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Irradiation of methanol ice on a sulfur-rich dust analogue at 25 K: a mid-infrared spectroscopic study

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Despite possibly representing a comparatively large reservoir of sulfur in extraterrestrial environments, the role of sulfur allotropes in the radiation-driven chemistry occurring in low-temperature ices in astrophysical media (e.g., pre-stellar nebulae or the outer Solar System) is an underexplored topic. Previous work has shown that the irradiation of astrophysical ice analogues composed of simple molecules on top of layers of allotropic sulfur results in the formation of simple, inorganic sulfur-bearing molecules in the ice phase. Our present work seeks to qualitatively determine whether the analogous irradiation of methanol on top of allotropic sulfur may lead to the formation of organosulfur molecules, as well as H₂S. Using *in situ* mid-infrared absorption spectroscopy, we have found compelling evidence for the formation of SO₂, CS₂, H₂SO₄, and a number of sulfur oxyanions, as well as tentative evidence for H₂S formation. Evidence for the formation of thiol molecules was inconclusive. Our experimental results are discussed in the context of their applicability to sulfur astrochemistry.

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1 Introduction

Although the extraterrestrial chemistry of sulfur continues to pose challenges to the research community,¹ it has become increasingly apparent in recent years that sulfur-rich refractory materials in the form of minerals or allotropes likely play an important role in this chemistry. Indeed, such sulfur-rich refractory materials have been detected in a wide variety of astrophysical environments: for instance, so-called GEMS (silicate glass with embedded metal and sulfides) and GEMS-like materials have been identified in chondritic meteorites^{2,3} and in interplanetary dust particles^{4,5} and are thought to be representative of primitive material originating from the pre-stellar nebula. Sulfide minerals of magnesium and iron have also been observed in the ejecta of (post-)asymptotic giant branch stars^{6,7}

and, moreover, iron sulfide minerals are thought to be the primary reservoir of sulfur in protoplanetary disks where they potentially account for >80% of the sulfur present there.⁸

Allotropes of elemental sulfur are also believed to be abundant in astrophysical media: Ruffle *et al.*⁹ suggested a mechanism by which interstellar gas-phase S⁺ ions could be depleted onto dust grain surfaces as diffuse interstellar nebulae evolve into denser structures, and recent Monte Carlo simulations by Cazaux *et al.*¹⁰ demonstrated that these adsorbed and neutralised ions could be converted to large allotropes within a few 10⁴ years. Within the cold (*i.e.*, 10–20 K) cores of quiescent pre-stellar nebulae, the energetic processing of sulfur-containing ices adsorbed on nanoscale dust grains by ultraviolet photons and galactic cosmic rays may also yield allotropic sulfur, as has been demonstrated by a number of experimental and computational studies.^{10–18} Within the Solar System, allotropic sulfur is a relatively common material, and is known to be the second-most abundant reservoir of sulfur on the surface of Jupiter's moon Europa.^{19,20} Moreover, allotropes of sulfur have been detected in comets such as 67P/Churyumov–Gerasimenko^{21,22} and asteroids such as 162173 Ryugu.²³

Recent work by Ferrari *et al.*²⁴ has shown that the fragmentation, and presumably subsequent reaction, of the S₈ allotrope is feasible under the low-temperature conditions typical of dense pre-stellar nebulae and icy outer Solar System environments. As such, allotropic sulfur could be an active participant

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in sulfur chemistry in these extraterrestrial settings. It recently occurred to us that, if allotropic sulfur is a reactive and relatively common material in these icy environments, then it is possible that the energetic processing of sulfur-free ices in contact with more refractory allotropic sulfur by galactic cosmic rays, stellar winds, or ultraviolet photons could result in the volatilisation of the sulfur and the synthesis of new sulfur-bearing molecules in the ice phase. This idea was in part inspired by previous experimental studies that demonstrated that the analogous irradiation of carbon-free astrophysical ice analogues on top of carbon-rich refractory material results in the synthesis of simple inorganic carbon-bearing molecules, such as CO and CO₂, in the ice phase.^{25–30}

To test this hypothesis, we recently performed experiments on the irradiation of a number of neat interstellar ice analogues (*i.e.*, O₂, CO, CO₂, and H₂O) on top of an allotropic sulfur layer using 1 MeV He⁺ ions as mimics of galactic cosmic rays.³¹ Experiments were nominally performed at 20 K, although those involving neat CO₂ and H₂O ices were also performed at 70 K so as to provide complementary data acquired under temperature conditions more relevant to icy outer Solar System bodies. Our experiments evidenced the radiolytic formation of a number of new sulfur-bearing inorganic molecules, such as SO₂, CS₂, OCS, and H₂SO₄ hydrates, and experiments performed at 70 K provided greater yields of these molecules.³¹ Although our previous study provided quantitative evidence for the formation of inorganic sulfur-bearing molecules as a result of the radiolytic processing of astrophysical ice analogues on top of sulfur-rich refractory material, it is interesting to note that we did not detect any organic sulfur-bearing products as a result of irradiating CO or CO₂ ices on top of allotropic sulfur and, additionally, we did not detect the formation of H₂S after the irradiation of H₂O ice on a layer of allotropic sulfur.

Such results are particularly interesting since both H₂S and organosulfur molecules have been proposed to be potentially significant reservoirs of sulfur in interstellar environments. In the case of H₂S, it is envisaged that the formation of this molecule proceeds as a result of the hydrogenation of sulfur atoms adsorbed on dust grains^{9,32} based on the previous laboratory observation of the analogous formation of CH₄, NH₃, and H₂O as a result of the hydrogenation of surface-adsorbed carbon, nitrogen, and oxygen atoms, respectively.^{33–36} In the case of organosulfur molecules, computational work by Laas and Caselli³⁷ suggested that the majority of sulfur in diffuse interstellar nebulae is sequestered into relatively simple organosulfur species trapped on dust grains as these nebulae evolve to denser structures. Indeed, analysis of the sulfur inventory of comet 67P/Churyumov–Gerasimenko has demonstrated that, not only is H₂S the most abundant sulfur-bearing molecule, but that complex organosulfur molecules are also present on the comet.^{21,22,38,39}

In this article, we describe the results of an infrared spectroscopic study aimed at extending the results of our previous study³¹ and better assessing the potential formation of H₂S and organosulfur molecules in extraterrestrial environments as a result of the energetic processing of sulfur-free ices in contact with allotropic sulfur. To achieve this, we have irradiated a neat

CH₃OH ice, prepared by condensation of the vapour on a layer of allotropic sulfur, using 1 MeV He⁺ ions as a mimic of space radiation. The selection of CH₃OH as a target ice was based on the knowledge that the irradiative processing of this ice by ions and electrons has been observed to yield a large number of complex organic molecules^{40–49} which, in the presence of allotropic sulfur, may possibly induce the formation of organosulfur species. Moreover, the high hydrogen atom density in the CH₃OH molecule may increase the propensity for radiolytic H₂S formation in this experiment. The irradiation was carried out at 25 K, since this temperature may be representative of the surfaces of some of the coldest icy outer Solar System bodies as well as warmer regions in the cold cores of pre-stellar nebulae; thereby making our study applicable to a variety of extraterrestrial environments.

2 Experimental methodology

The experimental protocol followed mirrored that used in our previous study.³¹ Experiments were carried out using the Ice Chamber for Astrophysics-Astrochemistry (ICA); a laboratory set-up dedicated to the study of radiation chemistry in astrophysical ice analogues.^{50,51} Briefly, the ICA (Fig. 1) is an ultrahigh-vacuum chamber within the centre of which is a rotatable and cryogenically cooled gold-coated copper sample holder hosting a series of infrared-transparent ZnSe deposition substrates onto which astrophysical ice analogues may be prepared through background condensation of dosed gases and vapours. To prepare astrophysical ice analogues composed of materials that are solid under standard conditions, a commercial evaporator (Createc OLED-40-10-WK-SHM) pre-loaded with the solid material of interest may be installed onto one of the side ports of the ICA. The nozzle of this evaporator may be brought into very close proximity (*i.e.*, within a few millimetres) of the substrate surface, thereby ensuring maximal condensation of sublimed solid material on the cooled



Fig. 1 Simplified top-view schematic diagram of the ICA set-up. Details on how the set-up was used to prepare and radiolytically process a CH₃OH ice on top of a sulfur layer can be found in text. Image reproduced with permission from Mifsud *et al.*³¹



deposition substrate rather than on any of the other internal surfaces of the ICA.

To prepare the sulfur-rich grain analogue required in this study, the sample holder was first cooled to 25 K and subsequently rotated to the face the nozzle of the evaporator, which had been pre-loaded with a few grams of pharmaceutical-grade sulfur. The sulfur was subsequently heated to 78 ± 3 °C and allowed to equilibrate at this temperature for a short while, prior to bringing the nozzle into close proximity of one substrate surface and opening its shutter to allow for the deposition of a relatively thick (~ 4 μm) sulfur layer. Once this layer had been prepared, the shutter was closed and the nozzle withdrawn from the chamber. The sample holder was then rotated to face an incident mid-infrared spectroscopic beam, and a reference background spectrum was acquired in transmission absorption mode. A neat CH_3OH astrophysical ice analogue was prepared on top of the sulfur layer by dosing vapours from a liquid sample (VLSI grade; supplied by VWR) into the main chamber through a fine regulating needle valve. To ensure that only CH_3OH was introduced into the chamber in this way, the liquid sample was first purged from any dissolved gases through multiple rounds of the freeze-pump-thaw cycle.

The deposition of the CH_3OH ice could be followed *in situ* using Fourier-transform mid-infrared transmission absorption spectroscopy over the $4000\text{--}650$ cm^{-1} range, thus allowing the amount of icy material deposited to be quantified. The molecular column density N (molecules cm^{-2}) of a deposited astrophysical ice analogue is related to the integrated absorbance S (cm^{-1}) of one of its characteristic absorption bands as:

$$N = \ln(10) \frac{S}{A_\nu} \quad (1)$$

where A_ν is the so-called integrated strength constant of that band (cm molecule^{-1}). The column density of a deposited ice is related to its thickness h (μm) as:

$$h = 10\,000 \frac{NM}{\rho N_A} \quad (2)$$

where M is the molar mass of the ice (g mol^{-1}), ρ is the ice density (g cm^{-3}), and N_A is the Avogadro constant. In the case of CH_3OH , $M = 32$ g mol^{-1} and ρ (25 K) = 0.636 g cm^{-3} .⁵² Furthermore, we have adopted an integrated strength constant of 1.61×10^{-17} cm molecule^{-1} for the C–O stretching mode located at approximately 1030 cm^{-1} .⁵²

The CH_3OH astrophysical ice analogue prepared in this study was grown to a thickness of 1.3 μm (*i.e.*, a column density of 1.56×10^{18} molecules cm^{-2}), after which a mid-infrared absorption spectrum was acquired. The ice-dust analogue was then exposed to a 1 MeV He^+ ion beam supplied by a 2 MV Tandem accelerator^{53,54}, with incident ions striking the ice at an angle of 36° to the surface normal. Using the *Stopping and Range of Ions in Matter* software,⁵⁵ the maximum range of the projectile ions in the ice-dust analogue was calculated to be 3.5 μm . Overall, the ice-dust analogue was irradiated to a total fluence of 10^{15} ions cm^{-2} over a two-hour period, and several mid-infrared absorption spectra were acquired at pre-defined

fluence intervals. The irradiation was halted during spectral acquisition, and spectra were acquired as an average of 128 co-added scans and at a resolution of 1 cm^{-1} .

3 Results and discussion

The mid-infrared absorption spectrum of CH_3OH ice prepared at 25 K on top of a layer of sulfur is portrayed in Fig. 2, and is very similar to that of a control experiment in which a purely amorphous CH_3OH ice of similar thickness was prepared at 20 K in the absence of sulfur *via* the background condensation of the vapour onto a ZnSe substrate. Moreover, both these spectra are very similar to literature spectra of amorphous CH_3OH acquired at low temperatures.^{56,57} It is therefore possible to conclude that the ice prepared on top of the sulfur layer at 25 K in this present study also adopted an amorphous structure. The exposure of the ice-dust analogue to a 1 MeV He^+ ion beam resulted in the gradual decay of the CH_3OH absorption bands and the growth of new features attributable to various radiolytic products (Fig. 3 and Table 1).

3.1 Products derived from methanol radiation chemistry

Although the main aim of this experiment was to identify new sulfur-bearing molecules that incorporated hydrogen, carbon, and/or oxygen from CH_3OH into their structure, a large number of products that formed exclusively from the radiolytic processing of CH_3OH (and thus did not include sulfur) could also be identified (Fig. 3 and Table 1). At low fluence (5.04×10^{12} ions cm^{-2}), a distinct absorption band could be identified at 1726 cm^{-1} which could be attributed to the formation of H_2CO as a result of the radiation-induced dehydrogenation of CH_3OH .⁷² This product accumulated as the delivered ion fluence increased, as could be



Fig. 2 Mid-infrared absorption spectra of CH_3OH ice on top of allotropic sulfur (black trace) and of an amorphous CH_3OH ice prepared at 20 K in the absence of sulfur as a control (red trace). The similarity between these spectra leads one to conclude that the black spectrum also represents an amorphous ice. Band assignments are based on those of Hudson *et al.*⁵⁸ Note that spectra are shifted along the vertical axis for clarity.





Fig. 3 Mid-infrared spectra acquired during the irradiation of CH_3OH ice on top of a layer of allotropic sulfur by 1 MeV He^+ ions. Panels show different regions of absorption, with emergent bands attributable to the synthesis of various product molecules highlighted (see Table 1 for full assignments). Note that panels B and C display difference spectra, in which the spectrum acquired at zero ion fluence is subtracted from all subsequently acquired spectra.

inferred from the increasing absorbance of this band. However, H_2CO is also prone to radiolytic dehydrogenation, as evidenced by the appearance of new absorption bands at 2138 cm^{-1} (due to CO)⁶⁹ and 1843 cm^{-1} (due to HCO)^{40,41,70,71} starting at fluences of $9.88 \times 10^{12}\text{ ions cm}^{-2}$ and $5.07 \times 10^{13}\text{ ions cm}^{-2}$, respectively. Indeed, at fluences beyond $2.12 \times 10^{14}\text{ ions cm}^{-2}$, the intensity of the H_2CO absorption band at 1726 cm^{-1} progressively declined as its radiolytic destruction became more efficient than its synthesis. It is to be noted that a band at 1196 cm^{-1} attributable to CH_2OH was observed in acquired mid-infrared spectra,^{40,41,71,77} thereby indicating that the radiation-induced loss of a single hydrogen atom from CH_3OH also occurred in our experiment.

Another radiolytic product that was formed early on in the experiment was CH_4 , which was identified through its main absorption band at 1303 cm^{-1} at a delivered ion fluence of $5.04 \times 10^{12}\text{ ions cm}^{-2}$.^{63,64} Similar to the case of H_2CO , the abundance of CH_4 within the irradiated ice initially increased with increasing ion fluence; however, under prolonged irradiation, the intensity of its absorption bands decreased due to the increased efficiency of its radiolytic destruction. Although a number of reaction pathways may contribute to the radiolytic synthesis of CH_4 from CH_3OH , one of particular interest is the direct loss of atomic oxygen from the latter molecule⁴¹ due to the ability of these highly reactive oxygen atoms to contribute to



the formation of new molecules. Indeed, oxygen atom addition to CO is believed to contribute to the synthesis of CO₂ in the ice,⁴¹ which was identified through its main absorption band at 2341 cm⁻¹.⁵⁹ Interestingly, both the ¹²C and ¹³C isotopologues of CO and CO₂ were detected in our experiment.

The radiolytic formation of H₂O was also observed starting at a fluence of 5.07 × 10¹³ ions cm⁻², but becoming really apparent in acquired mid-infrared spectra at fluences greater than 2.12 × 10¹⁴ ions cm⁻². Indeed, broad absorption bands attributable to H₂O were detected between ~3630–3020 (coincident with CH₃OH absorptions) and between ~1775–1540 cm⁻¹ (coincident with H₂CO absorptions), and continued to grow with increasing ion fluence.^{61,62} We exclude the possibility that the H₂O observed in our experiment was sourced from the condensation of contaminant water vapour in our experimental set-up on the basis of previous control experiments having determined that the integrated absorbances of the mid-infrared bands of such contaminant water vapour undergoing condensation over a two-hour period would be ~1% of those actually observed in the present study. Furthermore, the continued accumulation of H₂O during the 1 MeV He⁺ ion irradiation of CH₃OH on top of sulfur observed in this experiment is in good agreement with the observations of Palumbo *et al.*,⁸⁷ who studied the irradiation of neat CH₃OH ice using 3 keV He⁺ ions.

As noted previously, the irradiation of CH₃OH ice is known to result in the synthesis of a number of complex organic molecules and evidence for the formation of a number of such species is apparent in acquired spectra at wavenumbers below 1200 cm⁻¹ (Fig. 3, panel F). The reactions leading to the formation of these products, as well as their mid-infrared absorption spectra, have been elucidated in several studies,^{40–49,71,72,78–82,85,86} and so will not be described further in this article. However, on the basis

of the assignments made by these previous studies, we have been able to assign the absorption bands observed in our mid-infrared spectra to molecules such as dimethyl ether (CH₃OCH₃), methyl formate (HCOOCH₃), ethanol (CH₃CH₂OH), acetone (CH₃COCH₃), ethylene glycol (HOCH₂CH₂OH), and glycolaldehyde (HOCH₂CHO) (see Table 1 for assignments).

We note that a small absorption band identified at 1062 cm⁻¹ as a shoulder to the intense CH₃OH C–O stretching mode may have contributions from formic acid (HCOOH); specifically, from its C–H bending mode.⁸⁵ The radiolytic synthesis of HCOOH in our ice would be logical, especially given the detection of other, chemically related molecules such as H₂CO and HCOOCH₃ (Fig. 3 and Table 1). However, to the best of our knowledge, the synthesis of HCOOH as a result of the irradiation of CH₃OH has not been conclusively demonstrated by previous studies. Furthermore, the most intense absorption band in the spectrum of solid HCOOH at approximately 1700 cm⁻¹ (due to the C=O stretching mode) is not visible in our spectra; possibly due to it being obscured by the more intense absorption features of the more abundant product molecules H₂CO and H₂O. Therefore, in the absence of other confirmatory analysis techniques (such as mass spectrometric measurements of sublimed material obtained during post-irradiative warming of the ice), the identification of HCOOH in our experiment must remain tentative.

3.2 Products containing sulfur

In addition to those products yielded as a result of the radiolytic processing of CH₃OH, a number of sulfur-containing molecular products were also identified *via* mid-infrared absorption spectroscopy. Perhaps the most notable of these products were SO₂ and CS₂, whose absorption features were observed at 1351 and 1508 cm⁻¹, respectively.^{73–76} These molecules were also the

Table 1 Assignment of mid-infrared absorption bands that appeared in acquired spectra (Fig. 3) after the irradiation of a CH₃OH ice on a layer of sulfur at 25 K using 1 MeV He⁺ ions

Band position cm ⁻¹	Assignment	Ref.
3701	CO ₂	Isokoski <i>et al.</i> ; ⁵⁹ He & Vidal ⁶⁰
~ 3630–3020 (br., str.)	H ₂ O	Hagen <i>et al.</i> ; ⁶¹ Givan <i>et al.</i> ⁶²
3009	CH ₄	Chapados & Cabana; ⁶³ Gerakines & Hudson ⁶⁴
2976	CH ₃ SH (?) or CH ₃ CH ₂ SH (?)	Hudson; ⁶⁵ Hudson & Gerakines ⁶⁶
~ 2600–2525 (br., v. w.)	H ₂ S (?) or CH ₃ SH (?) or CH ₃ CH ₂ SH (?)	Hudson; ⁶⁵ Hudson & Gerakines; ⁶⁶ Yarnall & Hudson; ⁶⁷ Mifsud <i>et al.</i> ⁶⁸
2341 (str.)	CO ₂	Isokoski <i>et al.</i> ⁵⁹
2277 (w.)	¹³ CO ₂	Isokoski <i>et al.</i> ⁵⁹
2138 (str.)	CO	Gerakines <i>et al.</i> ⁶⁹
2092 (w.)	¹³ CO	Gerakines <i>et al.</i> ⁶⁹
1843 (v. w.)	HCO	Ewing <i>et al.</i> ; ⁷⁰ Bennett & Kaiser; ⁴⁰ Bennett <i>et al.</i> ; ⁴¹ Chen <i>et al.</i> ⁷¹
1726 (str.)	H ₂ CO	Hudson <i>et al.</i> ⁷²
~ 1775–1540 (br.)	H ₂ O	Hagen <i>et al.</i> ; ⁶¹ Givan <i>et al.</i> ⁶²
1508 (w.)	CS ₂	Yamada & Person; ⁷³ Sivaraman ⁷⁴
1351 (w.)	SO ₂	Schrifer-Mazzuoli <i>et al.</i> ; ⁷⁵ Yarnall & Hudson; ⁶⁷ Mifsud <i>et al.</i> ⁷⁶
1303	CH ₄	Chapados & Cabana; ⁶³ Gerakines & Hudson ⁶⁴
1246 (v. w.)	H ₂ CO	Hudson <i>et al.</i> ⁷²
1196 (w.)	CH ₂ OH	Jacox & Milligan; ⁷⁷ Bennett & Kaiser; ⁴⁰ Bennett <i>et al.</i> ; ⁴¹ Chen <i>et al.</i> ⁷¹
1161 (w.)	HCOOCH ₃ or CH ₃ OCH ₃	Terwisscha van Scheltinga <i>et al.</i> ; ^{78,79} Hudson <i>et al.</i> ⁸⁰
1089	CH ₃ CH ₂ OH or CH ₃ OCH ₃ or HOCH ₂ CH ₂ OH	Hudson <i>et al.</i> ; ^{80–82} Chen <i>et al.</i> ; ⁷¹ Terwisscha van Scheltinga <i>et al.</i> ⁷⁸
1062 (v. w.)	HSO ₃ ⁻ or SO ₄ ²⁻ or HCOOH (?)	Moore <i>et al.</i> ; ⁸³ Loeffler <i>et al.</i> ; ⁸⁴ Bergantini <i>et al.</i> ; ⁸⁵ Kaňuchová <i>et al.</i> ¹⁴
954 (v. w.)	S ₂ O ₅ ²⁻ or H ₂ SO ₄	Moore <i>et al.</i> ; ⁸³ Loeffler <i>et al.</i> ; ⁸⁴ Kaňuchová <i>et al.</i> ¹⁴
916 (v. w.)	HCOOCH ₃ or CH ₃ OCH ₃	Bennett <i>et al.</i> ; ⁴¹ Terwisscha van Scheltinga <i>et al.</i> ; ^{78,79} Hudson <i>et al.</i> ⁸⁰
890 (v. w.)	CH ₃ CH ₂ OH or HOCH ₂ CH ₂ OH or HSO ₄ ⁻	Hudson <i>et al.</i> ; ^{81,82} Loeffler <i>et al.</i> ; ⁸⁴ Terwisscha van Scheltinga <i>et al.</i> ⁷⁸
866 (v. w.)	HOCH ₂ CH ₂ OH or HOCH ₂ CHO or CH ₃ COCH ₃	Hudson <i>et al.</i> ^{81,86}



most common products observed in our previous study on the irradiation of various neat ices (*e.g.*, O₂, CO, CO₂) on top of a layer of sulfur by 1 MeV He⁺ ions,³¹ and so their formation in the present experiment is not entirely surprising. However, it is interesting to note that these products appeared at very different fluence points in the present experiment: SO₂ was formed early on, with tell-tale signs of absorption at 1351 cm⁻¹ being detected as early as delivered He⁺ ion fluences of 9.88 × 10¹² ions cm⁻². Conversely, the absorption band of CS₂ at 1508 cm⁻¹ only became detectable in acquired mid-infrared spectra at much higher fluences, starting at 6.01 × 10¹⁴ ions cm⁻².

Based on the results of previous mechanistical studies of sulfur radiation chemistry, it is possible to propose the most likely radical recombination reactions leading to the formation of SO₂ and CS₂.[†] In the case of SO₂, it is possible that a mechanism analogous to that described by Mayer⁸⁸ took place in the ice, in which electronically excited O₂ reacts with a sulfur allotrope S_n to yield a cyclic intermediate S_nO₂ which then decomposes to yield SO₂ and S_{n-1}. Alternatively, electronically excited sulfur atoms radiolytically liberated from the underlying allotropic layer may have undergone an insertion-type reaction with molecular oxygen, thereby directly yielding SO₂. This reaction has been demonstrated to be energetically barrierless at temperatures less than 40 K.^{89,90} Both these reaction mechanisms (Fig. 4) rely on the presence of O₂ within the ice. Although this species could not be detected in the present experiment due to it being infrared-inactive, it is nonetheless likely that it was formed to at least some extent as a result of the radiolytic processing of CH₃OH ice.

The reactions leading to the formation of CS₂ are somewhat more challenging to determine, as comparatively little prior astrochemical work has been performed with this molecule. Nonetheless, we propose a reaction scheme based on the known ability of CO molecules to capture sulfur atoms.⁹¹ In this scheme (Fig. 4), CO captures a radiolytically liberated and electronically excited sulfur atom to yield OCS which, upon capture of a second sulfur atom, produces some structural isomer of OCS₂, possibly dithiiranone or oxathiranethione.⁹²⁻⁹⁴ The OCS₂ intermediate, being unstable, may then decay to yield a variety of products, among which are CS₂ and atomic oxygen.^{93,94} We briefly note that neither OCS nor OCS₂ was detected in our experiments; however, this may be linked to the known radiolytic instability of these molecules,⁹² which may have precluded their accumulation in the irradiated ice. It is also important to note that the reaction between OCS and atomic sulfur need not necessarily yield OCS₂ and thence CS₂, as other reaction pathways have been identified by previous studies. For instance, a number of studies have demonstrated that this reaction may instead yield CO and S₂.⁹⁵⁻⁹⁹ Indeed, extensive branching of the reactions leading to the formation of CS₂ in this experiment may have limited the efficiency of its formation and may therefore explain the relatively

late appearance of CS₂ absorption features in acquired mid-infrared absorption spectra (Fig. 3, panel E).

In addition to SO₂ and CS₂, we have also found spectroscopic evidence for the formation of H₂SO₄ and a number of sulfur oxyanions, such as SO₄²⁻, HSO₄⁻, HSO₃⁻, and S₂O₅²⁻. The formation of these species as a result of the thermal and radiolytic processing of sulfur-rich ices mixed with H₂O (which, in our experiment, was present at fluences as early as 5.07 × 10¹³ ions cm⁻²) is well-known and has been described in detail by previous studies.^{1,13,14,19,83,84,100-109} This reaction scheme (Fig. 4) is thought to begin with the radiolytic formation of some structural isomer of H₂SO₂ from OH radicals and atomic sulfur.^{19,101} This lower oxoacid of sulfur then undergoes deprotonation followed by charge exchange with a neutral OH radical, before then reacting with another OH radical to yield HSO₃⁻.^{31,101} It is also possible for HSO₃⁻ to be formed as a result of the reaction between SO₂ and H₂O, giving off a proton in the process.^{14,51} Irrespective of how it is formed, HSO₃⁻ may then follow one of two reaction pathways: either dimerising to yield S₂O₅²⁻ (liberating H₂O in the process),^{14,51,110} or alternatively undergoing charge exchange with OH followed by reaction with a second OH radical accompanied by deprotonation to yield HSO₄⁻.^{31,101} This species may then undergo either protonation to yield H₂SO₄ or deprotonation to yield SO₄²⁻. We note that, as demonstrated by the experiments of Loeffler *et al.*,^{84,107} it is possible that the HSO₄⁻ and SO₄²⁻ products observed in our experiments are actually associated with H₂SO₄ as the monohydrate and tetrahydrate acids.

Finally, we sought evidence of the formation of organosulfur molecules and H₂S as a result of the irradiation of CH₃OH ice on top of a layer of sulfur. By examining difference spectra acquired during irradiation (Fig. 3, panels B and C), it was possible to note the emergence of a moderately intense band at 2976 cm⁻¹ as well as a very weak, broad absorption feature across the 2600–2525 cm⁻¹ wavenumber range. The positions of these bands are broadly coincident with the C–H and S–H stretching modes of thiol molecules and H₂S,⁶⁵⁻⁶⁸ which led us to suspect the presence of these molecules as radiolytic products. To better assess whether these molecules are indeed products in this experiment, we have directly compared these absorption bands with reference spectra of neat solid H₂S, methanethiol (CH₃SH), and ethanethiol (CH₃CH₂SH) acquired under low-temperature conditions (Fig. 5).⁶⁵⁻⁶⁸

Looking first at the S–H stretching mode of these molecules at approximately 2550 cm⁻¹, it is possible to note that the peaks of these bands are red-shifted by 18–42 cm⁻¹ compared to that observed in the present experiment (Fig. 5, panel A). Although this is a considerable shift, it should be noted that the positions of mid-infrared absorption bands of various sulfur-bearing molecules in low-temperature ice matrices have been reported to shift significantly depending on the composition of the matrix. For example, previous spectroscopic studies have shown that the S–H stretching mode of H₂S appears at about 2552 cm⁻¹ in the neat ice,^{67,68,111} but red-shifts to 2540 cm⁻¹ in a CH₃OH ice matrix and blue-shifts to 2561 and 2566 cm⁻¹ in H₂O and CO matrices, respectively.^{83,112} Furthermore, studies on the matrix isolation

[†] Although it is important to note that reactions mediated by ions may also contribute to the synthesis of SO₂ and CS₂ in our experiment, such reactions in low-temperature solids are poorly constrained and so will not be discussed any further here.



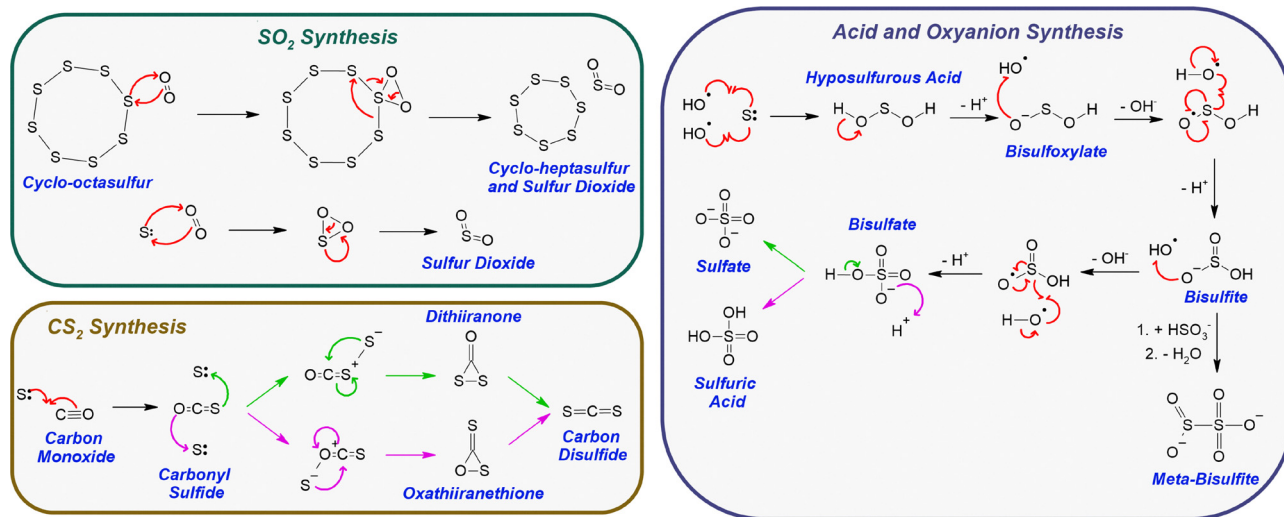


Fig. 4 Proposed mechanistic steps leading to the formation of the inorganic sulfur-bearing products of the irradiation of CH_3OH ice on top of sulfur using 1 MeV He^+ ions. Names of the sulfur-bearing products and intermediates in each scheme are given in blue text. Note that the mechanism proposed for the formation of CS_2 (especially the final step in which dithiirane or oxathiirane decays to CS_2 and atomic oxygen) is tentative and further studies are required to identify the exact route of formation of this molecule.

mid-infrared spectroscopy of H_2S in noble gas and N_2 matrices have demonstrated that this absorption feature may be blue-shifted to wavenumbers as high as 2649 cm^{-1} .^{113–116} Although we are unaware of any quantitative studies on the shifting of the S–H stretching mode of thiols when condensed at low temperatures in different matrices, we note that significant shifting has been observed for other sulfur-bearing molecules, such as OCS ,⁹² and so it is reasonable to assume that such composition-dependent shifting of bands also occurs in thiols.

Therefore, the match between the band observed at 2570 cm^{-1} in the present experiment and the S–H stretching modes of neat H_2S and the lower homologue thiols can be considered to be reasonable (Fig. 5, panel A), if not definitive. Further support for the presence of thiols was sought at higher wavenumber regions of the spectrum, where the C–H stretching modes of these molecules would be expected.^{65,66} In the present experiment, a band was observed to emerge at 2976 cm^{-1} as a result of irradiation (Fig. 3, panel B). Comparison of the position of this band to the C–H stretching modes of CH_3SH does not yield a good match; however, a very good match (*i.e.*, within 1 cm^{-1}) is observed with one of the bands associated with the C–H stretching mode of $\text{CH}_3\text{CH}_2\text{SH}$, although no matches could be made with the remaining bands (Fig. 5, panel B). We therefore conclude that although it is not possible to exclude the possible contribution of thiol molecules to the emergent band at 2976 cm^{-1} , there is insufficient evidence to propose that these molecules are indeed present. In the absence of other analytical techniques (*e.g.*, mass spectrometry) that could provide additional support for the presence of H_2S and organic thiol molecules as radiolytic products in the present experiment, the identification of these species must remain tentative and inconclusive, respectively.

Nevertheless, if H_2S and thiols are indeed present within the irradiated ice environment, then it is necessary to consider a plausible reaction sequence that could eventually lead to their

formation (Fig. 6). We speculate that H_2S is formed directly as a result of the hydrogenation of atomic sulfur liberated from the underlying allotropic layer. Our analysis of the non-sulfur-bearing radiolytic products observed in this experiment has already determined that the removal of hydrogen atoms from CH_3OH is an efficient process, and thus atomic hydrogen should be readily available to react with atomic sulfur. To the best of our knowledge, this hydrogenation reaction has not yet been studied experimentally under astrochemical conditions; however, computational studies have suggested that it is a favourable process which produces SH radicals as an intermediate species.^{32,117–119} Indeed, these SH radicals are the likely contributors to the formation of thiols: Santos *et al.*¹²⁰ recently demonstrated that these radicals are reactive under low-temperature astrochemical conditions, and may contribute to the formation of sulfur-bearing complex organic molecules (including thiols) when in the presence of organic species. Therefore, a perhaps straightforward route towards the formation of CH_3SH would be the radical combination reaction between SH and CH_3 ; this latter species being yielded either as a result of the radiolysis of CH_3OH or as a result of the dehydrogenation of CH_4 . The dehydrogenation of CH_3SH to CH_2SH radicals may also lead to the formation of $\text{CH}_3\text{CH}_2\text{SH}$ as a result of the radical addition reaction with CH_3 . Higher order thiol homologues may also be present within the ice, although it is likely that their abundance decreases with increasing chain length and branching. As such, we consider CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$ to be the most plausible thiol products in this experiment.

4 Astrochemical implications and conclusions

In this study, we exposed solid CH_3OH on top of a layer of allotropic sulfur at 25 K to 1 MeV He^+ ions in order to mimic the



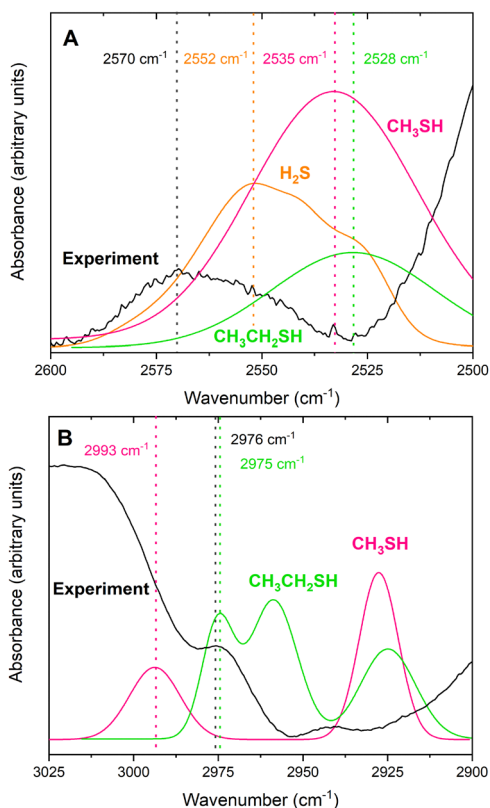


Fig. 5 Comparison of the absorption bands tentatively assigned to H_2S and thiols to reference spectra of these molecules. The reference spectrum of neat amorphous H_2S was taken from the work of Mifsud *et al.*,⁶⁸ while those of neat amorphous CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$ were digitised from the work of Hudson and Gerakines.⁶⁶ Note that the experimental spectra are difference spectra acquired at a fluence of 1×10^{15} ions cm^{-2} , while the intensities of the H_2S , CH_3SH , and $\text{CH}_3\text{CH}_2\text{SH}$ bands have been adjusted for ease of comparison.

processing of CH_3OH astrophysical ices on top of sulfur-rich interstellar dust grains or outer Solar System sulfur deposits by space radiation (*e.g.*, galactic cosmic rays or stellar winds). Of course, it is to be acknowledged that the compositional configuration of our experimental simulation is a simplified version of what may be expected in actual astrophysical ices,

where it is more likely that CH_3OH is mixed with other volatile ices and elemental sulfur is dispersed or chemically bound within refractory matrices. Nevertheless, such an experiment still provides useful insights into the radiation-driven chemical evolution of sulfur-bearing molecules in interstellar and outer Solar System environments. Our work, which builds upon our previous experimental efforts,³¹ has demonstrated that, aside from those products routinely observed as a result of the irradiation of CH_3OH ice, a number of sulfur-bearing products were observed to form, including SO_2 , CS_2 , H_2SO_4 , SO_4^{2-} , HSO_4^- , HSO_3^- , $\text{S}_2\text{O}_5^{2-}$ and, tentatively, H_2S . Insufficient evidence was found to substantiate the possible presence of simple thiols such as CH_3SH and $\text{CH}_3\text{CH}_2\text{SH}$.

These results have broad implications for our understanding of sulfur astrochemistry in both interstellar and outer Solar System environments, both of which continue to pose challenges to the research community.¹ In the context of interstellar chemistry, our results relate directly to the so-called ‘sulfur depletion problem’, wherein observed abundances of sulfur in diffuse nebulae align with its expected cosmic abundance but those observed in denser nebulae are up to three orders of magnitude lower than the expected cosmic abundance.^{9,121} Although the exact nature of the reservoir in which this ‘depleted sulfur’ is stored is still debated, increasing attention is being paid to the potential role of sulfur allotropes (which do not absorb over the mid-infrared¹²² and thus would not be detectable by telescopes operating in this spectroscopic range thereby contributing to the apparent depletion) in accommodating this missing sulfur. A potential mechanism for explaining the accumulation of allotropic sulfur chains and rings was proposed by Ruffle *et al.*,⁹ who suggested that S^+ ions in the diffuse interstellar medium undergo Coulomb-enhanced adsorption to negatively charged dust grains as the density of the medium increases in its evolution towards a pre-stellar nebula.

Several experimental studies have now also demonstrated that the irradiation of simple sulfur-bearing molecules (*e.g.*, H_2S or SO_2) under conditions relevant to dense, pre-stellar nebulae by ions and electrons mimicking space radiation results in the efficient production of sulfur allotropes.^{10–18} Indeed, recent work by Herath *et al.*¹⁸ has suggested that the irradiation of

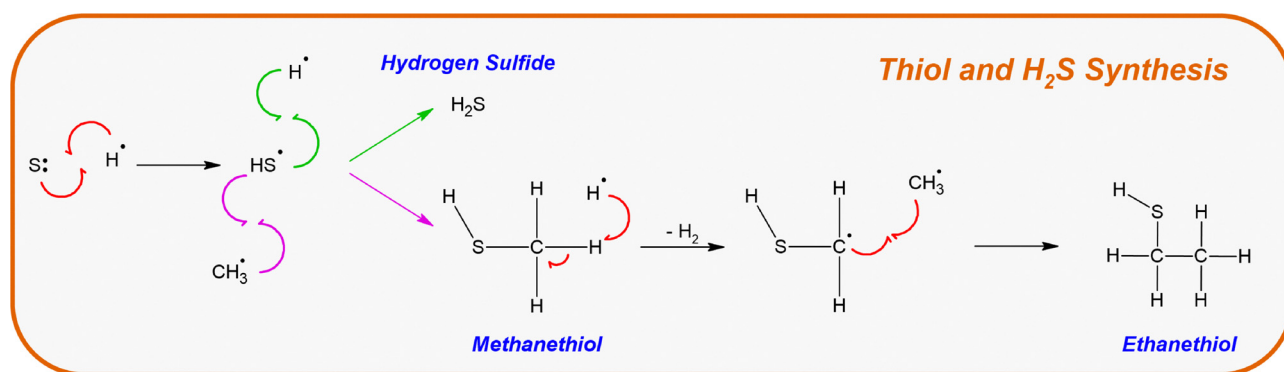


Fig. 6 Proposed mechanistic steps leading to the formation of H_2S and simple thiols as a result of irradiating CH_3OH ice on top of sulfur using 1 MeV He^+ ions. Names of sulfur-bearing products are given in blue text.



solid H₂S in the Taurus molecular cloud (a dense interstellar nebula home to hundreds of young stellar objects approximately 430 light-years away from the Earth) may produce 2.1×10^{27} kg of cyclo-octasulfur, which equates to just over 350 times the weight of the Earth. Such a result complements the previous finding of Cazaux *et al.*,¹⁰ whose Monte Carlo simulations demonstrated that refractory allotropic sulfur chains are formed as a result of the photo-processing of solid H₂S.

The formation of allotropic sulfur under interstellar nebula conditions has therefore been established, and the possibility of allotropic sulfur being a significant reservoir is seemingly plausible. This raises the question as to whether this allotropic sulfur is a participant in the radiolytic chemistry triggered in interstellar icy grain mantles within dense nebulae as a result of their interaction with galactic cosmic rays and stellar winds. Drawing inspiration from previous experimental studies that demonstrated that the irradiation of carbon-free ices on top of carbon-rich refractory materials results in the synthesis of CO and CO₂ in the ice phase,^{25–30} we sought to determine whether analogous reactions are possible when using a refractory sulfur layer. In our previous work,³¹ we showed that this is indeed the case, and that SO₂, CS₂, OCS, and H₂SO₄ hydrates are formed as a result of irradiating various neat ices (*i.e.*, O₂, CO, CO₂, and H₂O) on top of a layer of sulfur at 20 K using 1 MeV He⁺ ions. However, in that study, no detections of H₂S or organosulfur molecules were made.

We have extended our previous study³¹ by now considering the irradiation of CH₃OH, which is the most abundant complex organic molecule in interstellar icy grain mantles,¹²³ on top of a layer of allotropic sulfur. The irradiation of neat CH₃OH is known to result in a large number of complex organic species^{40–49} which, in the presence of allotropic sulfur, may be converted to organosulfur molecules. Moreover, it was hoped that the high hydrogen atom density on the CH₃OH molecule may be conducive to the synthesis of H₂S. Our results could only identify tentative evidence for the formation of H₂S, and inconclusive evidence for the formation of thiols such as CH₃SH and CH₃CH₂SH. The appearance of a broad but very weak absorption band centred at 2570 cm⁻¹ is seemingly coincident with the expected position of the S–H stretching modes of these molecules (Fig. 3 and 5). However, a poorer match between the emergent band at 2976 cm⁻¹ and the C–H stretching modes of the thiols means that we are unable to definitively state whether thiol molecules are indeed present as radiolytic products. That being said, the weak intensity of the putative S–H stretching mode at 2570 cm⁻¹ should not be considered to be evidence against the radiolytic synthesis of H₂S, since it is known that the formation of this molecule as a result of the hydrogenation of HS radicals can result in the reactive desorption of the H₂S product,¹²⁴ thereby reducing the yield in the ice phase.

What is more certain, however, is the synthesis of SO₂ and CS₂ in the present experiment, whose absorption features were definitively identified in acquired mid-infrared spectra (Fig. 3). A key finding of our study is the comparatively early synthesis of SO₂ compared to CS₂; the former being observed at ion fluences 60 times lower than the latter. Making use of literature data on

the lifetimes of interstellar ices and the 1 MeV He⁺ ion cosmic ray flux in dense nebulae, together with a few assumptions, it is possible to estimate the exposure time required to synthesise SO₂ and CS₂ from CH₃OH-rich ices on top of sulfur-rich interstellar dust grains. Moore *et al.*¹²⁵ gave the flux of 1 MeV protons in dense interstellar nebulae to be 10⁶ eV cm⁻² s⁻¹. Assuming that the average proton-to-helium ion compositional ratio of $\approx 9:1$ ¹²⁶ is invariant with particle energy and stopping power, this yields a 1 MeV He⁺ flux of 1.11×10^5 eV cm⁻² s⁻¹. If it is further assumed that all the kinetic energy of the projectile ions used in the present experiment was deposited into the ice-sulfur structure and that losses to processes such as ion recoil or bremsstrahlung are negligible, then the energy fluences at which SO₂ and CS₂ were first observed in the present experiment may be calculated to be 9.88×10^{18} and 6.01×10^{20} eV cm⁻², respectively. Dividing these energy fluences by the 1 MeV He⁺ ion cosmic ray flux derived earlier yields the exposure time required for SO₂ and CS₂ to be synthesised in this manner in dense interstellar nebulae. These exposure times are calculated to be 2.8×10^6 years (SO₂) and 1.7×10^8 years (CS₂). Given that the lifetime of interstellar ices in dense nebulae is thought to be about 10⁷ years,^{127,128} it is clear that the time required to generate CS₂ as a result of the irradiation of CH₃OH-rich ices on top of sulfur-rich dust grains exceeds the lifetime of the ice.

Of course, it is important to emphasise that these calculated exposure times are estimates that may be influenced by a number of factors. For instance, it is likely that the summed contribution to irradiative processing by other ions in galactic cosmic rays (particularly the more abundant protons) will reduce the time needed for SO₂ and CS₂ to be synthesised in this manner. Conversely, it is also possible that the rate of SO₂ and CS₂ synthesis in the present experiment was enhanced compared to what may be expected in actual astrophysical ices, where concentrations of CH₃OH and sulfur are very likely to be more dilute.

Nevertheless, this finding is particularly interesting in light of the fact that solid-phase SO₂ has been detected in astronomical observations of dense, quiescent, pre-stellar nebulae whereas CS₂ has yet to be detected.^{129–131} Given that it is known that SO₂ in interstellar icy grain mantles is most likely a radiolytic product and is not formed as a result of non-energetic atom or radical addition reactions,^{31,132} and that prior experimental evidence shows that the same is likely true for any putative CS₂ in interstellar ices,³¹ our present results suggest that the radiolytic formation of CS₂ in CH₃OH-rich interstellar ices on top of sulfur-rich grains during the quiescent dense nebula phase is not possible, and that this formation would likely need to occur in later evolutionary stages of the nebula (*e.g.*, during core collapse and proto-stellar formation) that are characterised by higher fluxes of radiation. If further studies on the radiolytic synthesis of CS₂ from other interstellar ice compositions containing sulfur (including those in which the sulfur is dispersed within the ice rather than layered below it) also demonstrate the need for exposure ages longer than the lifetime of the interstellar ice in the dense, quiescent nebula, then this could point towards a generic trend in which CS₂ is formed in



the solid-phase only in the later evolutionary stages of interstellar nebulae.

Turning our attention to the utility of our results to understanding sulfur chemistry in Solar System environments, the experimental conditions under which our study was performed are perhaps most applicable to cometary bodies due to the low temperature (*i.e.*, 25 K) at which the irradiation was performed as well as the fact that many comets are known to be comparatively rich in CH₃OH (Table 2). Importantly, the small sulfur allotropes S₂ and S₃ have been detected on several comets; perhaps most notably on comet 67P/Churyumov–Gerasimenko by the ROSINA mass spectrometric instrument aboard the *Rosetta* mission.³⁹ These small allotropes may be fragments of larger, more stable forms of sulfur present on the comet that could be active participants in radiolytically driven chemistry.

Our results suggest that, if the radiolytically driven reaction between CH₃OH and allotropic sulfur is indeed a significant contributor to the diversity of sulfur molecules detected on comets, then SO₂ and CS₂ should be among the most abundant neutral molecules present. Comparing this result to the known molecular composition of a number of comets (Table 2), it is possible to note that this is indeed the case. After H₂S (which is by far the most abundant cometary sulfur-bearing species), the most common sulfur molecules are SO₂, OCS, and CS₂ which are all present at abundances of a few tenths of a percent relative to H₂O. However, our results fail to reproduce the OCS and H₂S abundances in comets. As discussed previously, the non-detection of OCS in the present experiment is likely due to the known radiolytic instability of this molecule⁹² which would have precluded its formation and accumulation in the ice during irradiation by the He⁺ ion beam. Instead, previous experimental studies have suggested that OCS is predominantly formed as a result of solid-phase neutral-neutral reactions in pre-stellar nebulae,^{31,132,135–137} and so should have been preserved in cold ices that went on to form comets during the birth and evolution of the Solar System.

The high abundance of H₂S observed in comets (typically at least an order of magnitude greater than that of other sulfur-bearing molecules; see Table 2) is also likely the result of primordial H₂S formed in the pre-stellar nebula being incorporated into cold ices during Solar System evolution. As such, it is most likely that the chemistry leading to the formation of novel sulfur-bearing species in comets is overwhelmingly driven by the reaction of H₂S with other constituents of the cometary ice, and previous experimental studies have shown that such

reactions can lead to the formation of molecules such as H₂S₂, SO₂, CS₂, and OCS.^{83,92,138} Nevertheless, our results suggest that the radiolytically driven reaction between elemental sulfur and CH₃OH ice in comets and similar cold outer Solar System bodies may still contribute to the synthesis of novel sulfur-bearing molecules; even if such a reaction is not the dominant factor in controlling the overall sulfur chemistry.

Lastly, we note that the irradiation of CH₃OH ice on top of allotropic sulfur at 25 K also gave rise to a number of sulfur oxyanions, many of which are associated with solid H₂SO₄ hydrates at low temperatures (Fig. 3 and Table 1). In the outer Solar System, these species are perhaps best associated with the so-called ‘radiolytic sulfur cycle’ occurring on the icy surface of Jupiter’s moon Europa wherein radiation from the giant Jovian magnetosphere drives the cycling of sulfur through different molecular forms over a timescale of approximately 4000 years.²⁰ A key species in this cycle is elemental sulfur, which is believed to form as a result of the radiation-induced reduction of SO₂.^{11,14,16,139} Observational evidence for the existence of polymeric forms of sulfur on the surface of Europa, likely formed as a result of the irradiation of lower allotropes, has also been demonstrated.²⁰ The key reactions in which elemental sulfur is involved are oxidation-type processes that regenerate H₂SO₄ hydrates. Previous experimental work by Carlson *et al.*¹⁹ on the irradiation of sulfur grains frozen in H₂O ice at 77 K demonstrated the synthesis of SO₄²⁻ anions, and that the amount of SO₄²⁻ formed is dependent on the weight fraction of sulfur in the mixture as well as on the size of the grains. These results echoed the results of previous studies on the gamma-ray irradiation of colloidal suspensions of sulfur, which demonstrated the facile synthesis of H₂SO₄.^{100,101,140} Our recent experiments on the irradiation of H₂O ice deposited on top of a layer of allotropic sulfur at 70 K using 1 MeV He⁺ ions also demonstrated the efficient formation of H₂SO₄ hydrates,³¹ thus corroborating the results of previous studies.

In this present work, we have demonstrated that H₂SO₄ hydrates can also be produced as a result of the irradiation of CH₃OH ice on top of elemental sulfur. Although the presence of CH₃OH ice on Europa has yet to be confirmed, it is reasonable to assume that it is present as a minor surface component. This assumption is based on the known presence of CH₃OH in ices in pre-stellar nebulae¹²³ as well as its tentative detection on the surface of the icy ocean world Enceladus.¹⁴¹ Our present results therefore highlight the fact that the radiolytic regeneration of H₂SO₄ hydrates from elemental sulfur on Europa may also

Table 2 Abundances of CH₃OH and various sulfur-bearing molecules in a selection of comets relative to the abundance of H₂O. Data compiled from the works of Rodgers and Charnley,¹³³ Bockelée-Morvan *et al.*,¹³⁴ Calmonte *et al.*,²¹ and Rubin *et al.*²²

Comet	Abundance relative to H ₂ O							
	CH ₃ OH	H ₂ S	SO ₂	OCS	CS ₂	S ₂	CH ₃ SH	CH ₃ CH ₂ SH
67P/Churyumov–Gerasimenko	0.002	0.0110	0.0013	0.0004	0.00006	0.00002	0.0004	0.000006
C/1995 O1 (Hale–Bopp)	0.024	0.0100–0.0150	0.0015–0.0021	0.0028–0.0046	0.0020	—	—	—
C/1996 B2 (Hyakutake)	0.020	0.0054–0.0080	—	0.0010–0.0021	0.0010	< 0.00010	—	—
1P/Halley	0.018	0.0041	—	—	0.0020	—	—	—
153P/Ikeya–Zhang	0.025	0.0082	—	< 0.0020	< 0.0010	0.00004	—	—



proceed as a result of energetic processes involving CH_3OH , although there is some ambiguity as to whether the allotropic sulfur reacts directly with CH_3OH itself or with the H_2O produced as a result of its radiolysis. In any case, the presence of CH_3OH (and, presumably, any other icy species containing hydrogen and oxygen) on Europa presents another potential route to the formation of these acid hydrates, although the contribution of this reaction to the overall abundance of acid hydrates is anticipated to be significantly smaller due to the lower concentrations of CH_3OH on the European surface. Nevertheless, such a result is at the very least indicative of the potential complexity of the radiolytic sulfur cycle taking place on Europa.

In conclusion, the results of this mid-infrared spectroscopic study demonstrated that the irradiation of CH_3OH ice on top of elemental sulfur at 25 K using 1 MeV He^+ ions as a mimic of space radiation results in the synthesis of a number of new molecules similar to those obtained during the irradiative processing of neat CH_3OH ice (including several complex organic molecules), as well as various sulfur-bearing species. These sulfur-bearing molecules include SO_2 , CS_2 , H_2SO_4 , and the sulfur oxyanions SO_4^{2-} , HSO_4^- , HSO_3^- , and $\text{S}_2\text{O}_5^{2-}$. Tentative evidence for the formation of H_2S was also observed, while the identification of thiol molecules was inconclusive. These results underscore the complexity of radiolytically driven sulfur chemistry in astrophysical environments, and also highlight the role played in this chemistry by allotropic sulfur.

Author contributions

Conceptualisation: D. V. Mifsud, O. Auriacombe; data Curation: D. V. Mifsud, Z. Kaňuchová; formal analysis: D. V. Mifsud; funding acquisition: O. Auriacombe, S. Ioppolo, N. J. Mason; investigation: D. V. Mifsud, P. Herczku, S. T. S. Kovács, R. Rácz, B. Sulik, Z. Juhász; methodology: D. V. Mifsud, P. Herczku, S. T. S. Kovács, R. Rácz, B. Sulik, Z. Juhász; project administration: D. V. Mifsud, D. Qasim, S. Ioppolo, N. J. Mason; resources: O. Auriacombe, I. Vajda, I. Rajta, S. Biri, S. Ioppolo, N. J. Mason; supervision: S. Ioppolo, N. J. Mason; validation: D. V. Mifsud, P. Herczku, S. T. S. Kovács, R. Rácz, D. Qasim, B. Sulik, Z. Juhász, U. Raut; writing – original draft: D. V. Mifsud; writing – review & editing: D. V. Mifsud, Z. Kaňuchová, O. Auriacombe, P. Herczku, R. Rácz, S. T. S. Kovács, D. Qasim, B. Sulik, Z. Juhász, I. Vajda, I. Rajta, U. Raut, S. Biri, S. Ioppolo, N. J. Mason.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article in the form of raw mid-infrared absorption spectra are available online at the Mendeley Data repository (DOI: <https://doi.org/10.17632/grzgmwcpm.1>).

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