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Stability of Sulphur Dimers (S_2) in Cometary Ices

O. Mousis¹, O. Ozgurel², J. I. Lunine³, A. Luspay-Kuti⁴, T. Ronnet¹, F. Pauzat², A. Markovits², and Y. Ellinger²
¹Aix Marseille Université, CNRS, LAM (Laboratoire d'Astrophysique de Marseille) UMR 7326, F-13388, Marseille, France; olivier.mousis@lam.fr
²Laboratoire de Chimie Théorique, Sorbonne Universités, UPMC Univ. Paris 06, CNRS UMR 7616, F-75252 Paris CEDEX 05, France
³Department of Astronomy and Carl Sagan Institute, Space Sciences Building Cornell University, Ithaca, NY 14853, USA
⁴Department of Space Research, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78228, USA
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Abstract

S_2 has been observed for decades in comets, including comet 67P/Churyumov–Gerasimenko. Despite the fact that this molecule appears ubiquitous in these bodies, the nature of its source remains unknown. In this study, we assume that S_2 is formed by irradiation (photolysis and/or radiolysis) of S-bearing molecules embedded in the icy grain precursors of comets and that the cosmic ray flux simultaneously creates voids in ices within which the produced molecules can accumulate. We investigate the stability of S_2 molecules in such cavities, assuming that the surrounding ice is made of H_2S or H_2O . We show that the stabilization energy of S_2 molecules in such voids is close to that of the H_2O ice binding energy, implying that they can only leave the icy matrix when this latter sublimates. Because S_2 has a short lifetime in the vapor phase, we derive that its formation in grains via irradiation must occur only in low-density environments such as the ISM or the upper layers of the protosolar nebula, where the local temperature is extremely low. In the first case, comets would have agglomerated from icy grains that remained pristine when entering the nebula. In the second case, comets would have agglomerated from icy grains condensed in the protosolar nebula and that would have been efficiently irradiated during their turbulent transport toward the upper layers of the disk. Both scenarios are found consistent with the presence of molecular oxygen in comets.

Key words: astrobiology – comets: general – comets: individual (67P/Churyumov–Gerasimenko) – methods: numerical – solid state: volatile

1. Introduction

The nature of the source of sulphur dimers (S_2) observed in comets is still unknown. The first detection of S_2 in a celestial body was in the UV spectra of Comet IRAS-Araki-Alcock (C/1983 H1) acquired with the *International Ultraviolet Explorer* (IUE) space observatory (Ahearn et al. 1983). Emission bands of S_2 were subsequently identified in many comets observed with IUE in the eighties, including 1P/Halley (Krishna Swamy & Wallis 1987). S_2 was also identified in comets Hyakutake (C/1996 B2), Lee (C/1999 H1), and Ikeya-Zhang (C/2002 C1; Laffont et al. 1998; Kim et al. 2003; Boice & Reylé 2005). More recently, S_2 has been detected in comet 67P/Churyumov–Gerasimenko (hereafter 67P/C-G) by the ROSINA mass spectrometer on board the *Rosetta* spacecraft at a distance of ~ 3 au from the Sun in 2014 October ($\sim 4\text{--}13 \times 10^{-6}$ with respect to water; Le Roy et al. 2015; Calmonte et al. 2016). All of these observations suggest that S_2 is ubiquitous in comets.

Because the lifetime of S_2 is very short in comae (approximately a few hundred seconds at most; Reylé & Boice 2003), two main scenarios have been invoked in the literature to account for its presence in comets. In the first scenario, S_2 is the product of reactions occurring in the coma. Ethylene was thus proposed to act as a catalyst allowing the formation of S_2 molecules in the inner coma (Saxena & Misra 1995; Saxena et al. 2003). Also, the presence of atomic S (as the photodissociation product of CS_2) reacting with OCS was suggested to form S_2 in comae (A’Hearn et al. 2000). However, models depicting the chemistry occurring in cometary comae show that these two mechanisms do not account for the observed levels of S_2 (Rodgers & Charnley 2006).

In the second scenario, S_2 molecules are believed to be of parent nature and reside in cometary ices (Ahearn et al. 1983;

Ahearn & Feldman 1985; Feldman 1987; Grim & Greenberg 1987; A’Hearn 1992). Ahearn & Feldman (1985) proposed that the UV photolysis of S-bearing species embedded in ISM ices could form sufficient amounts of S_2 that remains trapped in the icy matrix. Since then, a number of mechanisms based on UV or X-ray irradiation have been proposed, starting mainly from H_2S (the most abundant S-bearing volatile observed in comets; Irvine et al. 2000; Bockelée-Morvan et al. 2004) and H_2S_2 , and involving radicals like HS and HS_2 (Grim & Greenberg 1987; Jiménez-Escobar & Muñoz-Caro 2011; Jiménez-Escobar et al. 2012). It has also been proposed that S_2 could be formed from the radiolysis of S-bearing compounds in cometary ices (Ahearn & Feldman 1985; Calmonte et al. 2016) despite the fact that so far, there is no experimental proof showing that this mechanism is effective.

In the present study, we postulate that S_2 is formed from H_2S molecules embedded in icy grains by irradiation of UV, X-ray, and cosmic ray fluxes (CRF), whether icy grain precursors of comets formed in the protosolar nebula or the ISM. Because radiolysis generated by the impact of cosmic rays simultaneously creates voids in ices within which the produced molecules can accumulate (Carlson et al. 2009; Mousis et al. 2016b), we investigate the stability of S_2 molecules in such cavities, assuming that the surrounding ice is made of H_2S or H_2O . We show that the stabilization energy of S_2 molecules in such voids is close to that of the H_2O ice binding energy, implying that they can only leave the icy matrix when this latter sublimates. We finally discuss the implications of our results for the origin of cometary grains, with a particular emphasis on those agglomerated by comet 67P/C-G.

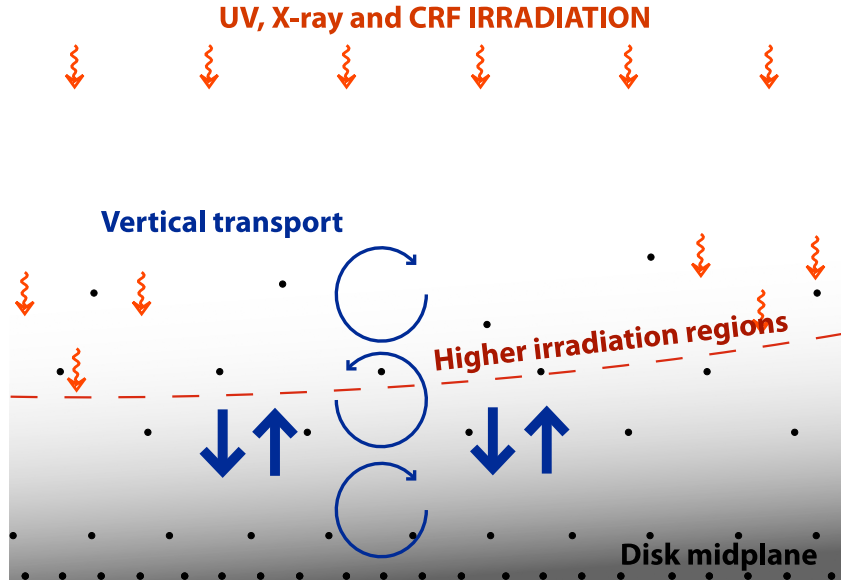


Figure 1. Illustration of the vertical transport of small icy grains toward disk regions where they are efficiently irradiated. Dust is concentrated in the midplane of the disk due to gravitational settling and gas drag. However, turbulent eddies lift the icy grains toward the upper regions and also drag them down because the direction of the velocity is random and coherent during a timescale comparable to the local keplerian period. Small dust grains finally spend a non-negligible fraction of their lifetime in the disk’s upper regions, where the irradiation attenuation is low.

2. Irradiation of Icy Grains

Three irradiation mechanisms leading to the formation of S_2 are considered in this study. The first two mechanisms, namely UV and X-ray irradiation, have been proven to produce S_2 from H_2S and H_2S_2 (Grim & Greenberg 1987; Jiménez-Escobar & Muñoz-Caro 2011; Jiménez-Escobar et al. 2012). Experiments have shown that S_2 can be produced and stabilized in icy grains over thicknesses of a few tenths of microns. Despite the lack of experimental data, radiolysis has also been considered as a potential candidate for S_2 formation from S-bearing compounds in cometary icy grains (Ahearn & Feldman 1985). This mechanism has recently been proposed to explain the detection of S_2 in 67P/C-G (Calmonte et al. 2016) and is often invoked to account for its presence in Europa’s exosphere (Carlson et al. 1999; Cassidy et al. 2010). Cosmic rays reach deeper layers than photon irradiation and simultaneously creates voids in which some irradiation products such as O_2 or here S_2 can be sequestered (Mousis et al. 2016b). Whatever the irradiation process considered, we assume that, once S_2 has been created and trapped in the microscopic icy grains, the latter agglomerated and formed the building blocks of comets.

3. Stability of S_2 Molecules in an Icy Matrix

The S_2 stabilization energy arises from the electronic interaction between the host support (H_2O ice or H_2S ice) and the S_2 foreign body. The stabilization energy is evaluated as

$$E_{\text{stab}} = (E_{\text{ice}} + E_{S_2}) - E, \quad (1)$$

where E_{S_2} is the energy of the isolated molecule, E_{ice} the energy of the pristine solid host and E is the total energy of the [host + S_2] complex, with all entities optimized in isolation.

All simulations are carried out by means of the Vienna ab-initio simulation package (Kresse & Hafner 1993, 1994; Kresse & Furthmüller 1996; Kresse & Joubert 1999). The long range interactions in the solid and the hydrogen bonding being the

critical parameters in the ices, we use the PBE generalized gradient approximation functional (Perdew et al. 1996), in the (PBE+D2) version corrected by Grimme et al. (2010), that has been specifically designed to deal with the present type of problem. This theoretical tool has proved to be well adapted to model bulk and surface ice structures interacting with volatile species (Lattalais et al. 2011, 2015; Ellinger et al. 2015; Mousis et al. 2016b). More details on the computational background can be found in the aforementioned publications.

Since S_2 is created well inside the icy grain mantles, the initial description of the irradiated ice is taken as that of the internal structures of ice clusters obtained from Monte-Carlo simulations of ice aggregates constituted of hundreds of water molecules. The important point in the simulations by Buch et al. (2004) is that the core of the aggregates consists in crystalline domains of apolar hexagonal ice Ih . However, in the present context, the irradiation creates significant defects inside the ice, namely, voids and irradiation tracks that, at least locally, modify the crystalline arrangement.

3.1. S_2 Embedded in H_2O Ice

Because H_2O is the dominant volatile in comets (Bockelée-Morvan et al. 2004), most of the cavities created by CRF irradiation are expected to be surrounded by H_2O molecules. Table 1 shows the stabilization energy of S_2 as a function of the size of these cavities. How the S_2 stabilization evolves as a function of their size is summarized below.

1. Starting with no H_2O removed, we find no stabilization for the inclusion of S_2 in the ice lattice. It is in fact an endothermic process, as it is for O_2 inclusion (Mousis et al. 2016b).
2. With one H_2O removed, we have an inclusion structure for which stabilization is negative, meaning that S_2 cannot stay in such a small cavity.
3. With somewhat larger cavities obtained by removing two to four adjacent H_2O molecules from the ice lattice, we

Table 1Computed Stabilization Energies (eV) of S₂ Interacting with H₂O Ice or H₂S Ice

Environment	H ₂ O Ice	H ₂ S Ice
Adsorption	0.28	...
Inclusion ($n = 1$) ^a	-0.12	0.30
Inclusion ($n = 2$)	0.28	0.45
Inclusion ($n = 4$)	0.50	0.40
Inclusion (fine track)	0.51	0.41
Inclusion (large track)	0.53	0.50

Note.

^a n = number of H₂O or H₂S molecules destroyed to create the void in which S₂ is trapped.

obtain increasing stabilization energies from 0.3 to 0.5 eV.

4. With larger cavities that form along the irradiation track, the stabilization energies are found to be at least of the order of 0.5 eV.

In short, as soon as the space available is sufficient, the energy stabilizes around 0.5 eV. This stabilization energy is (1) higher (more stabilizing) than what is found in the case of O₂ (0.2–0.4 eV; Mousis et al. 2016b) and (2) larger than that of a water dimer (~0.25 eV). Hence, the presence of S₂ should not perturb the ice structure until it is ejected into the coma via sublimation with the surrounding H₂O molecules. The results of our computations are consistent with the laboratory experiments of Grim & Greenberg (1987) who showed that S₂ remains trapped in icy grains until they are heated up to ~160 K, a temperature at which water ice sublimates at PSN conditions.

3.2. S₂ Embedded in H₂S Ice

H₂S behaves similarly to H₂O because of its ability to establish hydrogen bonds. This implies that small domains of H₂S could have formed in the bulk of the ice and served as local sources for the formation of S₂. The stabilization of these aggregates is addressed by numerical simulations in which H₂S entities are progressively introduced by replacing an equal number of H₂O molecules in the water-ice lattice. Table 2 shows the stabilization energies with values around 0.5 and 0.75 eV for neighboring and far away H₂S, respectively. Consequently, substituting several neighboring H₂O by H₂S is a possibility to be considered if the H₂S is abundant enough, thus creating small islands of H₂S within the water ice.

If small clumps of H₂S ices in the bulk of water ice are a plausible hypothesis, as suggested by the aforementioned numbers, then the proper conditions are realized for the in situ formation of S₂ by deep irradiation. The case in which H₂S molecules replace H₂O along the irradiation track is a less favorable situation but it could be at the origin of the S_n oligomers observed in some laboratory experiments (Meyer et al. 1972; Jiménez-Escobar et al. 2012). We evaluate the stabilization of S₂ in H₂S clumps, assuming that they behave as pure condensates. The results, presented in Table 1 and summarized below, are quite close to those derived for water ice.

1. With one H₂S removed, we have a substitution structure whose stabilization is on the order of 0.30 eV.

Table 2Computed Stabilization Energies (eV) of H₂S Interacting with H₂O Ice

Environment	H ₂ S
Adsorption	0.61
Substitution ($n = 1$) ^a	0.77
Substitution ($n = 2$ far away)	0.73
Substitution ($n = 2$ close)	0.56
Substitution ($n = 3$ close)	0.50
Substitution (irradiation track)	0.51

Note.

^a n = number of H₂O molecules replaced by H₂S.

2. With larger cavities obtained by removing two to four adjacent H₂S molecules, we obtain increasing stabilization energies between 0.40 and 0.45 eV.
3. With even larger cavities, extended in the direction of the irradiation, the stabilization energies are found to be similar to the preceding ones, between 0.40 and 0.50 eV.

Again we find that the presence of S₂ should not perturb the ice structure, even when trapped in H₂S clumps, until the latter sublimate, due to increasing local temperature.

4. Implications for Cometary Ices

It has recently been shown that the radiolysis of icy grains in low-density environments, such as the presolar cloud, may induce the production of amounts of molecular oxygen high enough to be consistent with the quantities observed in 67P/C-G (Mousis et al. 2016b). Higher density environments such as the PSN midplane were excluded because the timescales needed to produce enough O₂ in cometary grains exceeded by far their lifetimes in the disk. Also, the efficiency of ionization by cosmic rays in the PSN midplane is now questioned because of the deflection of galactic CRF by the stellar winds produced by young stars (Cleeves et al. 2013, 2014).

On the other hand, because the lifetime of S₂ is very short in the gas phase (approximately a few hundred seconds at most; Reylé & Boice 2003), its formation conditions are even more restrictive than those required for O₂. Assuming that S₂ indeed formed from H₂S or any other S-bearing molecule via UV, X-ray, or CRF irradiation, this implies that this molecule never left the icy matrix in the time interval between its formation and trapping. In other words, S₂ never condensed from the PSN before being trapped in cometary grains. This stringent constraint requires S₂ to form within icy grains irradiated by CRF in low-density environments such as ISM, where the local temperature is extremely cold. In this picture, comets, including 67P/C-G, would have agglomerated in the PSN from icy grains originating from ISM, whose compositions and structures remained pristine when entering the nebula.

Alternatively, because the CRF irradiation should be poorly attenuated in the upper layers of the PSN, these regions also constitute an adequate low-density environment, allowing the formation of S₂ in cometary grains. Turbulence plays an important role in the motion of small dust grains that are well coupled to the gas (see Figure 1). Micron-sized grains initially settled in the midplane are entrained by turbulent eddies and diffuse radially and vertically with an effective viscosity roughly equal to that of the gas for such small particles (see Ciesla 2010, 2011 for details). Consequently, solid particles

follow a Gaussian distribution in the vertical direction. The scale height of dust (corresponding to the standard deviation of the distribution) is a fraction of the gas scale height, this fraction being larger and possibly equal to the gas scale height in the cases of small grains and higher degrees of turbulence (Dubrulle et al. 1995; Youdin & Lithwick 2007).

The vertical transport of solids exposes them to very different disk environments. Dust grains are stochastically transported to high altitude and low-density regions above the disk midplane. Ciesla (2010) developed a numerical simulation to integrate the motion of individual particles and showed that micron-sized grains spent $\sim 32\%$ of their lifetime at altitudes above the scale height of the disk, including $\sim 5\%$ at heights above four times its scale height, regardless of the distance from the Sun. In such low-density environments, photochemistry plays a primordial role, as demonstrated by Ciesla & Sandford (2012), because UV photons are weakly attenuated at those heights. This also holds for the CRF irradiation of grains that should be substantially enhanced compared to the dose received by particles residing in the midplane. Under those circumstances, the production of S_2 should be favored in icy grains over several cycles of vertical transport toward the surface of the disk. This scenario should also favor the formation of O_2 from irradiation of H_2O ice (see Mousis et al. 2016b for details).

5. Discussion and Conclusions

It is reasonable to assume that the multiple forms of irradiation hitting the microscopic icy grains in low-density environments such as ISM or the upper layers of protoplanetary disks can lead both to the formation of S_2 molecules and the development of cavities in these grains, in which the molecule remains sequestered. The same scenario has been proposed for O_2 formation and stabilization in cometary icy grains (Mousis et al. 2016b). In the case of S_2 formation, the possibility of forming the dimer via the radiolysis of S-bearing ices remains an open question. Future experimental work is needed to check the viability of this mechanism.

The possible formation of S_2 in icy grains via their irradiation in ISM, together with the short lifetime of this molecule in the gas phase, leads to the plausible possibility that comets agglomerated from pristine amorphous grains that never vaporized when entering the PSN, as already envisaged for the origin of 67P/C-G's material (Rubin et al. 2015a; Mousis et al. 2016b). On the other hand, the formation of S_2 in icy grains that migrated toward the upper layers of the disk is compatible with their condensation in the PSN midplane. This mechanism leaves open the possibility that these grains are made of crystalline ices and clathrates, as proposed by Mousis et al. (2016a) and Luspay-Kuti et al. (2016) to account for several pre-perihelion compositional measurements made by the *Rosetta* spacecraft in 67P/C-G. The same process could explain the presence of O_2 measured in situ in comets 67P/C-G and 1P/Halley (Bieler et al. 2015; Rubin et al. 2015b). Interestingly, whatever the ice structure considered for the icy grains, the voids allowing the stabilization of S_2 can be considered as analogs of clathrates in terms of cage sizes and intermolecular interactions.

The fact that one H_2S replacing one H_2O has little influence on the stability of the solid lattice is a favorable situation for the formation of a mixed ice. It is plausible that some segregation occurs with the formation of H_2S islands in the bulk of

crystalline or amorphous water ice. Then, the proper conditions would be realized for the in situ formation of S_2 , especially if we remember that the formation of one S_2 requires at least the destruction of two imprisoned sulphur species. The plausible formation of H_2S clumps is a strong argument in favor of a non-uniform distribution of S_2 within cometary ices. Note that in the case of irradiation of crystalline grains condensed in the PSN and transported toward the upper layers of the disk, the formed S_2 may be entrapped in clathrates (Grim & Greenberg 1987), also forming a solid phase distinct from water ice in cometary grains.

The immediate consequence of the presence of distinct S_2 -bearing solid phases is the difficulty to predict the S_2 correlation with H_2O or H_2S in 67P/C-G from *Rosetta* measurements. The S_2/H_2O abundance ratio is directly linked to the region of the comet whose desorption is observed. Contrary to O_2 whose apparent good correlation with H_2O is explained by its trapping in water ice (Bieler et al. 2015; Mousis et al. 2016b), no global trend should be drawn between the variation of S_2 and H_2O abundances if S_2 is distributed within both the S-bearing and H_2O ices. Indeed, S_2 may be released simultaneously from the H_2O layer present close to the surface and from H_2S clusters localized deeper in the subsurface. Our results are supported by the ROSINA data collected between 2015 May (equinox) and 2015 August (perihelion), showing that there is no clear correlation of S_2 with H_2O or H_2S in 67P/C-G (Calmonte et al. 2016). These observations allow us to exclude the trapping of S_2 in a dominant ice reservoir. If S_2 was mainly trapped in H_2S -bearing ice, then the outgassing rates of S_2 and H_2S should have been well correlated during the period sampled by the ROSINA instrument. The same statement applies if S_2 had been essentially trapped in water ice.

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