface and those which sublime from it. The corresponding vapor pressure, $p_v(T_b)$ (in Pa), is expressed as

$$p_v(T_B) = nkT_B \tag{5}$$

in which k is the Boltzmann constant ($1.38\,10^{-23}\,\mathrm{J\,K^{-1}}$) and n the number density of the gas molecules. However, in our experimental set-up the subliming molecules are pumped off and result in a decrease of the sample thickness. The number of molecules that sublime per unit time and unit area is then given by:

$$\frac{dN}{dt} = \frac{n}{2}\,v_x(T_B) \tag{6}$$

in which $v_x(T_B)$ is the mean velocity perpendicular to the surface (in $\mathrm{m\,s^{-1}}$) and is approximately given by the Maxwell-Boltzmann distribution as:

$$v_x(T_B) = \sqrt{\frac{2kT_B}{\pi M}} \tag{7}$$

The corresponding decrease of the sample thickness, $\frac{dh}{dt}$ ($\mathrm{m\,s^{-1}}$), is found by substituting Eqs. (5) and (7) into Eq. (6):

$$\frac{dh}{dt} = \frac{p_v(T_B)}{\rho}\sqrt{\frac{M}{2\pi kT_B}} \tag{8}$$

In Eqs. (7) and (8) M is the molecular mass of an argon atom ($6.7\,10^{-26}$ kg) and ρ the mass density of argon ($1.755\,10^3\,\mathrm{kg\,m^{-3}}$;

Pallark, 1964). Eq. (8) becomes

$$\frac{dh}{dt} = 1.6\,10^{-5}\,\frac{p_v(T_B)}{\sqrt{T_B}} \qquad (9a)$$

For different temperatures the decrease of the argon thickness is listed in Table 6a. With this table we calculate that in 40 min the sample thickness at 30 K is decreased with 0.9 μm, which is only 3% of the original value after deposition at 12 K. This number is ten times less than the observed decrease for SH and S_2. Although this is only a crude approximation of the actual evaporation process, we conclude, within the limits of our accuracy, that the decrease of the number of SH and S_2 molecules at 30 K cannot be the result of evaporation with argon alone. Thus there is no doubt that the higher matrix temperatures enhance diffusion and recombination (polymerization) reactions, which is consistent with the prolonged glowing of the samples upon heating. In all our experiments a residue remained on the substrate indicating that indeed polymerization had occurred confirming the earlier suggestions.

Additional information is gained by monitoring the chemiluminescence upon heating of the argon samples. During the first warming cycle to 30 K strong chemiluminescence peaks are observed at 17 K and 25 K respectively. The corresponding spectra are attributed to $A\,{}^3\Sigma_u^+ \rightarrow X\,{}^3\Sigma_g^-$ fluorescence of O_2 recombination (12–25 K) and to the very strong $a\,{}^3B_1 \rightarrow X\,{}^1A_1$ phosphorescence of SO_2 recombination (18–36 K) (Smardzewski, 1978). Since SO_2 luminescence is orders of magnitude stronger, it obscures possible S_2 chemiluminescence. No special efforts were taken to avoid the problem of the small O_2 impurities in the samples. Potential luminescence of SO in the 500–700 nm region was too weak to be observed.

Table 6a. The evaporation rate for argon at different temperatures. The numbers are calculated using Eq. (9a) and vapor pressures by Honig and Hook (1960). Conversion factor for p_v (Torr) to p_v (Pa) is 1.33 × 10^2 (Allen, 1955)

T_B(K)	$p_v(T_B)$(Torr)	dh/dt (μm s^{-1})
25.2	10^{-9}	4.2×10^{-7}
26.8	10^{-8}	4.1×10^{-6}
28.6	10^{-7}	3.9×10^{-5}
30.6	10^{-6}	3.8×10^{-4}
33.1	10^{-5}	3.7×10^{-3}
35.9	10^{-4}	3.5×10^{-2}
39.2	10^{-3}	3.4×10^{-1}
43.2	10^{-2}	3.2

Table 6b. The evaporation rate for water at different temperatures. The numbers are calculated using Eq. (9b) and vapor pressures by Honig and Hook (1960). Conversion factor for p_v (Torr) to p_v (Pa) is 1.33 × 10^2 (Allen, 1955)

T_B(K)	$p_v(T_B)$(Torr)	dh/dt (μm s^{-1})
137.0	10^{-9}	2.27×10^{-7}
144.5	10^{-8}	2.21×10^{-6}
153.0	10^{-7}	2.15×10^{-5}
162.0	10^{-6}	2.09×10^{-4}
173.0	10^{-5}	2.02×10^{-3}
185.0	10^{-4}	1.96×10^{-2}
198.5	10^{-3}	1.89×10^{-1}
215.0	10^{-2}	1.81

In the temperature cycles (12 → 35 → 12 K and 12 → 38 → 12 K) the sample continued to glow at a rather constant rate for a long period of time, but the chemiluminescence signals were too weak to record spectra.

The behavior of S_2 in dirty ices is studied by recording the induced fluorescence signal upon warmup. Heating begins immediately after the cooler is turned off resulting ultimately in a heating rate of 1 K min^{-1}. The behavior of the $B \rightarrow X$ fluorescence of S_2 in several samples is shown in Fig. 6. In all these mixtures, which consist mainly of H_2O, a sharp rise of the emission signal is observed above 130 K. The signal reaches a maximum at ~160 K. Above this temperature the signal drops to zero. Since a similar type of behavior is observed in all water rich experiments, this can probably be ascribed to the phase change of amorphous (H_2O(as)) into polycrystalline ice ($H_2O\,I_c$). Hagen et al. (1981) have discussed this transformation extensively on the basis of infrared spectroscopy and stated that the transformation proceeds rapidly as a result of heat liberation (Patashnick et al., 1974). The observed increase of S_2 fluorescence from 130 to 150 K seems to follow the phase transition of the water ice. Apparently the coupling of the S_2 molecules to the water ice is weakened as the water molecules rearrange into a purely crystalline form. The dissipation of the excitation energy of S_2 via vibrational modes of H_2O becomes less efficient so that the increase of

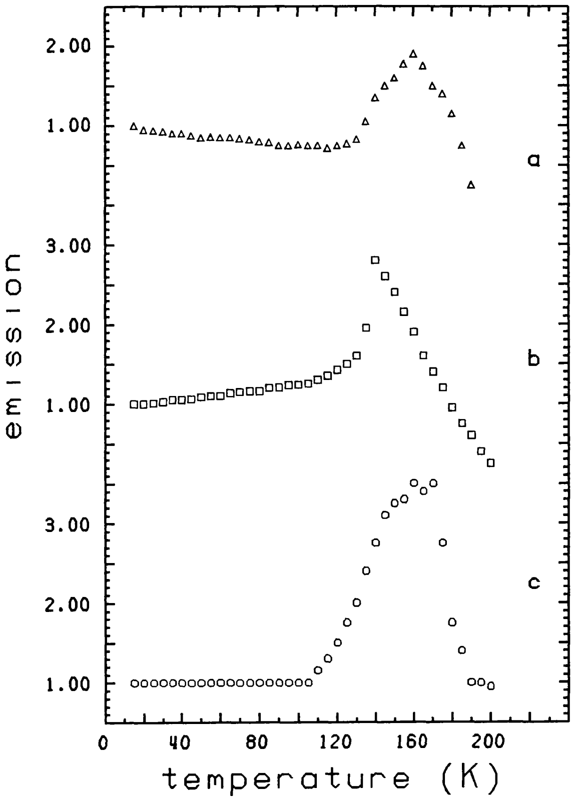

Fig. 6. Relative strength of the S_2 emission signal at 433 nm upon heating of several photolyzed dirty ices; $H_2O/H_2S = 10/1$ **(a)**, $H_2O/CO/H_2S = 10/1/1$ **(b)** and $H_2O/CO/H_2S = 10/2/1$ **(c)**

the S_2 fluorescence signal is not due to an increase of the number of S_2 molecules.

Although, above 150 K, the water I_c can transform into hexagonal ice, $H_2O\,I_h$ (Fletcher, 1971), under our experimental conditions the water molecules will start to evaporate (Honig and Hook, 1960). In a similar way as for argon we calculate with Eq. (8) the evaporation rate for H_2O; $M = 3.0\,10^{-26}$ kg and $\rho = 0.94\,10^3\,\mathrm{kg\,m^{-3}}$ (Hagen et al., 1981):

$$\frac{dh}{dt} = 2 \times 10^{-5}\,\frac{p_v(T_B)}{\sqrt{T_B}} \tag{9b}$$

From the listed values in Table 6b we conclude that at temperature $T_B = 173$ K the evaporation rate is $0.12\,\mu\mathrm{m\,min^{-1}}$, while at 185 K it is a factor 10 higher. These values indicate that water ice in vacuum evaporates quickly at temperatures above 170 K. Such a behavior has been experimentally observed in our laboratory as well as by other groups (e.g. Bar-Nun et al., 1985 and references therein). The observed decrease of the S_2 emission above 160–170 K is explained as follows: (i) The S_2 molecules are released from the substrate simultaneously with water either as a pure substance or as a clathrate hydrate. (ii) Evaporation of the water ice leaves S_2 molecules on the substrate which polymerize into larger more stable sulfur aggregates. Probably both mechanisms occur.

The main conclusion from this study is that S_2, which is not a fully saturated molecule, but also not a radical, can survive in a water ice even at high temperature until it is freed from its trap by the evaporation of the surrounding water molecules. The strong binding forces between the water molecules apparently inhibit S_2 diffusion and subsequent reactions. This makes the use of the observed reactivity of S_2 molecules in annealed argon matrices for astrophysical applications highly questionable. The consequences of the results are extensively discussed in the next section.

4. Discussion

4.1. Interstellar photochemical aspects

Both the fluorescence and ultraviolet absorption studies have convincingly demonstrated that S_2 is formed when astrophysical molecular ices are photoprocessed with vacuum UV. Although, strictly speaking, recombination reactions between diffusing sulfur atoms on a grain surface may also lead to S_2 formation, this process is exceedingly inefficient because the time needed for a complete scanning of the grain surface by a heavy atom is much larger than that for a hydrogen atom. Consequently the chemistry of unsaturated atoms and molecules will be dominated by hydrogen recombination reactions (d'Hendecourt et al., 1985), so that essentially all sulfur atoms on a grain surface are converted into SH and H_2S and will remain inside the grain mantle as long as no other processing (photo or thermal) takes place. The grains are, of course, always subjected to photoprocessing by the interstellar radiation field which will modify the composition of the mantle. This process has been extensively discussed in many papers (e.g. Greenberg, 1982b, 1984; d'Hendecourt et al., 1986). In general, not only is S_2 expected to be a parent molecule in interstellar or cometary ices as a result of photolysis, but also such other molecules as: CS_2, HSOH, SO_2 and OCS. If it can be shown that all these molecules are the result of UV photolysis only, it will provide further support for the comet/interstellar dust connection (Greenberg, 1986). Chemiluminescence and infrared studies similar to that of Grim and d'Hendecourt (1986) are strongly suggested to determine the possible origin of dirty ice components.

An important application of this study is the comparison between the relative abundances of various molecules in the experiments and the observed ratios in comets. In Sect. 3.2 we derived, for simultaneous photolysis, S_2 abundances relative to H_2S of about 0.012 for Ar/H_2S and 0.008 for $Ar/H_2O/CO/CH_4/H_2S$ mixtures (Table 4). The value of this ratio increased to 0.06 in one experiment when the photolysis occurred after deposition. The slight decrease, as observed for the more complex mixtures, is explained by a competition between the possible reaction channels for photolytic sulfur atoms. Since concentration studies have shown that $[S_2]/[H_2S]$ is not critically dependent on the initial H_2S concentration, we assume here that in photoprocessed astrophysical ices $[S_2]/[H_2S]$ will be roughly between 0.01 and 0.06. Because photochemical processing in the interstellar medium is much greater than can be simulated in the laboratory, this assumption appears to be quite reasonable.

In order to compare these numbers with S_2 production rates in comets we have to scale the S_2 to H_2O. For this, we assume that in comets $[H_2S]/[H_2O] = 0.023$ based on the cosmic abundance of S relative to O (Cameron, 1973). From our experiments we calculate $[S_2]/[H_2O]$ to be between $2\,10^{-4}$ and $1.4\,10^{-3}$, which is consistent with the mean value $[S_2]/[OH] = 5\,10^{-4}$ obtained for comet IRAS-Araki-Alcock 1983VII (A'Hearn et al., 1983). Relative abundances for CS and SO are also calculated (Table 7). Since the abundances of S_2 and CS relative to H_2O in our experiments are in essential agreement with the observed values for comets, we feel that this provides additional evidence that comets formed out of the photoprocessed interstellar dust particles.

4.2. Thermal evolution of the cometary ices

4.2.1. Laboratory evidence

Two important questions yet to be answered are: (i) How warm do the grains become during comet aggregation and (ii) to what degree will the mantle composition persist when the grains are thermally processed? Two different heating processes are considered here: (i) a sudden increase of the temperature by grain-

Table 7. A comparison of experimental molecular abundances (relative to H_2O) with molecular production rates (relative to OH) in comets.

Molecule X	Expected ratio based on experiments $[X]/[H_2O]$	Observed ratio in comets $[X]/[OH]$
S_2	$2\,10^{-4} - 1.4\,10^{-3}$	$5\,10^{-4\,a}$
CS_2	$9.2\,10^{-4}$	$2\,10^{-4} - 3\,10^{-3\,a,b,c}$
SO	$3\,10^{-4}$	?[d]

[a] A'Hearn et al. (1983)

[b] Weaver et al. (1981)

[c] Azoulay and Festou (1986)

[d] SO has been tentatively identified in IRAS-Araki-Alcock 1983 VII Wallis (private communication)

grain collisions and (ii) a gradual temperature increase, for instance when the grains enter the solar nebula.

Although the effects of grain collisions have been discussed elsewhere (Greenberg et al., 1986) we will review here the main aspects. As has been shown by d'Hendecourt et al. (1982) grain collision speeds $>40\,\mathrm{m\,s^{-1}}$ can raise the grain temperature above 25 K and chain reactions and explosions will consume most, if not all, reactive species in a fully irradiated grain mantle. This process certainly modifies the mantle composition very substantially and probably most volatile species will evaporate when (local) explosions occur. The critical parameter in this process is the radical concentration, which is assumed to be $\sim 1\%$. However, if this value is decreased as a result of radical diffusion and recombination, the radical energy storage will be too low to trigger any explosive grain mantle events.

Van IJzendoorn et al. (1986b) have experimentally shown that in interstellar clouds with a mean temperature of ~ 15 K, 50% of the initial (1%) radical composition will survive about 10^6 yr. They also showed that once the comet is fully formed and in the Oort cloud ($T < 10$ K) all radicals ($>99\%$) will survive for longer than 4.5 10^9 yr. These results are based on HCO diffusion in slightly annealed dirty ice mixtures leading to glyoxal formation. How the chemical composition of interstellar ices is modified by diffusion of varieties of radicals (and molecules, e.g. CO) as a function of temperature and time, is a subject requiring further investigation. One important aspect will be addressed in this paper: "*Will the S_2 molecules diffuse and react (with radicals) under similar conditions?*" In other words: "*Can the S_2 molecule be used as a discriminant for the formation temperature of comets?*" as suggested by A'Hearn and Feldman (1985).

It has been argued in Sect. 3.4 that the disappearance of S_2 in argon matrices upon heating most likely resulted from recombination reactions leading to larger sulfur aggregation (Meyer et al., 1972; Barnes et al., 1974) but also from simultaneous evaporation with the argon. The conclusion that S_2 is a volatile and reactive species is in agreement with the experiments by Hopkins and Brown (1975). However, an argon matrix is not representative of the interstellar medium and, therefore, these results *cannot* be applied conclusively to the interstellar case. In contrast, the temperature studies of S_2 in H_2O rich (60–100%) ices show a completely different behavior, as demonstrated by monitoring the S_2 fluorescence signal upon warmup (Fig. 6). The increase of the emission signal above 130 K seems to be correlated with the phase transition from amorphous to cubic ice. A possible evaporation of S_2 by squeezing out of the ice upon transformation as proposed by Bar-Nun et al. (1985) could not be observed in our experiments, but is nevertheless likely to occur. When the temperature exceeds 160 K, the S_2 decrease is explained by polymerization and evaporation with the water molecules.

All experiments performed have led us to conclude that S_2 appears to have lost its volatility and reactivity in a water rich dirty ice. The ice acts as a matrix consisting of water molecules. The cage effect of the hydrogen bondings between the water molecules appears to slow down the diffusion processes. This trapping (or clathrate formation) becomes almost perfect if the dilution of the trapped species remains low, a condition that was satisfied in our experiments.

From theoretical interpretations of ice band observations in molecular clouds (Greenberg, 1982b; Van de Bult et al., 1985; Whittet et al., 1985) and from chemical modelling (d'Hendecourt et al., 1985) the H_2O fraction in interstellar grain mantles is most likely within the 50–80% range. Consistent with this, Delsemme (1985, 1986) shows that H_2O is indeed the major constituent (up to 80%) of cometary ices. The astrophysical application of all these results is that the S_2 molecule cannot be simply used as a tracer to discriminate the formation temperature of comets as long as its volatility and reactivity is completely governed by the water ice. Diffusion time scales play an important role. If aggregation time scales were as short as the time scales for solar heating of the comet, one could show the following: Suppose there is some mechanism by which the S_2 molecules disappear out of a dirty ice at a particular temperature T_0. Then, even if the comet formation temperature was lower than this value we would still not be able to observe S_2 if the cometary ice mantle is heated by solar radiation to $T > T_0$, because then, the S_2 molecules would have vanished out of the cometary ice by the same mechanism that would have eliminated them from the interstellar grain mantles.

4.2.2. Observational evidence

Although the laboratory approach has not yet provided strict information on comet aggregation temperatures, we can focus on another aspect of the experimental results. The observation that the disappearance of S_2 above 160 K is correlated with the evaporation of water ice led to the conclusion that it is trapped in the ice, probably as some clathrate (Delsemme and Swings, 1952). The possibility of trapping volatile species at high temperatures has been recognized earlier. For instance, Lacy et al. (1984) have shown that a significant amount of CO can be trapped, even at temperatures as high as 85 K, in a dirty ice mixture. The occlusion of volatile species (CO, CH_4 and N_2) in an amorphous ice has been described qualitatively and quantitatively by Bar-Nun et al. (1985), by monitoring the mass spectra upon heating. They show that a significant amount of the volatile gases can be trapped in an amorphous water ice. They also demonstrate that trapped molecules are squeezed out of the ice when it transforms from amorphous to cubic form. Upon further heating, the volatile gases are released simultaneously with water. The relative number of volatile molecules trapped by clathrate formation is restricted to $\sim 15\%$ of the water molecules (Delsemme and Miller, 1970), although in amorphous ices this amount may be exceeded (see results in Bar-Nun et al., 1985).

Under astrophysical conditions, condensation on and photoprocessing of grain mantles lead to a mixture of molecules. Therefore, it is likely that volatile species, such as CO and CO_2, were mixed in the interstellar ices *before* aggregation occurred. Since CO, after H_2, is the most abundant molecule in the interstellar medium, it is believed to be present in grain mantles in significant amounts. Although it is still not 100% clear whether or not CO is a constituent of the cometary ices (Feldman, 1983; Delsemme, 1986), we note here that in fact CO is the precursor of CO_2 in interstellar grain mantles (d'Hendecourt et al., 1985, 1986; Grim and d'Hendecourt, 1986). By combining the observational data on the 3.07 μm "ice" band and the 4.67 μm CO band of several interstellar sources (Lacy et al., 1984; Van de Bult et al., 1985; Whittet et al., 1985), we calculate the mean $[CO]/[H_2O]$ ratio in the grain mantles towards these objects. The column densities for CO and H_2O are derived as follows:

$$N_x = \int_{\nu_1}^{\nu_2} \ln(I/I_0) d\nu / A_x \qquad (10)$$

Table 8. Observed ratios of CO relative to H_2O in grain mantles towards several interstellar sources. The total number of absorbers in column 4 and 5 are calculated by combining Eqs. (2) and (10) and the following integrated absorbance values for CO and H_2O: $A_{CO} = 1.1\,10^{-17}$ cm molecule^{-1} (Jiang et al., 1975), $A_{H_2O} = 1.6\,10^{-16}$ cm molecule^{-1} (Hagen et al., 1981); no corrections have been made for dilution effects (Greenberg et al., 1983b)

Source	$\int \tau_v(H_2O)dv$ (cm^{-1})	$\int \tau_v(CO)dv$ (cm^{-1})	N_{H_2O} ($\times 10^{18}$ cm^{-2})	N_{CO} ($\times 10^{18}$ cm^{-2})	N_{CO}/N_{H_2O}	Ref.
W33 A	>1620	10.4	>10	1.0	<0.10	2,3
NGC 7538/IRS 9	985	17.0	6.2	1.6	0.26	2,3
NGC 7538/IRS 1	540	0.9	3.4	0.1	0.03	1,2,3
W3/IRS 5	1025	1.0	6.4	0.1	0.02	1,2,3
HL Tau	210	<0.44	1.3	<0.04	<0.03	4,5
Elias 1	180	0.88	1.1	0.08	0.07	4,5
Elias 16	440	6.7	2.5	0.61	0.23	4,5
BN	530	<0.55	3.3	<0.05	<0.02	6,7
GL 989	515	3.5	3.2	0.35	0.11	6,7
GL 2136	1310	1.5	8.2	0.13	0.02	6,7

References: (1) Soifer et al., 1976. (2) Willner et al., 1982. (3) Lacy et al., 1984. (4) Van de Bult et al., 1985. (5) Whittet et al., 1985. (6) Geballe, 1986. (7) Greenberg et al., 1987

in which N_x is the column density of species X, $\int_{v_1}^{v_2} \ln(I/I_0)dv =$ the integrated absorbance over the absorption profile and $A_x =$ the integrated absorbance value. We use in our calculation $A_{CO} = 1.1\,10^{-17}$ cm molecule^{-1} (Jiang et al., 1975) and $A_{H_2O} = 1.6\,10^{-16}$ cm molecule^{-1} (Hagen et al., 1981). The latter cross section is for pure water ice; an H_2O fraction of 70% in the mantle will reduce the integrated absorbance value by roughly 20% (Greenberg et al., 1983b).

From Table 8, where the calculated values for several objects are listed, we notice that the mean $[CO]/[H_2O]$ ratio in grain mantles towards NGC 7538/IRS 9 and Elias 16 is as large as ~ 0.20–0.25. This value is consistent with grain mantle model calculations (d'Hendecourt et al., 1985) and the high ratio observed for CO relative to OH emission in comet West (Feldman and Brune, 1976). In stars with circumstellar dust (HL Tau), the mean CO fraction is much smaller undoubtedly as a result of the higher temperature history.

Finally, these data and the fact that comet evaporation is controlled by water molecules (Delsemme, 1985, 1986) argue against the essential assumption in the comet formation model of Yamamoto et al. (1983, 1985), which is that the sublimation of a dirty ice mantle is controlled by separate volatilities of the various components of the ice.

In short, we hope to have demonstrated that differences in the mantle compositions of interstellar and cometary ices can be explained as a consequence of a combined interstellar gas and grain chemistry, whereas the mean temperature of the grains can modify the mantle composition as long as the H_2O fraction does not become too large. To what degree the temperature may affect the mantle composition will be subject of a further study in which we intend to investigate the diffusivity of CO molecules in amorphous ices at different temperatures. For this, infrared spectroscopy will be an important tool coupled to mass spectroscopy techniques as described in Bar-Nun et al. (1985). When the H_2O fraction is between 60 and 80%, according to model calculations (d'Hendecourt et al., 1985), we may expect small but significant variations in composition as a result of different thermal evolution of comets. The fact that almost all comets have equal compositions (Weaver et al., 1981) indicates that they may also share a common thermal evolution. As a result of the many uncertainties and parameters we are not able to draw any quantitative conclusions on the formation temperature of comets. The observational data *do not rule out* comets being formed by coagulation of interstellar grains in regions where the temperature was fairly high for short times. The only restriction for the comet aggregation that can be given on this basis is that the temperature in the formation region was such that *substantial diffusion over ~ 0.1 µm did not take place during the total aggregation time.* Although this study does not rule out the possibility that comets were formed in the Uranus-Neptune region, diffusion over 10^6 yr in even 80% water-rich mixtures may be sufficient at $T \sim 30$–40 K to require formation much further out.

5. Conclusions

The observation of S_2 as a parent molecule in comet IRAS-Araki-Alcock 1983 VII has led A'Hearn and Feldman (1985) to suggest that S_2 would be a constituent of all comets. We have shown that it must have been formed as a result of photochemical processes in accreted mantles of precometary grains. In the model of Greenberg (1977, 1982a, 1983a) interstellar grains are irradiated by ultraviolet photons in the interstellar medium before they become incorporated in the solar system. In this paper we have shown that ultraviolet photolysis of H_2S in dirty ices consisting of H_2O, CO and CH_4 produces S_2 and other new molecular species containing sulfur atoms. The presence of S_2, SH, SO, CS is well established, while trace amounts of HSO, OCS, SO_2 and HSOH are inferred. Observed fractional abundances of S_2 and CS are in agreement with production rates for these species in IRAS-Araki-Alcock 1983 VII and other comets.

As a next step we have investigated the diffusivity and reactivity of the S_2 molecules upon thermal heating in an attempt to deduce a possible maximum formation temperature of comets. We have considered two heating processes: first, instantaneous heating by grain collisions; second, a gradual heating by radiation processes. The first mechanism, according to the grain collision model of d'Hendecourt et al. (1982), assumes a high radical concentration ($\sim 1\%$) and leads to a restriction of the grain collision speed. If this restriction is correct, it implies that the grains in the interstellar medium have not collided with speeds exceeding $40 \mathrm{~m~s}^{-1}$ and the same restriction also accounts for the coagulation of the precometary grains in the presolar nebula.

A slow and gradual annealing of photolyzed water rich ices shows that the S_2 molecules remain trapped in the amorphous material until the water molecules evaporate. The astrophysical relevance of these observations is that S_2, and in fact any other volatile molecule that has been formed in-situ in interstellar ices by high energetic processing, cannot be simply used as a discriminant to establish the temperature of the precometary formation region as long as H_2O is the dominant species of the grain mantles. We have also argued that the observations of S_2 in the coma of IRAS-Araki-Alcock 1983 VII *imply* that there is no mechanism by which S_2 can have been eliminated from interstellar ices, for it would have also disappeared when the cometary mantle is heated by solar radiation making S_2 observation *in the coma* impossible.

We have shown that observation of S_2 and CO emission bands in cometary comas is not in contradiction with possible comet formation regions where the temperature exceeded 40 K, but that formation in the Uranus-Neptune region is yet to be fully justified.

One aspect of S_2, its chemical reactivity, is not fully solved. In this study it has been shown that when the matrix material (Ar or H_2O) evaporates, S_2 disappears as a result of a combination of evaporation and polymerization. Consequently the reactivity of S_2 in an "explosive" environment, i.e. high radical concentration, could not be investigated in detail. We must emphasize that although we have not been able to use the S_2 molecule as a probe for the formation temperature of comets as suggested by A'Hearn and Feldman (1985), our experiments do not completely rule out this possibility. The outcome of this study points in that direction, but final evidence may only be achieved by applying techniques other than UV spectroscopy and Laser Induced Fluorescence to this problem.

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