PHOTOCHEMICAL S_2: EVIDENCE FOR INTERSTELLAR GRAINS IN COMETS

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ABSTRACT

The formation of S_2 by ultraviolet photo-processing of interstellar ices is shown to be a plausible explanation for the observation of this molecule in comet IRAS-Araki-Alcock 1983VII. Not only S_2 is expected to be in cometary ices but also products such as SH, SO, CS, CS_2, HSO, OCS etc. The composition of the processed interstellar analog ices is compared with molecular production rates in comets. It appears that when the water fraction is high (> 60-80%) S_2, and other volatile species, can remain trapped in the cometary ice for a long period of time (> 10^8 years) as long as T $\leq$ 100 K.

Keywords: interstellar photochemistry, molecules, composition, evolution, laboratory simulation.

1. INTRODUCTION

The observation of S_2 close to the nucleus of IRAS-Araki-Alcock 1983VII (A'Hearn et al. 1983) has been unique in a sense that this molecule had never been observed in the interstellar medium before in spite of extensive radio observations in dark clouds (Liszt 1978). Although some other sulfur species (i.e. S, CS) have also been detected in cometary comae (Weaver et al. 1981), the interstellar gas phase is known to contain many more sulfur molecules (Mann and Williams 1980). Interstellar grain mantles have been observed which contain OCS and H_2S (Geballe et al. 1985). It has furthermore been deduced that the dust in the protostellar object W33A shows clear evidence that the formation of the molecules OCS and XCN is the result of ultraviolet photoprocessing.

In this study we focus on the suggestion that the S_2 observed in comets must have been formed in interstellar grain mantles by energetic photoprocessing (A'Hearn and Feldman 1985). Although it has been demonstrated that ion bombardment of H_2S and sulfur creates S_2 (Boring et al. 1985), it can be shown that the total energy absorbed by the grain as a result of cosmic ray irradiation during its lifetime in the interstellar medium is negligible compared to the total energy absorbed from the interstellar ultraviolet radiation field (Greenberg 1986). Therefore it can be assumed that ultraviolet photoprocessing is the dominant mechanism for S_2 production. Although the presence of S_2 in interstellar grain mantles has not been established yet, its presence can be inferred from the observations of H_2S and OCS in grain mantles towards W33A (Geballe et al. 1985) in combination with sulfur recombination experiments in low temperature argon matrices (Smardzewski 1978, Lee and Pimentel 1979).

After first demonstrating that S_2 is indeed formed by ultraviolet irradiation, we consider the amount of S_2 produced by this process in order to have a comparison with the amounts of S_2 and CS relative to OH in IAA 1983VII. Finally, we study the warmup behavior of S_2 in argon matrices as well as in dirty ice mixtures to find answers to the suggestion made by A'Hearn and Feldman (1985) that S_2 possibly can be used to discriminate the comet formation temperature.

2. EXPERIMENTAL RESULTS

2.1 Formation of S_2

Figure 1 shows the formation of S_2 observed by means of Laser Induced Fluoresence (LIF) after the photolysis of H_2S in various concentrations and mixtures. For instance, in a photolyzed argon/H_2S = 1000/1 mixture (figure 1a) strong and sharp emission lines due to $B'' \, ^3\Pi_u \to X \, ^3\Sigma_g^-$ fluorescence of $^{32}S^{32}S$ are observed (Brewer and Brabson 1966, Bondybey and English 1978). The other sharp, but weaker, progression results from emission of $^{32}S^{34}S$, while the broad high frequency satellite can be ascribed to $B \, ^3\Sigma_u^- \to X \, ^3\Sigma_g^-$ fluorescence of S_2. For a complete discussion of all emission spectra the reader is referred to Grim and Greenberg (1986).

If we add other molecules (e.g. H_2O, CO and CH_4) to the argon/H_2S samples, we observe similar spectra although the locations of the $B \, ^3\Sigma_u^- \to X \, ^3\Sigma_g^-$ emission bands shift slightly with respect to those in the irradiated argon/H_2S matrices, indicating perturbation of the S_2 energy states.

In photolyzed dirty ice mixtures, therefore, we expect the $B'' \, ^3\Pi_u \to X \, ^3\Sigma_g^-$ emission system of undisturbed S_2 molecules to disappear. This is shown in the LIF spectrum after the photolysis of an H_2O/H_2S = 10/1 sample (figure 2a), where the emission comes only from the $B \, ^3\Sigma_u^-$ state of S_2. Coupling of S_2 to neighbouring molecules increases the number of channels for radiationless decay of the excited S_2 molecules, thus weakening and also broadening the emission signals. Finally, if we go to more complex dirty ice mixtures, for example $H_2O/CO/CH_4/H_2S$ = 5/2/2/1 (figure 2b), the S_2 fluorescence is hard to distinguish from a broad background fluorescence signal.

Figure 1:
Observed fluorescence lines of the B → 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/$H_2O/CO/CH_4/H_2S$ = 1000/1/1/1/1 after warming to 38 K and recooling to 12 K (c). Emission is in arbitrary units.
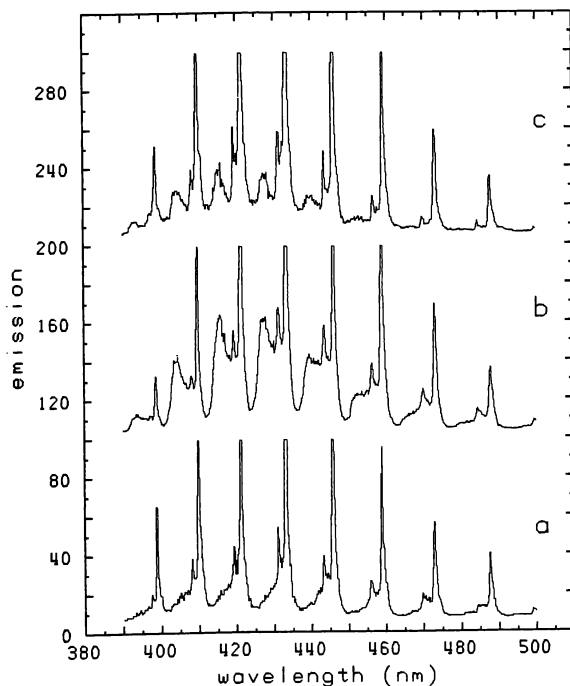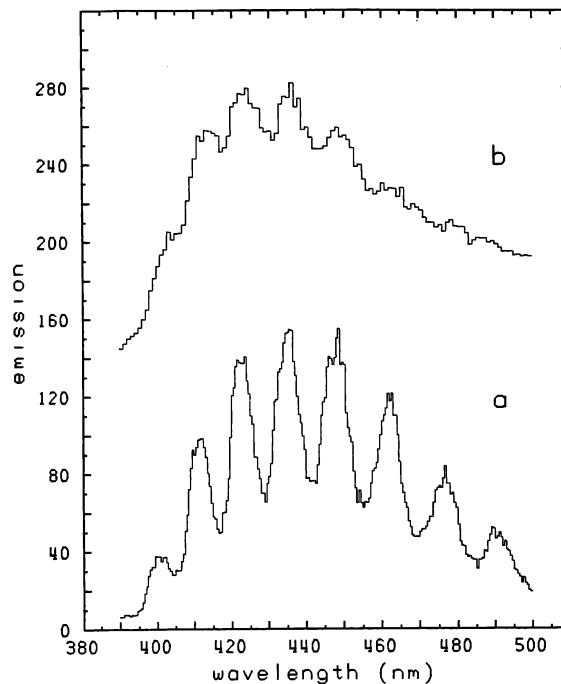
Figure 2:
Same as for figure 1: H_2O/H_2S = 10/1 at 12 K (a), $H_2O/CO/CH_4/H_2S$ = 5/2/2/1 at 12 K (b).

2.2 Formation of species other than S$_2$

In the LIF studies only S$_2$ has been positively identified. In the 550-750 nm region of photolyzed dirty ices another emission system appeared that could not originate from S$_2$ (Grim and Greenberg 1986). This system is characteristic of an S=0 stretching vibration and probably results from excited SO, HSO and/or HSOH molecules.

The ultraviolet spectra taken from photolyzed argon samples demonstrate the formation of SH and CS radicals, and possible also of SO (figure 3). The last molecule, however, shows only one major band in this spectral region that coincides with an absorption band of the CS radical (Hsu 1981). Probably both molecules contribute to the 261 nm absorption profile.

In the 550-650 nm region of a photolyzed H$_2$O/H$_2$S = 10/1 dirty ice a weak absorption system has been observed which is probably due to $^2A' \leftarrow {}^2A''$ absorption of HSO (Grim and Greenberg 1986). In relation to other experimental results (e.g. Geballe et al. 1985) the formation of trace amounts of HSOH, SO$_2$, CS$_2$ and OCS can be inferred, although these species have not been detected in these experiments.

2.3 Rate of formation

An important question to be answered is "How many S$_2$ molecules are formed by ultraviolet photolysis?" From the ultraviolet absorption spectra it is possible to calculate the number of absorbers by using the following expression for the oscillator strength in S.I.-units:

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

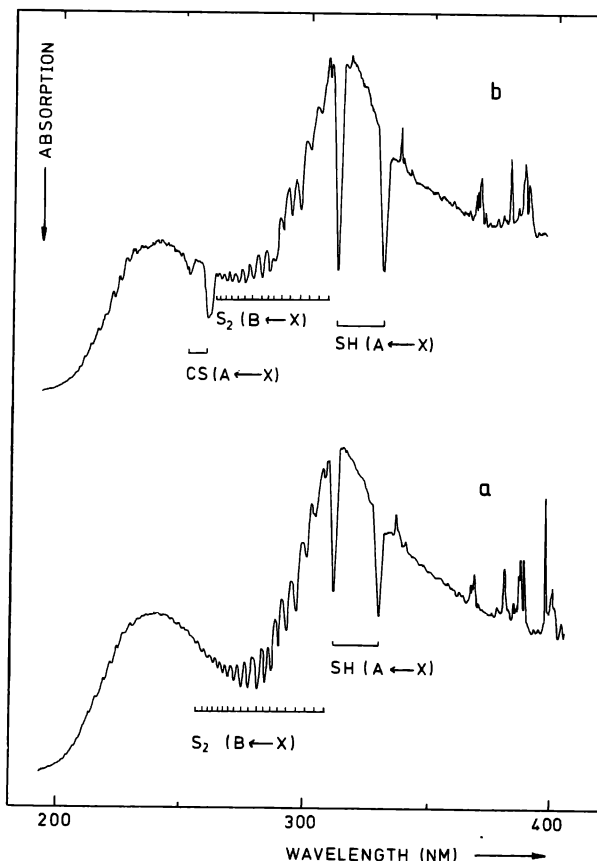while the integrated absorbance value can be approximated by

$$\int_{\nu_1}^{\nu_2} \tau_\nu \, d\nu = \frac{1}{N1} \tau \, \Delta\nu \tag{2}$$

(Person 1981), where N1 is the number of absorbers per unit area, τ the optical depth $(\ln(I/I_0))$ and $\Delta\nu$ the full width of the absorption line at half maximum. Substituting all constants in (1) we obtain:

$$N_{tot} = 54\ \tau\ \Delta\nu\ f^{-1} \tag{3}$$

In table 1 we summarize the ratios of the absorbing species relative to the total number of H$_2$S molecules present in the sample for three experiments. In table 1a the values are tabulated for an experiment in which the UV photolysis occurred simultaneously with the deposition of the Ar/H$_2$S = 300/1 matrix. In table 1b similar values are shown for the same mixture, but now the UV photolysis occurred after deposition. Finally, in table 1c the values for an Ar/H$_2$O/CO/CH$_4$/H$_2$S = 300/1/1/1/1 matrix with simultaneous deposition and irradiation are tabulated.

Figure 3:
Ultraviolet absorption spectrum at 12 K of photolyzed Ar/H$_2$S = 300/1 (a) and Ar/H$_2$O/CO/CH$_4$/H$_2$S = 300/1/1/1/1 (b) obtained with the hydrogen discharge lamp.

Experiment	X	$\lambda(nm)$	f	τ	$\Delta\nu(s^{-1})$	[X]/[H_2S]
a) $Ar/H_2S=300/1$ [1]	HS	330	1.1×10^{-3}	0.49	9.4×10^{12}	0.10
	S_2	282	4.5×10^{-3}	0.35	7.1×10^{12}	0.015
		293	4.5×10^{-3}	0.24	6.2×10^{12}	0.009
b) $Ar/H_2S=300/1$ [2]	HS	312	1.1×10^{-3}	0.16[3]	7.8×10^{12}	0.30[3]
				0.02[4]		0.18[4]
	S_2	293	4.5×10^{-3}	0.023[3]	7.1×10^{12}	0.02[3]
				0.20[4]		0.06[4]
c) $Ar/H_2O/CO/CH_4/H_2S=300/1/1/1/1$ [1]						
	HS	312	1.1×10^{-3}	0.69	7.2×10^{12}	0.14
	CS	261	7.3×10^{-3}	0.47	1.6×10^{13}	0.04
	SO	261	1.8×10^{-2}	0.47	1.6×10^{13}	0.013
	S_2	293	4.5×10^{-3}	0.20	4.8×10^{12}	0.008

Table 1: Production rates of relevant molecules in some typical experiments. The numbers have been calculated using equation (3) in combination with the deposition rate of the mixture.
[1]: UV simultaneously with deposition
[2]: UV after deposition
[3]: after 2 hrs UV
[4]: after 6.5 hrs UV

2.4 Temperature dependence

Following the suggestion made by A'Hearn and Feldman (1985) we have examined the behavior of the S_2 molecules upon warmup of the photoprocessed samples using either ultraviolet spectroscopy (argon matrices) or Laser Induced Fluorescence (dirty ices) to measure the possible decrease with increasing temperature.

Figure 4 shows the emission of S_2 molecules in various mixtures as a function of the temperature. In all mixtures with a high water concentration (> 60%) we observe a strong increase of the emission at T ~ 130 K. The signal increases to ~ 160 K and above this temperature it drops to zero. The remarkable temperature behavior of the S_2 emission seems to follow the phase transition of water from amorphous to cubic ice (Hagen et al. 1981). Due to this phase transition the coupling of the S_2 molecules with water apparently becomes weakened, so that the emission signal increases. At T > 160 K the water molecules start to evaporate and it is then quite possible that the S_2 molecules are simultaneously released either as a pure substance or as some clathrate hydrate. The second explanation for the decrease of the S_2 emission is that polymerization reactions occur similar to what has been observed in argon matrices. The formation of a room temperature stable residue favors the last explanation. Probably both processes occur (Grim and Greenberg 1986).

Figure 4:
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).
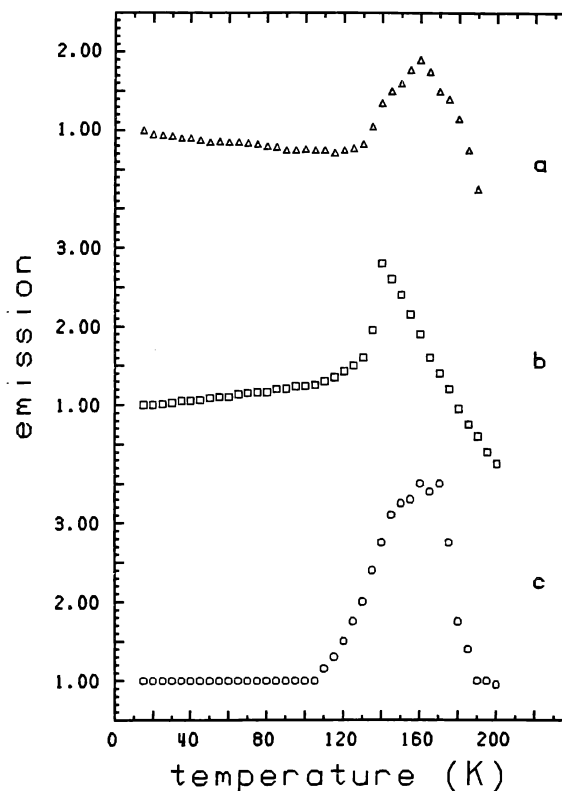
3. DISCUSSION

3.1 Interstellar photochemistry

All experiments have convincingly demonstrated that S_2 is formed when interstellar analog ices are exposed to ultraviolet radiation. Not only do we expect the formation of S_2 in interstellar ices, but also other sulfur molecules such as SH, CS, SO, HSO, HSOH, SO_2, CS_2, HCS_2 and OCS. The importance of photochemical processing of interstellar grain mantles for interstellar gas phase chemistry has been recognized earlier (Greenberg 1982, d'Hendecourt et al. 1986) and now a direct link is found to the composition of cometary ice. As a matter of fact, S_2 will not be the only photochemical product present in comets. If CO_2 is definitely found to be a parent molecule in the ice, and not a product as a result of the coma chemistry, this then will provide additional evidence for photoprocessed interstellar material in comets, for it has been demonstrated that CO_2 can only be formed in grain mantles by ultraviolet radiation (Grim and d'Hendecourt 1986).

The $[S_2]/[H_2S]$ ratio in interstellar ices, expected on the basis of our experimental results, will be between 0.008 and 0.06. Applying the cosmic abundance of elemental sulfur to oxygen we calculate a value of $[S_2]/[H_2O]$ between 2×10^{-4} and 1.4×10^{-3}. A review of the expected abundances for S_2, CS_2 and SO relative to H_2O is given in table 2, where the values are compared with the observed ratios of these molecules relative to cometary OH. The table shows that the values experimentally derived are consistent with the observed production rates, indicating that photo# chemistry of interstellar ices is a plausible mechanism to account for the observed composition of cometary ices. Secondly, we have shown that the high concentration of water in cometary ices is in agreement with infrared observations towards several interstellar objects showing that the interstellar ice mantles consist of at least 60% H_2O (Van de Bult et al. 1985, Grim and Greenberg 1986).

3.2 Implications for the evolution of cometary ices

The astrophysical relevance of these experiment to comet formation temperature limites is studied by examining the warmup behavior of S_2

molecule	expected ratio based on experiments	observed ratio in comets
[X]	$[X]/[H_2O]$	$[X]/[OH]$
S_2	2×10^{-4}–1.4×10^{-3}	5×10^{-4} (1)
CS_2	9.2×10^{-4}	2×10^{-4}–3×10^{-3} (1,2,3)
SO	3×10^{-4}	? (4)

(1): A'Hearn et al. (1983)
(2): Weaver et al. (1981)
(3): Azoulay and Festou (1986)
(4): SO has been tentatively identified in IAA 1983VII (Wallis 1986).

Table 2: A comparison of experimental molecular abundances with observational data.

in dirty ices. As has been described in section 2.4 the fluorescence signal of S_2 did not change significantly until the water molecules started to evaporate indicating that the S_2 molecule remained trapped in the ice. As a matter of fact, as long as the water concentration remains high (> 60%) we expect all volatile molecules to be trapped and prevented from evaporation. Also the strong cage effect of H_2O will not allow any diffusion of the S_2 molecules. However, as the temperature of the ice increases, say to ~ 100 K and higher, the trapping becomes weaker. When the water molecules evaporate, the S_2 molecules may evaporate along with them or polymerize on the surface of the ice to form larger sulfur aggregates. Both mechanisms are shown to be plausible (see section 2.4). This means that for the astrophysical counterpart we expect a similar behavior.

The presence of S_2, and other volatile species, in IRAS-Araki-Alcock 1983VII unfortunately does not reveal details on the thermal evolution of the cometary ices during and after its aggregation. It tells us only that the ices have not been processed to temperatures higher than 100#130 K, the temperature at which the ice starts to evaporate. The presence of S_2 provides, however, direct evidence for photoprocessing of the ices, the most likely place having been in the mantles of the interstellar grains. The differences in the ultimate composition of the cometary (interstellar) ices are explained as a consequence of a combined interstellar gas and grain chemistry (d'Hendecourt et al. 1985, 1986).

4. CONCLUSION

Considering the fact that S_2 is a parent molecule in IRAS-Araki-Alcock 1983VII and that it must have been formed by photoprocessing of interstellar ice mantles, we expect S_2 to be present in all comets. According to the model in which interstellar ices are incorporated in the comet during its coagulation (Greenberg 1982, 1983) we also expect the presence of other photochemical products in the cometary ices (e.g. CO_2, SO, OCS, CS_2 etc.). The observation that water is the major component in cometary ices as well in interstellar ices is in agreement with this model. For species other than H_2O only small fractions are to be expected ($\leq$ few %). The numbers of S_2 and CS formation in the laboratory are shown to be consistent with observational data.

An important aspect of the water ice is that it is capable of trapping considerable amounts of volatile species up to high temperatures as long the H_2O concentration remains well above 60%. Therefore, the use of a volatile species as a discriminant for the comet formation temperature is not possible. As a matter of fact, the only restriction to be set is that the cometary particles upon coagulation have not been heated to T > 100 K. Diffusion effects over astrophysically reasonable time scales for comet formation at temperatures T < 100 K are under consideration.

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