

SOFT X-RAY IRRADIATION OF H₂S ICE AND THE PRESENCE OF S₂ IN COMETS

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ABSTRACT

Little is known about the effects of X-rays in interstellar ices. To understand the sulfur depletion in dense clouds and the presence of S₂ in comets, we simulated experimentally the soft X-ray processing (0.3 keV) of H₂S ice for the first time. Experiments were performed under ultrahigh vacuum conditions at 8 K using infrared and quadrupole mass spectrometry to monitor the solid and gas phases, respectively. A UV irradiation experiment using a similar dose was made for comparison. After X-ray irradiation, an infrared absorption appears near 4.0 μm which is attributed to H₂S₂ formation in the ice. This identification is also supported by the desorption at 133 K of *m/z* 66, 65, 64, corresponding to the mass fragments of H₂S₂. The H₂S₂ species is expected to be present in interstellar and cometary ices that were processed by X-rays. Further irradiation leads to dissociation of this molecule forming S₂ and larger S-molecules up to S₈, which may explain the depletion of sulfur in dense clouds. CS₂ was so far the parent molecule proposed for S₂ formation in comets. But the abundance of H₂S₂, formed by irradiation of pure H₂S or H₂S in an H₂O–ice matrix, should be larger than that of CS₂ in the ice, the latter requiring a carbon source for its formation. Based on our experimental results, we propose that S₂ in comets could be formed by dissociation of H₂S₂ in the ice.

Key words: ISM: molecules – methods: laboratory – X-rays: ISM

1. INTRODUCTION

Sulfur is depleted in dense clouds, Class 0 and Class I sources (e.g., Buckle & Fuller 2003), and hot cores (Wakelam et al. 2004). Because of the high hydrogen abundances and the mobility of hydrogen in the ice matrix, sulfur atoms impinging in interstellar and circumstellar ice mantles are expected to form H₂S preferentially. There are only upper limits of the solid H₂S abundance (e.g., Jiménez-Escobar & Muñoz Caro 2011), and the only S-bearing molecule unambiguously detected in ice mantles is OCS, because of its large band strength in the infrared (Geballe et al. 1985; Palumbo et al. 1995) and maybe SO₂ (Boogert et al. 1997). OCS is formed by UV or ion irradiation of H₂S ice containing CH₃OH or CO (Ferrante et al. 2008; Garozzo et al. 2010). Upon UV irradiation, H₂S is also the precursor of more complex species such as S-polymers (Jiménez-Escobar & Muñoz Caro 2011), which could be the reservoir of the depleted sulfur (Wakelam et al. 2005; Garozzo et al. 2010).

The most abundant interstellar ice molecules are common to cometary ices (e.g., Bockelée-Morvan et al. 2000). Therefore, the abundance of H₂S in comets, up to 1.5% relative to H₂O as inferred from millimeter and submillimeter observations (Bockelée-Morvan et al. 2000, 2010; Boissier et al. 2007), also suggests that this molecule should be present in interstellar icy grain mantles. Other S-species (CS₂, SO₂, OCS, and H₂CS) were detected in comet Hale–Bopp with abundances between 0.02% and 0.4% (Bockelée-Morvan et al. 2000). Observations of S₂ in the coma of comet IRAS–Araki–Alcock showed that this species came from, or very close to, the nucleus (A’Hearn et al. 1983). Later, S₂ was tentatively detected in comet Hyakutake and is probably ubiquitous in comets, but its detection requires a sufficiently short distance from the comet to Earth (Laffont et al. 1996). The origin of S₂ in comets is unclear (Bockelée-Morvan et al. 2004). The reactions induced by ions or UV photons in ices containing H₂S were studied experimentally (e.g., Grim & Greenberg 1987; Moore et al. 2007; Ferrante

et al. 2008; Garozzo et al. 2010; Jiménez-Escobar & Muñoz Caro 2011). But no experiments were dedicated to study X-ray irradiation of H₂S ice. X-rays could play a significant role in energetic ice processing in various astrophysical environments such as circumstellar regions around protostars and young solar-type stars, especially when the X-ray flux exceeds the UV flux (Ribas et al. 2005). We report here the irradiation of pure H₂S ice with soft X-rays of 0.3 keV to explore the role played by X-rays in the formation of other S-bearing molecules in icy environments. In particular, we discuss the possible contribution of X-rays to the formation of S₂ in comets. The low flux of our X-ray source mimics more realistic astrophysical conditions and its spectrum peaked at 0.3 keV matches the peak of the quiet X-ray emission of today’s Sun. Such a low flux demands long irradiation times of one day, sensitive detection techniques, and optimum ultrahigh vacuum conditions to detect irradiation products unambiguously.

Section 2 describes the experimental protocol and Section 3 reports the results. The conclusions and astrophysical implications are presented in Section 4.

2. IRRADIATION EXPERIMENTS

The experiments were performed using the Interstellar Astrochemistry Chamber (ISAC). This setup and the standard experimental protocol are described in Muñoz Caro et al. (2010). ISAC is an ultrahigh vacuum chamber, with pressure in the range $P = (2.5\text{--}4.0) \times 10^{-11}$ mbar, where an ice layer is made by deposition of a gas mixture onto a cold finger at 8 K. The ice is monitored in situ by a transmittance Fourier Transform Infrared (FTIR) spectrometer, and the volatile species are detected by a Quadrupole Mass Spectrometer (QMS). Solid H₂S (Praxair 99.8%) was irradiated using an electron impact X-ray source built at the X-ray Astronomy Calibration and Testing facility of the INAF–Osservatorio Astronomico di Palermo. The X-ray flux at the sample position was 6.1×10^9 photons cm⁻² s⁻¹

Table 1
Log of Experiments

Exp. No.	$N(\text{H}_2\text{S})$ (cm^{-2})	E Fluence (photons cm^{-2})	Restricted Dose (eV molecule^{-1})	$N(\text{H}_2\text{S}_2)$ (cm^{-2})	$\frac{N(\text{H}_2\text{S}_2)}{N(\text{H}_2\text{S})}$
1. Blank	2.6×10^{18}	0.0	0.0
2. X-ray	2.9×10^{18}	1.2×10^{17}	0.033 ^a	8.3×10^{15}	2.9×10^{-3}
3. X-ray	2.6×10^{18}	1.5×10^{17}	0.046 ^a	8.6×10^{15}	3.3×10^{-3}
4. UV	$6.9 \times 10^{17\text{a}}$	6.9×10^{16}	0.10	1.7×10^{16}	2.5×10^{-2}

Note.

^a This value of the column density corresponds to an absorption of about 99% of the incident UV photons. The column density of the deposited H_2S ice was about a factor of three larger.

corresponding to $2.3 \times 10^{12} \text{ eV cm}^{-2} \text{ s}^{-1}$. The X-ray spectrum was obtained with a C anode and has a main peak at the C $K\alpha$ line and a tail at higher energies due to the bremsstrahlung continuum above the absorption edge (see Figure 1 of Ciaravella et al. 2011). Although the absorption edge of the sulfur K shell is at $\sim 2.5 \text{ keV}$, where the X-ray flux of our lamp is negligible, the L shell of sulfur atoms can efficiently be ionized given their large photoelectric cross-section around the C $K\alpha$ line threshold.

H_2S was deposited with a rate of 1.8 ML s^{-1} where one monolayer (ML) corresponds to a column density of $1.0 \times 10^{15} \text{ molecules cm}^{-2}$. After irradiation, the ice is warmed up at a constant rate of 1 K min^{-1} . FTIR spectra with a spectral resolution of 1 cm^{-1} were acquired before and after irradiation, as well as during warm-up every 10 K. The ice molecules desorbing inside the chamber during warm-up were continuously monitored by QMS.

3. RESULTS

The log of experiments is given in Table 1. Experiment N1 is a blank using the same experimental protocol as the X-ray experiments, but with no irradiation, while N2 and N3 involved X-ray irradiation of the H_2S ice. For comparison we also performed a UV irradiation experiment, N4, using a microwave-stimulated hydrogen flow discharge lamp with a UV photon flux of $2.5 \times 10^{14} \text{ photons cm}^{-2} \text{ s}^{-1}$ at the sample position (Muñoz Caro et al. 2010). While the irradiation time in X-ray experiments was close to 24 hr, in the UV experiment the total irradiation time was only 30 s to obtain a dose comparable to that of the X-ray experiments.

The column density of the deposited ice, $N(\text{H}_2\text{S})$ in the second column of Table 1, was calculated using the formula

$$N = \int_{\Delta\nu} \frac{\tau_\nu d\nu}{A}, \quad (1)$$

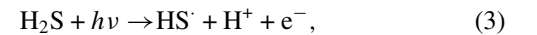
where N is the column density in cm^{-2} , τ_ν is the optical depth of the band, $d\nu$ is the wavenumber differential in cm^{-1} , and A is the band strength in cm molecule^{-1} . The adopted band strength for H_2S at 8 K is $A(\text{H}_2\text{S}) = 2.0 \times 10^{-17} \text{ cm molecule}^{-1}$ (Jiménez-Escobar & Muñoz Caro 2011). The photon fluence, in photons cm^{-2} , is given by the product $I_0 \cdot t$, where I_0 is the photon flux and t is the irradiation time. For the X-ray and UV experiments, the energy fluence expressed in eV cm^{-2} , third column of Table 1, is obtained by integrating the emission spectra of the X-ray and UV lamps, respectively. By taking into account the absorbance of the ice at different energies, the total energy absorbed by the ice during the X-ray irradiation was $\mathcal{E}_{\text{abs}} = 9.8 \times 10^{16}$ and $1.2 \times 10^{17} \text{ eV cm}^{-2}$ in the N2 and N3 experiments, respectively. The restricted dose \mathcal{D} in absorbed eV molecule^{-1} ,

fourth column of Table 1, was obtained from

$$\mathcal{D} = \frac{\mathcal{E}_{\text{abs}}}{N(\text{H}_2\text{S})} \quad (2)$$

in these experiments. The UV absorption cross-section of solid H_2S is unknown. As an approximation, we adopted the $\text{Ly}\alpha$ cross-section for H_2S in the gas phase, $9.01 \times 10^{-16} \text{ cm}^2 \text{ nm}$ (Lee et al. 1987) in the spectral range of the UV lamp [121.2–159.3 nm] corresponding to $6.7 \times 10^{-18} \text{ cm}^2$ per photon of average energy 9.2 eV. That value corresponds to an absorption of 99% of the impinging photons for $N(\text{H}_2\text{S}) = 6.9 \times 10^{17} \text{ molecules cm}^{-2}$. The restricted dose for the UV experiment given in the fourth column of Table 1 was estimated using the above $N(\text{H}_2\text{S})$ value. The fifth column in Table 1 provides the column density of H_2S_2 , $N(\text{H}_2\text{S}_2)$, formed by X-ray or UV irradiation of H_2S ice. This value divided by the column density of H_2S , $N(\text{H}_2\text{S})$ from the second column, is given in the last column of Table 1.

Figure 1 displays the infrared spectra of pure H_2S upon X-ray irradiation (top panels), UV irradiation (middle panels), and the blank experiment with no irradiation (bottom panels); see the caption for explanation. During irradiation, a new band at $2501 \pm 4 \text{ cm}^{-1}$ ($4.0 \mu\text{m}$) appears in both the X-ray and the UV experiments, attributed by Isoniemi et al. (1999) to complexes of H_2S_2 , probably the $\text{H}_2\text{S}_2\text{-H}_2\text{S}$ complex. The reaction scheme induced by X-rays is probably similar to that induced by UV photons. The process begins with HS^\cdot radical formation as



followed by the reaction of two HS^\cdot radicals



The H_2S_2 molecule is expected to be formed by X-ray irradiation in our experiments rather than HS_2 at 2483 cm^{-1} (Jiménez-Escobar & Muñoz Caro 2011) due to the very low dose employed, as it occurs with the UV experiment we report here using a comparable low dose. If the dose is increased, H_2S_2 is subsequently photolyzed yielding HS_2 ; see the top panel of Figure 6 of Jiménez-Escobar & Muñoz Caro (2011), following the reaction scheme of Isoniemi et al. (1999). The integrated absorbances of H_2S_2 for X-ray experiments N2 and N3 of Table 1 are 0.072 and 0.075 cm^{-1} , corresponding to dose values of 0.033 and $0.046 \text{ eV molecule}^{-1}$. The integrated absorbance of H_2S_2 produced in the UV experiment was 0.144 cm^{-1} corresponding to experiment N4 of Table 1 for a dose of $0.10 \text{ eV molecule}^{-1}$. Therefore, since a linear dependence of the integrated absorbance with the dose was observed for restricted dose values below $0.1 \text{ eV molecule}^{-1}$, it is possible to

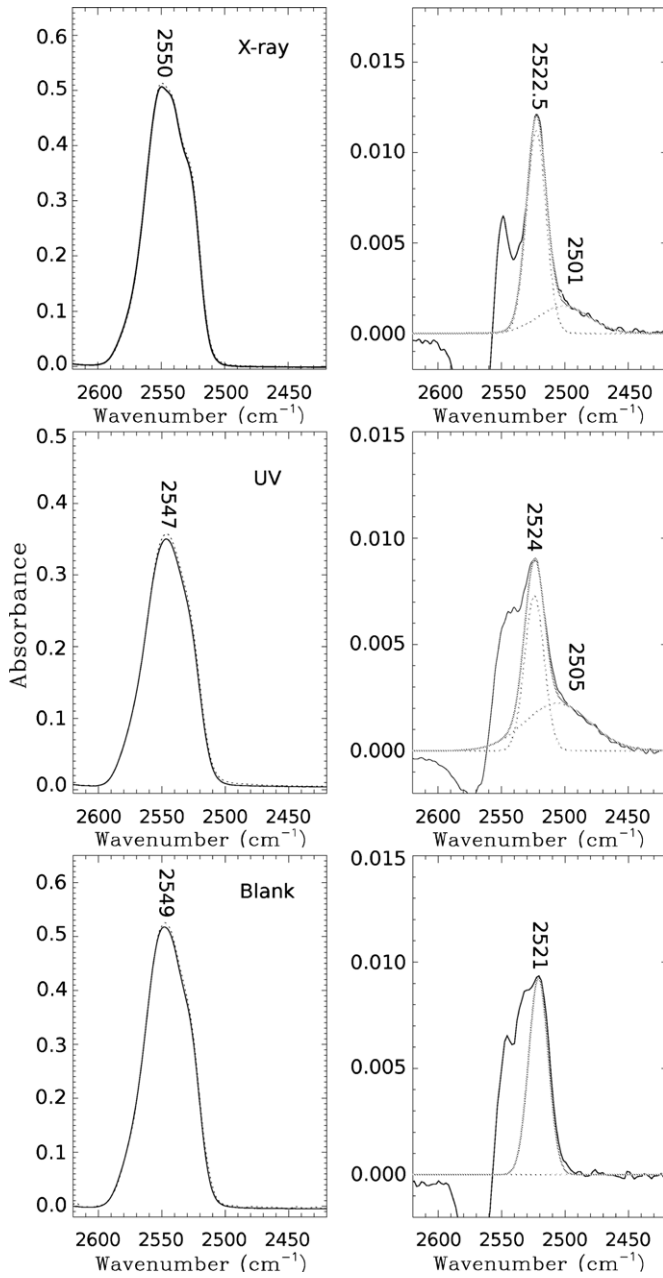


Figure 1. Infrared spectra of experiments N3 (X-ray irradiation), N4 (UV irradiation), and N1 (blank with no irradiation); see Table 1. Left panels show the absorption band of deposited H_2S ice (solid line), and after irradiation for the X-ray and UV experiments (dotted line), showing little difference due to the low dose of irradiation. Right panels show the subtraction of the spectra made after and before irradiation displayed in the left panels (solid line). Deconvolutions using two Gaussians are superposed (dotted lines) and the best fit made by addition of the two Gaussians (gray line).

extrapolate those results to the same dose value in experiments N2 and N3 for X-rays, and N4 for UV, we obtain a ratio of

$$\frac{A_{\text{int}}(\text{H}_2\text{S}_2, \text{X-ray})}{A_{\text{int}}(\text{H}_2\text{S}_2, \text{UV})} = \begin{cases} 1.5 & \text{for N2} \\ 1.1 & \text{for N3} \end{cases}, \quad (5)$$

where $A_{\text{int}}(\text{H}_2\text{S}_2)$ is the integrated absorbance. This indicates that the production yield of H_2S_2 is similar in the UV and X-ray experiments, but there can be an important error in this value introduced by the estimated value of the dose in the UV experiment, which depends on the value of $N(\text{H}_2\text{S})$ corresponding to 99% UV absorption. This value cannot be

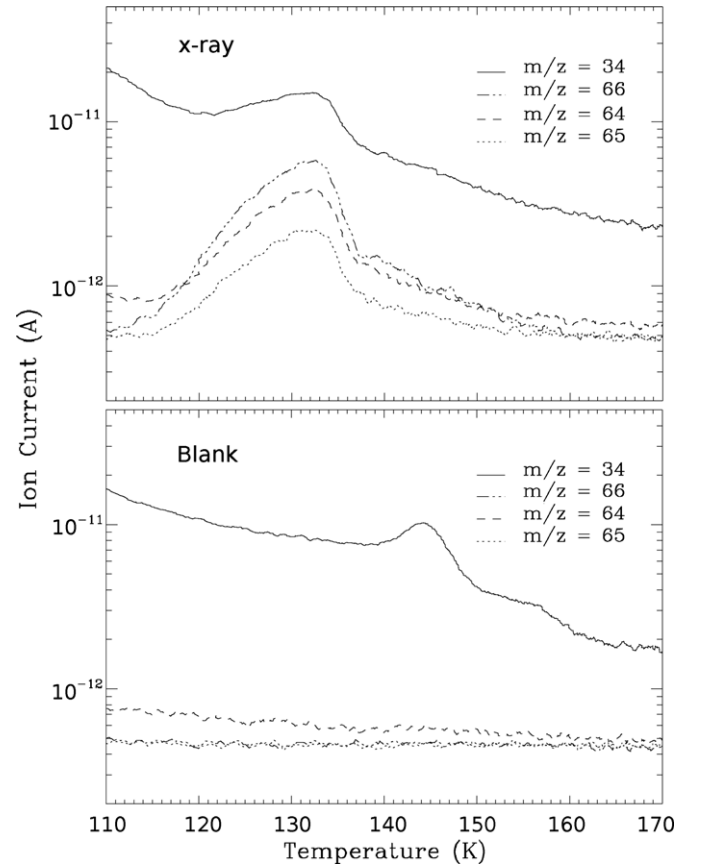


Figure 2. TPD curves corresponding to X-ray irradiation of H_2S ice, experiment N3 of Table 1 (top panel) and the blank with no irradiation, experiment N1 (bottom panel). The traces, in order of decreasing ion current, correspond to the tail of the desorption of H_2S ($m/z = 34$) and the m/z values 66, 64, and 65 for the desorption of the H_2S_2 product near 133 K in the X-ray experiment. The peaks superposed on the desorption tail of H_2S ($m/z = 34$) are due to H_2S co-desorption induced by the release of H_2S_2 in the X-ray experiment, and co-desorption with a trace of background-accreted water in the blank experiment.

estimated properly if the UV absorption cross-section of H_2S ice is not well known. The infrared band strength of solid H_2S_2 was to our knowledge not reported in the literature, but it is expected to be lower than that of H_2S . Analyzing the infrared spectra of short UV irradiation of H_2S experiments (less than 1 minute irradiation to reduce the formation of secondary products like HS_2^- and S_2), we obtained a value of $A(\text{H}_2\text{S}_2)$ similar to that of $A(\text{H}_2\text{S})$, but this estimation could be affected by a large error, mainly due to the small amount of product formed. We therefore used the value $A(\text{H}_2\text{S}_2) = 2.0 \times 10^{-17} \text{ cm molecule}^{-1}$ to convert the integrated absorbance to the column density of produced H_2S_2 , see fifth column of Table 1. The temperature-programmed desorption (TPD) data of X-ray irradiated H_2S ice, experiment N3, is shown in the top panel of Figure 2. The $m/z = 34$ peak corresponds to the tail of the desorption of H_2S that occurs around 95 K. Jiménez-Escobar & Muñoz Caro (2011) show an H_2S desorption temperature peaking at 84 K. This discrepancy is caused by the large difference in ice thickness; see, e.g., Acharyya et al. (2007) for a description of this phenomenon.

For comparison, the TPD data of the blank experiment with no irradiation, experiment N3, are shown in the bottom panel. The desorption peaks of $m/z = 64$ (S_2^+), 65 (HS_2^+), and 66 (H_2S_2^+) around 133 K are only observed in the X-ray-irradiated H_2S ice experiment. This value of the desorption

temperature agrees with that observed in UV irradiation of H₂S ice experiments (Grim & Greenberg 1987; Jiménez-Escobar & Muñoz Caro 2011), and the relative m/z values correspond to the fragmentation of H₂S₂ molecules impinging in the filament of the QMS after desorption from the irradiated ice during warm up. Formation of S₂ in our X-ray experiments, which would contribute to $m/z = 64$, is negligible because it would not account for $m/z = 65$ and 66 and desorbs at higher temperatures, above 200 K (Jiménez-Escobar & Muñoz Caro 2011). Therefore, the infrared and QMS data support the formation of H₂S₂ by soft X-ray irradiation of H₂S ice.

4. DISCUSSION AND ASTROPHYSICAL IMPLICATIONS

Soft X-ray processing of H₂S ice led to the formation of H₂S₂, as in UV irradiation and proton bombardment experiments (Jiménez-Escobar & Muñoz Caro 2011; Moore et al. 2007). In addition to H₂S₂, other species including S₂ were formed by UV irradiation of pure H₂S or H₂S in an H₂O ice matrix (Jiménez-Escobar & Muñoz Caro 2011). We show that for the same low-energy dose in absorbed eV molecule⁻¹, both X-ray and UV irradiation led to H₂S₂. The low X-ray flux used in our experiments resembles astrophysical conditions but the dose was insufficient to induce significant formation of HS₂ and S₂ by photodissociation of the H₂S₂ product. Also, a higher X-ray flux would be required to easily detect photoproducts in experiments where H₂S is diluted in an H₂O ice matrix.

X-ray and UV irradiation of H₂S leading to H₂S₂, which photodissociates in the ice forming S₂, could explain the detection of S₂ in comets. Other S₂ formation channels appear to be less favorable. Formation of S₂ in the gas phase is unlikely as well as direct formation of S₂ from reaction of two S atoms in the ice. CS₂, the precursor of CS, has been proposed to lead also to S₂ (A'Hearn et al. 1983). However, the formation of S₂ should preferentially proceed by irradiation of H₂S, the molecule expected to be more abundant in ice mantles (Grim & Greenberg 1987) and up to 6–30 times more abundant than CS in comets (Biver et al. 2002; Bockelée-Morvan et al. 2010). The proposition of H₂S₂ as a parent molecule of S₂ in comets has implications for its formation in the nucleus or the coma. While gas phase photodissociation of H₂S₂ forms mainly SH radicals, in the solid phase the main product is S₂, formed by direct photodissociation or via the formation of HS₂ as an intermediate species (Isoniemi et al. 1999; Jiménez-Escobar & Muñoz Caro 2011). S₂ is therefore expected to be present in the nucleus, rather than formed in the coma. In addition, we observed experimentally that CS₂, H₂S₂, and S₂ have similar desorption temperatures and would be released to the coma almost simultaneously explaining the observed coma composition.

The production of S₂ in comet IRAS-Araki-Alcock 1983d was 2×10^{25} molecules s⁻¹, about 5×10^{-4} that of OH (A'Hearn et al. 1983). For comet Hyakutake, the production rate was between 6.5×10^{24} and 1.0×10^{25} molecules s⁻¹ and an abundance of $(5-9) \times 10^{-3}$ relative to water (Laffont et al. 1998). To estimate the X-ray fluence required to form the S₂ observed in comets, we can compare the S₂/H₂S abundance ratio to experiments. For Hyakutake, the production rate of H₂S was $(0.45 \pm 0.2) \times 10^{27}$ molecules s⁻¹ measured on April 10–12, and therefore S₂/H₂S ~ 0.018 . For comet IRAS-Araki-Alcock, the S₂/CS abundance ratio was 1.0, but the abundance of H₂S was not measured, and we assume an average cometary value

of H₂S/CS = 6.25 (Biver et al. 2002). Therefore,

$$\frac{S_2}{H_2S} = \frac{S_2}{CS} \times \left[\frac{H_2S}{CS} \right]^{-1} = 0.16. \quad (6)$$

The same value varies from 0.033 to 0.41, if we consider S₂/H₂O = 5×10^{-4} (A'Hearn et al. 1983) and H₂S/H₂O = 0.12%–1.5% measured for 11 comets (Biver et al. 2002). The value S₂/H₂S ~ 0.018 of comet Hyakutake is more reliable because it was obtained from direct observations of this comet. This value is about 5.5 times larger than that obtained in X-ray experiment N3 of Table 1 for H₂S₂/H₂S. Therefore, a dose of at least $0.05 \times 5.5 = 0.28$ eV molecule⁻¹ would be required to account for the observed S₂ abundance if all the H₂S₂ molecules are converted to S₂. For UV photons, assuming an optically thin ice in the UV, this dose is 0.072 eV molecule⁻¹. If H₂S is diluted in an H₂O–ice matrix the required irradiation doses are expected to be higher, although at least for UV irradiation the S₂/H₂S ratio is not critically dependent on the initial H₂S concentration (Grim & Greenberg 1987). Assuming that the X-rays emitted by a young solar-type star at 10 AU account for $2 \times 10^{11-13}$ eV cm⁻² s⁻¹ (Ciaravella et al. 2011), a gas-to-ice ratio of 10^{-4} (e.g., Öberg et al. 2009), an estimated ice X-ray absorption of about 1% for a silicate-core grain of 0.1 μm size with a 0.01 μm thickness ice mantle, and an ice column density of the order of 10^{19} molecules cm⁻² around low-mass protostars (Öberg et al. 2009), the X-ray dose of 0.28 eV required to account for the S₂ abundance observed in comets, see above, roughly corresponds to between $4.4 \times (10^5-10^3)$ yr for the lower and upper X-ray flux limits, respectively.

The results obtained in this work open a new route to the formation of S₂ in comets. UV photons likely irradiated submicron-sized pre-cometary grains in the local dense cloud or later in the solar nebula. More energetic photons or cosmic rays are required to process grain agglomerates leading to cometesimals. The presence of X-rays inside the cloud where the UV flux is low, about 10^4 photons cm⁻² s⁻¹ (Cecchi-Pestellini & Aiello 1992), the high X-ray flux produced by the young Sun, and the larger penetration depth of X-rays in the ice compared to UV photons, suggest that X-rays played a significant role in the formation of S₂ in comets, and that this molecule could be present in interstellar and circumstellar ice mantles, contributing to the observed sulfur depletion in these regions.

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