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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 H<sub>2</sub>S. Using *in situ* mid-infrared absorption spectroscopy, we have found compelling evidence for the formation of SO<sub>2</sub>, CS<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, and a number of sulfur oxyanions, as well as tentative evidence for H<sub>2</sub>S 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,<sup>1</sup> 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<sup>2,3</sup> and in interplanetary dust particles<sup>4,5</sup> 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<sup>6,7</sup>

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.<sup>8</sup>

Allotropes of elemental sulfur are also believed to be abundant in astrophysical media: Ruffle *et al.*<sup>9</sup> suggested a mechanism by which interstellar gas-phase S<sup>+</sup> 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.*<sup>10</sup> demonstrated that these adsorbed and neutralised ions could be converted to large allotropes within a few 10<sup>4</sup> 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.<sup>10–18</sup> 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.<sup>19,20</sup> Moreover, allotropes of sulfur have been detected in comets such as 67P/Churyumov–Gerasimenko<sup>21,22</sup> and asteroids such as 162173 Ryugu.<sup>23</sup>

Recent work by Ferrari *et al.*<sup>24</sup> has shown that the fragmentation, and presumably subsequent reaction, of the S<sub>8</sub> 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 CO<sub>2</sub>, in the ice phase.<sup>25–30</sup>

To test this hypothesis, we recently performed experiments on the irradiation of a number of neat interstellar ice analogues (*i.e.*, O<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O) on top of an allotropic sulfur layer using 1 MeV He<sup>+</sup> ions as mimics of galactic cosmic rays.<sup>31</sup> Experiments were nominally performed at 20 K, although those involving neat CO<sub>2</sub> and H<sub>2</sub>O 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 SO<sub>2</sub>, CS<sub>2</sub>, OCS, and H<sub>2</sub>SO<sub>4</sub> hydrates, and experiments performed at 70 K provided greater yields of these molecules.<sup>31</sup> 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 CO<sub>2</sub> ices on top of allotropic sulfur and, additionally, we did not detect the formation of H<sub>2</sub>S after the irradiation of H<sub>2</sub>O ice on a layer of allotropic sulfur.

Such results are particularly interesting since both H<sub>2</sub>S and organosulfur molecules have been proposed to be potentially significant reservoirs of sulfur in interstellar environments. In the case of H<sub>2</sub>S, it is envisaged that the formation of this molecule proceeds as a result of the hydrogenation of sulfur atoms adsorbed on dust grains<sup>9,32</sup> based on the previous laboratory observation of the analogous formation of CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O as a result of the hydrogenation of surface-adsorbed carbon, nitrogen, and oxygen atoms, respectively.<sup>33–36</sup> In the case of organosulfur molecules, computational work by Laas and Caselli<sup>37</sup> 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 H<sub>2</sub>S the most abundant sulfur-bearing molecule, but that complex organosulfur molecules are also present on the comet.<sup>21,22,38,39</sup>

In this article, we describe the results of an infrared spectroscopic study aimed at extending the results of our previous study<sup>31</sup> and better assessing the potential formation of H<sub>2</sub>S 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

CH<sub>3</sub>OH ice, prepared by condensation of the vapour on a layer of allotropic sulfur, using 1 MeV He<sup>+</sup> ions as a mimic of space radiation. The selection of CH<sub>3</sub>OH 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<sup>40–49</sup> which, in the presence of allotropic sulfur, may possibly induce the formation of organosulfur species. Moreover, the high hydrogen atom density in the CH<sub>3</sub>OH molecule may increase the propensity for radiolytic H<sub>2</sub>S 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.<sup>31</sup> 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.<sup>50,51</sup> 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

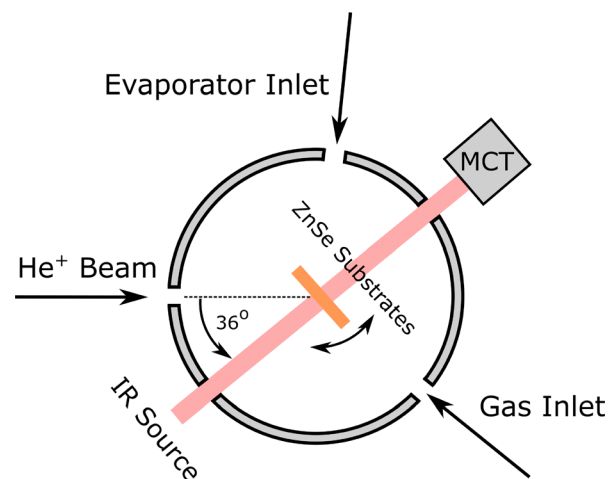


Fig. 1 Simplified top-view schematic diagram of the ICA set-up. Details on how the set-up was used to prepare and radiolytically process a CH<sub>3</sub>OH ice on top of a sulfur layer can be found in text. Image reproduced with permission from Mifsud *et al.*<sup>31</sup>



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  $78 \pm 3$  °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 ( $\sim 4$   $\mu\text{m}$ ) 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  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  ice could be followed *in situ* using Fourier-transform mid-infrared transmission absorption spectroscopy over the  $4000\text{--}650$   $\text{cm}^{-1}$  range, thus allowing the amount of icy material deposited to be quantified. The molecular column density  $N$  (molecules  $\text{cm}^{-2}$ ) of a deposited astrophysical ice analogue is related to the integrated absorbance  $S$  ( $\text{cm}^{-1}$ ) of one of its characteristic absorption bands as:

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

where  $A_\nu$  is the so-called integrated strength constant of that band ( $\text{cm molecule}^{-1}$ ). The column density of a deposited ice is related to its thickness  $h$  ( $\mu\text{m}$ ) as:

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

where  $M$  is the molar mass of the ice ( $\text{g mol}^{-1}$ ),  $\rho$  is the ice density ( $\text{g cm}^{-3}$ ), and  $N_A$  is the Avogadro constant. In the case of  $\text{CH}_3\text{OH}$ ,  $M = 32$   $\text{g mol}^{-1}$  and  $\rho$  (25 K) =  $0.636$   $\text{g cm}^{-3}$ .<sup>52</sup> Furthermore, we have adopted an integrated strength constant of  $1.61 \times 10^{-17}$   $\text{cm molecule}^{-1}$  for the C–O stretching mode located at approximately  $1030$   $\text{cm}^{-1}$ .<sup>52</sup>

The  $\text{CH}_3\text{OH}$  astrophysical ice analogue prepared in this study was grown to a thickness of  $1.3$   $\mu\text{m}$  (*i.e.*, a column density of  $1.56 \times 10^{18}$  molecules  $\text{cm}^{-2}$ ), after which a mid-infrared absorption spectrum was acquired. The ice-dust analogue was then exposed to a 1 MeV  $\text{He}^+$  ion beam supplied by a 2 MV Tandem accelerator<sup>53,54</sup>, with incident ions striking the ice at an angle of  $36^\circ$  to the surface normal. Using the *Stopping and Range of Ions in Matter* software,<sup>55</sup> the maximum range of the projectile ions in the ice-dust analogue was calculated to be  $3.5$   $\mu\text{m}$ . Overall, the ice-dust analogue was irradiated to a total fluence of  $10^{15}$  ions  $\text{cm}^{-2}$  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  $1$   $\text{cm}^{-1}$ .

### 3 Results and discussion

The mid-infrared absorption spectrum of  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  acquired at low temperatures.<sup>56,57</sup> 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  $\text{He}^+$  ion beam resulted in the gradual decay of the  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  into their structure, a large number of products that formed exclusively from the radiolytic processing of  $\text{CH}_3\text{OH}$  (and thus did not include sulfur) could also be identified (Fig. 3 and Table 1). At low fluence ( $5.04 \times 10^{12}$  ions  $\text{cm}^{-2}$ ), a distinct absorption band could be identified at  $1726$   $\text{cm}^{-1}$  which could be attributed to the formation of  $\text{H}_2\text{CO}$  as a result of the radiation-induced dehydrogenation of  $\text{CH}_3\text{OH}$ .<sup>72</sup> This product accumulated as the delivered ion fluence increased, as could be



Fig. 2 Mid-infrared absorption spectra of  $\text{CH}_3\text{OH}$  ice on top of allotropic sulfur (black trace) and of an amorphous  $\text{CH}_3\text{OH}$  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.*<sup>58</sup> Note that spectra are shifted along the vertical axis for clarity.





Fig. 3 Mid-infrared spectra acquired during the irradiation of  $\text{CH}_3\text{OH}$  ice on top of a layer of allotropic sulfur by 1 MeV  $\text{He}^+$  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,  $\text{H}_2\text{CO}$  is also prone to radiolytic dehydrogenation, as evidenced by the appearance of new absorption bands at  $2138\text{ cm}^{-1}$  (due to  $\text{CO}$ )<sup>69</sup> and  $1843\text{ cm}^{-1}$  (due to  $\text{HCO}$ )<sup>40,41,70,71</sup> 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  $\text{H}_2\text{CO}$  absorption band at  $1726\text{ cm}^{-1}$  progressively declined as its radiolytic destruction became more efficient than its synthesis. It is to be noted that a band at  $1196\text{ cm}^{-1}$  attributable to  $\text{CH}_2\text{OH}$  was observed in acquired mid-infrared spectra,<sup>40,41,71,77</sup> thereby indicating that the radiation-induced loss of a single hydrogen atom from  $\text{CH}_3\text{OH}$  also occurred in our experiment.

Another radiolytic product that was formed early on in the experiment was  $\text{CH}_4$ , which was identified through its main absorption band at  $1303\text{ cm}^{-1}$  at a delivered ion fluence of  $5.04 \times 10^{12}\text{ ions cm}^{-2}$ .<sup>63,64</sup> Similar to the case of  $\text{H}_2\text{CO}$ , the abundance of  $\text{CH}_4$  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  $\text{CH}_4$  from  $\text{CH}_3\text{OH}$ , one of particular interest is the direct loss of atomic oxygen from the latter molecule<sup>41</sup> 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 CO<sub>2</sub> in the ice,<sup>41</sup> which was identified through its main absorption band at 2341 cm<sup>-1</sup>.<sup>59</sup> Interestingly, both the <sup>12</sup>C and <sup>13</sup>C isotopologues of CO and CO<sub>2</sub> were detected in our experiment.

The radiolytic formation of H<sub>2</sub>O was also observed starting at a fluence of 5.07 × 10<sup>13</sup> ions cm<sup>-2</sup>, but becoming really apparent in acquired mid-infrared spectra at fluences greater than 2.12 × 10<sup>14</sup> ions cm<sup>-2</sup>. Indeed, broad absorption bands attributable to H<sub>2</sub>O were detected between ~3630–3020 (coincident with CH<sub>3</sub>OH absorptions) and between ~1775–1540 cm<sup>-1</sup> (coincident with H<sub>2</sub>CO absorptions), and continued to grow with increasing ion fluence.<sup>61,62</sup> We exclude the possibility that the H<sub>2</sub>O 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 H<sub>2</sub>O during the 1 MeV He<sup>+</sup> ion irradiation of CH<sub>3</sub>OH on top of sulfur observed in this experiment is in good agreement with the observations of Palumbo *et al.*,<sup>87</sup> who studied the irradiation of neat CH<sub>3</sub>OH ice using 3 keV He<sup>+</sup> ions.

As noted previously, the irradiation of CH<sub>3</sub>OH 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<sup>-1</sup> (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,<sup>40–49,71,72,78–82,85,86</sup> 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 (CH<sub>3</sub>OCH<sub>3</sub>), methyl formate (HCOOCH<sub>3</sub>), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), acetone (CH<sub>3</sub>COCH<sub>3</sub>), ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH), and glycolaldehyde (HOCH<sub>2</sub>CHO) (see Table 1 for assignments).

We note that a small absorption band identified at 1062 cm<sup>-1</sup> as a shoulder to the intense CH<sub>3</sub>OH C–O stretching mode may have contributions from formic acid (HCOOH); specifically, from its C–H bending mode.<sup>85</sup> The radiolytic synthesis of HCOOH in our ice would be logical, especially given the detection of other, chemically related molecules such as H<sub>2</sub>CO and HCOOCH<sub>3</sub> (Fig. 3 and Table 1). However, to the best of our knowledge, the synthesis of HCOOH as a result of the irradiation of CH<sub>3</sub>OH has not been conclusively demonstrated by previous studies. Furthermore, the most intense absorption band in the spectrum of solid HCOOH at approximately 1700 cm<sup>-1</sup> (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 H<sub>2</sub>CO and H<sub>2</sub>O. 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 CH<sub>3</sub>OH, a number of sulfur-containing molecular products were also identified *via* mid-infrared absorption spectroscopy. Perhaps the most notable of these products were SO<sub>2</sub> and CS<sub>2</sub>, whose absorption features were observed at 1351 and 1508 cm<sup>-1</sup>, respectively.<sup>73–76</sup> 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 CH<sub>3</sub>OH ice on a layer of sulfur at 25 K using 1 MeV He<sup>+</sup> ions

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



most common products observed in our previous study on the irradiation of various neat ices (*e.g.*, O<sub>2</sub>, CO, CO<sub>2</sub>) on top of a layer of sulfur by 1 MeV He<sup>+</sup> ions,<sup>31</sup> 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: SO<sub>2</sub> was formed early on, with tell-tale signs of absorption at 1351 cm<sup>-1</sup> being detected as early as delivered He<sup>+</sup> ion fluences of 9.88 × 10<sup>12</sup> ions cm<sup>-2</sup>. Conversely, the absorption band of CS<sub>2</sub> at 1508 cm<sup>-1</sup> only became detectable in acquired mid-infrared spectra at much higher fluences, starting at 6.01 × 10<sup>14</sup> ions cm<sup>-2</sup>.

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 SO<sub>2</sub> and CS<sub>2</sub>.<sup>†</sup> In the case of SO<sub>2</sub>, it is possible that a mechanism analogous to that described by Mayer<sup>88</sup> took place in the ice, in which electronically excited O<sub>2</sub> reacts with a sulfur allotrope S<sub>n</sub> to yield a cyclic intermediate S<sub>n</sub>O<sub>2</sub> which then decomposes to yield SO<sub>2</sub> and S<sub>n-1</sub>. 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 SO<sub>2</sub>. This reaction has been demonstrated to be energetically barrierless at temperatures less than 40 K.<sup>89,90</sup> Both these reaction mechanisms (Fig. 4) rely on the presence of O<sub>2</sub> 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 CH<sub>3</sub>OH ice.

The reactions leading to the formation of CS<sub>2</sub> 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.<sup>91</sup> 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 OCS<sub>2</sub>, possibly dithiiranone or oxathiranethione.<sup>92-94</sup> The OCS<sub>2</sub> intermediate, being unstable, may then decay to yield a variety of products, among which are CS<sub>2</sub> and atomic oxygen.<sup>93,94</sup> We briefly note that neither OCS nor OCS<sub>2</sub> was detected in our experiments; however, this may be linked to the known radiolytic instability of these molecules,<sup>92</sup> 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 OCS<sub>2</sub> and thence CS<sub>2</sub>, 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 S<sub>2</sub>.<sup>95-99</sup> Indeed, extensive branching of the reactions leading to the formation of CS<sub>2</sub> in this experiment may have limited the efficiency of its formation and may therefore explain the relatively

late appearance of CS<sub>2</sub> absorption features in acquired mid-infrared absorption spectra (Fig. 3, panel E).

In addition to SO<sub>2</sub> and CS<sub>2</sub>, we have also found spectroscopic evidence for the formation of H<sub>2</sub>SO<sub>4</sub> and a number of sulfur oxyanions, such as SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, HSO<sub>3</sub><sup>-</sup>, and S<sub>2</sub>O<sub>5</sub><sup>2-</sup>. The formation of these species as a result of the thermal and radiolytic processing of sulfur-rich ices mixed with H<sub>2</sub>O (which, in our experiment, was present at fluences as early as 5.07 × 10<sup>13</sup> ions cm<sup>-2</sup>) is well-known and has been described in detail by previous studies.<sup>1,13,14,19,83,84,100-109</sup> This reaction scheme (Fig. 4) is thought to begin with the radiolytic formation of some structural isomer of H<sub>2</sub>SO<sub>2</sub> from OH radicals and atomic sulfur.<sup>19,101</sup> 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 HSO<sub>3</sub><sup>-</sup>.<sup>31,101</sup> It is also possible for HSO<sub>3</sub><sup>-</sup> to be formed as a result of the reaction between SO<sub>2</sub> and H<sub>2</sub>O, giving off a proton in the process.<sup>14,51</sup> Irrespective of how it is formed, HSO<sub>3</sub><sup>-</sup> may then follow one of two reaction pathways: either dimerising to yield S<sub>2</sub>O<sub>5</sub><sup>2-</sup> (liberating H<sub>2</sub>O in the process),<sup>14,51,110</sup> or alternatively undergoing charge exchange with OH followed by reaction with a second OH radical accompanied by deprotonation to yield HSO<sub>4</sub><sup>-</sup>.<sup>31,101</sup> This species may then undergo either protonation to yield H<sub>2</sub>SO<sub>4</sub> or deprotonation to yield SO<sub>4</sub><sup>2-</sup>. We note that, as demonstrated by the experiments of Loeffler *et al.*,<sup>84,107</sup> it is possible that the HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> products observed in our experiments are actually associated with H<sub>2</sub>SO<sub>4</sub> as the monohydrate and tetrahydrate acids.

Finally, we sought evidence of the formation of organosulfur molecules and H<sub>2</sub>S as a result of the irradiation of CH<sub>3</sub>OH 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<sup>-1</sup> as well as a very weak, broad absorption feature across the 2600–2525 cm<sup>-1</sup> wavenumber range. The positions of these bands are broadly coincident with the C–H and S–H stretching modes of thiol molecules and H<sub>2</sub>S,<sup>65-68</sup> 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 H<sub>2</sub>S, methanethiol (CH<sub>3</sub>SH), and ethanethiol (CH<sub>3</sub>CH<sub>2</sub>SH) acquired under low-temperature conditions (Fig. 5).<sup>65-68</sup>

Looking first at the S–H stretching mode of these molecules at approximately 2550 cm<sup>-1</sup>, it is possible to note that the peaks of these bands are red-shifted by 18–42 cm<sup>-1</sup> 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 H<sub>2</sub>S appears at about 2552 cm<sup>-1</sup> in the neat ice,<sup>67,68,111</sup> but red-shifts to 2540 cm<sup>-1</sup> in a CH<sub>3</sub>OH ice matrix and blue-shifts to 2561 and 2566 cm<sup>-1</sup> in H<sub>2</sub>O and CO matrices, respectively.<sup>83,112</sup> Furthermore, studies on the matrix isolation

<sup>†</sup> Although it is important to note that reactions mediated by ions may also contribute to the synthesis of SO<sub>2</sub> and CS<sub>2</sub> in our experiment, such reactions in low-temperature solids are poorly constrained and so will not be discussed any further here.



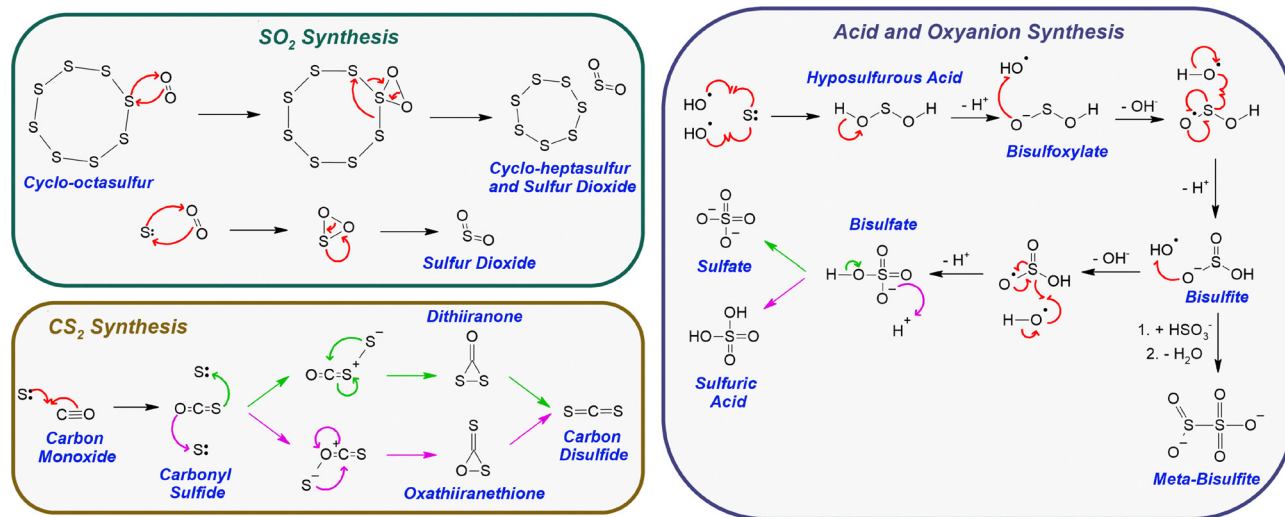


Fig. 4 Proposed mechanistic steps leading to the formation of the inorganic sulfur-bearing products of the irradiation of  $\text{CH}_3\text{OH}$  ice on top of sulfur using 1 MeV  $\text{He}^+$  ions. Names of the sulfur-bearing products and intermediates in each scheme are given in blue text. Note that the mechanism proposed for the formation of  $\text{CS}_2$  (especially the final step in which dithiirane or oxathiirane decays to  $\text{CS}_2$  and atomic oxygen) is tentative and further studies are required to identify the exact route of formation of this molecule.

mid-infrared spectroscopy of  $\text{H}_2\text{S}$  in noble gas and  $\text{N}_2$  matrices have demonstrated that this absorption feature may be blue-shifted to wavenumbers as high as  $2649\text{ cm}^{-1}$ .<sup>113–116</sup> 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  $\text{OCS}$ ,<sup>92</sup> 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  $2570\text{ cm}^{-1}$  in the present experiment and the S–H stretching modes of neat  $\text{H}_2\text{S}$  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.<sup>65,66</sup> In the present experiment, a band was observed to emerge at  $2976\text{ cm}^{-1}$  as a result of irradiation (Fig. 3, panel B). Comparison of the position of this band to the C–H stretching modes of  $\text{CH}_3\text{SH}$  does not yield a good match; however, a very good match (*i.e.*, within  $1\text{ cm}^{-1}$ ) 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  $2976\text{ cm}^{-1}$ , 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  $\text{H}_2\text{S}$  and organic thiol molecules as radiolytic products in the present experiment, the identification of these species must remain tentative and inconclusive, respectively.

Nevertheless, if  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  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  $\text{CH}_3\text{OH}$  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.<sup>32,117–119</sup> Indeed, these SH radicals are the likely contributors to the formation of thiols: Santos *et al.*<sup>120</sup> 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  $\text{CH}_3\text{SH}$  would be the radical combination reaction between SH and  $\text{CH}_3$ ; this latter species being yielded either as a result of the radiolysis of  $\text{CH}_3\text{OH}$  or as a result of the dehydrogenation of  $\text{CH}_4$ . The dehydrogenation of  $\text{CH}_3\text{SH}$  to  $\text{CH}_2\text{SH}$  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  $\text{CH}_3$ . 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  $\text{CH}_3\text{SH}$  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  $\text{CH}_3\text{OH}$  on top of a layer of allotropic sulfur at 25 K to 1 MeV  $\text{He}^+$  ions in order to mimic the





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

processing of  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  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,<sup>31</sup> has demonstrated that, aside from those products routinely observed as a result of the irradiation of  $\text{CH}_3\text{OH}$  ice, a number of sulfur-bearing products were observed to form, including  $\text{SO}_2$ ,  $\text{CS}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{HSO}_3^-$ ,  $\text{S}_2\text{O}_5^{2-}$  and, tentatively,  $\text{H}_2\text{S}$ . Insufficient evidence was found to substantiate the possible presence of simple thiols such as  $\text{CH}_3\text{SH}$  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.<sup>1</sup> 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.<sup>9,121</sup> 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-infrared<sup>122</sup> 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.*,<sup>9</sup> who suggested that  $\text{S}^+$  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.*,  $\text{H}_2\text{S}$  or  $\text{SO}_2$ ) under conditions relevant to dense, pre-stellar nebulae by ions and electrons mimicking space radiation results in the efficient production of sulfur allotropes.<sup>10–18</sup> Indeed, recent work by Herath *et al.*<sup>18</sup> has suggested that the irradiation of

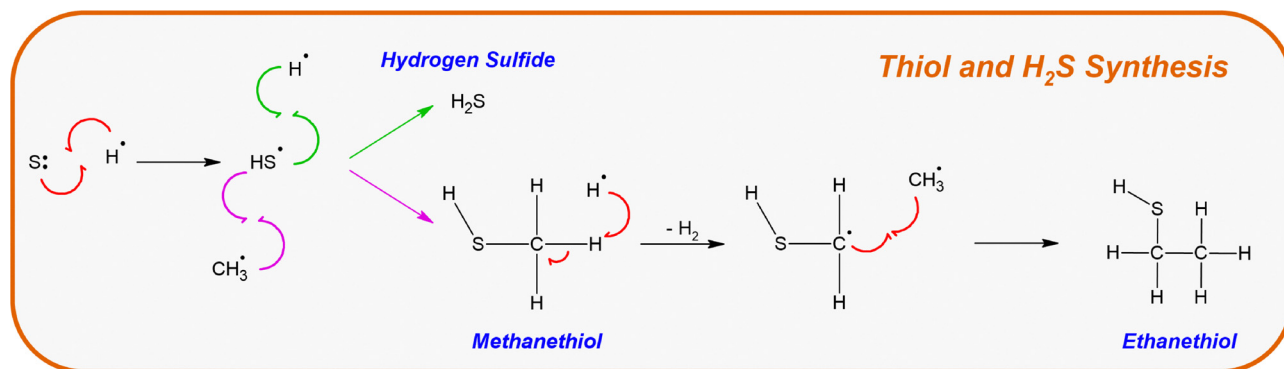


Fig. 6 Proposed mechanistic steps leading to the formation of  $\text{H}_2\text{S}$  and simple thiols as a result of irradiating  $\text{CH}_3\text{OH}$  ice on top of sulfur using 1 MeV  $\text{He}^+$  ions. Names of sulfur-bearing products are given in blue text.



solid H<sub>2</sub>S 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  $2.1 \times 10^{27}$  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.*,<sup>10</sup> whose Monte Carlo simulations demonstrated that refractory allotropic sulfur chains are formed as a result of the photo-processing of solid H<sub>2</sub>S.

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 CO<sub>2</sub> in the ice phase,<sup>25–30</sup> we sought to determine whether analogous reactions are possible when using a refractory sulfur layer. In our previous work,<sup>31</sup> we showed that this is indeed the case, and that SO<sub>2</sub>, CS<sub>2</sub>, OCS, and H<sub>2</sub>SO<sub>4</sub> hydrates are formed as a result of irradiating various neat ices (*i.e.*, O<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O) on top of a layer of sulfur at 20 K using 1 MeV He<sup>+</sup> ions. However, in that study, no detections of H<sub>2</sub>S or organosulfur molecules were made.

We have extended our previous study<sup>31</sup> by now considering the irradiation of CH<sub>3</sub>OH, which is the most abundant complex organic molecule in interstellar icy grain mantles,<sup>123</sup> on top of a layer of allotropic sulfur. The irradiation of neat CH<sub>3</sub>OH is known to result in a large number of complex organic species<sup>40–49</sup> 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 CH<sub>3</sub>OH molecule may be conducive to the synthesis of H<sub>2</sub>S. Our results could only identify tentative evidence for the formation of H<sub>2</sub>S, and inconclusive evidence for the formation of thiols such as CH<sub>3</sub>SH and CH<sub>3</sub>CH<sub>2</sub>SH. The appearance of a broad but very weak absorption band centred at 2570 cm<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> should not be considered to be evidence against the radiolytic synthesis of H<sub>2</sub>S, 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 H<sub>2</sub>S product,<sup>124</sup> thereby reducing the yield in the ice phase.

What is more certain, however, is the synthesis of SO<sub>2</sub> and CS<sub>2</sub> 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 SO<sub>2</sub> compared to CS<sub>2</sub>; 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<sup>+</sup> ion cosmic ray flux in dense nebulae, together with a few assumptions, it is possible to estimate the exposure time required to synthesise SO<sub>2</sub> and CS<sub>2</sub> from CH<sub>3</sub>OH-rich ices on top of sulfur-rich interstellar dust grains. Moore *et al.*<sup>125</sup> gave the flux of 1 MeV protons in dense interstellar nebulae to be 10<sup>6</sup> eV cm<sup>-2</sup> s<sup>-1</sup>. Assuming that the average proton-to-helium ion compositional ratio of  $\approx 9:1$ <sup>126</sup> is invariant with particle energy and stopping power, this yields a 1 MeV He<sup>+</sup> flux of  $1.11 \times 10^5$  eV cm<sup>-2</sup> s<sup>-1</sup>. 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 SO<sub>2</sub> and CS<sub>2</sub> were first observed in the present experiment may be calculated to be  $9.88 \times 10^{18}$  and  $6.01 \times 10^{20}$  eV cm<sup>-2</sup>, respectively. Dividing these energy fluences by the 1 MeV He<sup>+</sup> ion cosmic ray flux derived earlier yields the exposure time required for SO<sub>2</sub> and CS<sub>2</sub> to be synthesised in this manner in dense interstellar nebulae. These exposure times are calculated to be  $2.8 \times 10^6$  years (SO<sub>2</sub>) and  $1.7 \times 10^8$  years (CS<sub>2</sub>). Given that the lifetime of interstellar ices in dense nebulae is thought to be about 10<sup>7</sup> years,<sup>127,128</sup> it is clear that the time required to generate CS<sub>2</sub> as a result of the irradiation of CH<sub>3</sub>OH-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 SO<sub>2</sub> and CS<sub>2</sub> to be synthesised in this manner. Conversely, it is also possible that the rate of SO<sub>2</sub> and CS<sub>2</sub> synthesis in the present experiment was enhanced compared to what may be expected in actual astrophysical ices, where concentrations of CH<sub>3</sub>OH and sulfur are very likely to be more dilute.

Nevertheless, this finding is particularly interesting in light of the fact that solid-phase SO<sub>2</sub> has been detected in astronomical observations of dense, quiescent, pre-stellar nebulae whereas CS<sub>2</sub> has yet to be detected.<sup>129–131</sup> Given that it is known that SO<sub>2</sub> 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,<sup>31,132</sup> and that prior experimental evidence shows that the same is likely true for any putative CS<sub>2</sub> in interstellar ices,<sup>31</sup> our present results suggest that the radiolytic formation of CS<sub>2</sub> in CH<sub>3</sub>OH-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 CS<sub>2</sub> 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 CS<sub>2</sub> 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 CH<sub>3</sub>OH (Table 2). Importantly, the small sulfur allotropes S<sub>2</sub> and S<sub>3</sub> have been detected on several comets; perhaps most notably on comet 67P/Churyumov–Gerasimenko by the ROSINA mass spectrometric instrument aboard the *Rosetta* mission.<sup>39</sup> 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 CH<sub>3</sub>OH and allotropic sulfur is indeed a significant contributor to the diversity of sulfur molecules detected on comets, then SO<sub>2</sub> and CS<sub>2</sub> 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 H<sub>2</sub>S (which is by far the most abundant cometary sulfur-bearing species), the most common sulfur molecules are SO<sub>2</sub>, OCS, and CS<sub>2</sub> which are all present at abundances of a few tenths of a percent relative to H<sub>2</sub>O. However, our results fail to reproduce the OCS and H<sub>2</sub>S 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 molecule<sup>92</sup> which would have precluded its formation and accumulation in the ice during irradiation by the He<sup>+</sup> 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,<sup>31,132,135–137</sup> 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 H<sub>2</sub>S<sub>2</sub>, SO<sub>2</sub>, CS<sub>2</sub>, and OCS.<sup>83,92,138</sup> Nevertheless, our results suggest that the radiolytically driven reaction between elemental sulfur and CH<sub>3</sub>OH 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 CH<sub>3</sub>OH 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 H<sub>2</sub>SO<sub>4</sub> 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.<sup>20</sup> A key species in this cycle is elemental sulfur, which is believed to form as a result of the radiation-induced reduction of SO<sub>2</sub>.<sup>11,14,16,139</sup> 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.<sup>20</sup> The key reactions in which elemental sulfur is involved are oxidation-type processes that regenerate H<sub>2</sub>SO<sub>4</sub> hydrates. Previous experimental work by Carlson *et al.*<sup>19</sup> on the irradiation of sulfur grains frozen in H<sub>2</sub>O ice at 77 K demonstrated the synthesis of SO<sub>4</sub><sup>2-</sup> anions, and that the amount of SO<sub>4</sub><sup>2-</sup> 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 H<sub>2</sub>SO<sub>4</sub>.<sup>100,101,140</sup> Our recent experiments on the irradiation of H<sub>2</sub>O ice deposited on top of a layer of allotropic sulfur at 70 K using 1 MeV He<sup>+</sup> ions also demonstrated the efficient formation of H<sub>2</sub>SO<sub>4</sub> hydrates,<sup>31</sup> thus corroborating the results of previous studies.

In this present work, we have demonstrated that H<sub>2</sub>SO<sub>4</sub> hydrates can also be produced as a result of the irradiation of CH<sub>3</sub>OH ice on top of elemental sulfur. Although the presence of CH<sub>3</sub>OH 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 CH<sub>3</sub>OH in ices in pre-stellar nebulae<sup>123</sup> as well as its tentative detection on the surface of the icy ocean world Enceladus.<sup>141</sup> Our present results therefore highlight the fact that the radiolytic regeneration of H<sub>2</sub>SO<sub>4</sub> hydrates from elemental sulfur on Europa may also

**Table 2** Abundances of CH<sub>3</sub>OH and various sulfur-bearing molecules in a selection of comets relative to the abundance of H<sub>2</sub>O. Data compiled from the works of Rodgers and Charnley,<sup>133</sup> Bockelée-Morvan *et al.*,<sup>134</sup> Calmonte *et al.*,<sup>21</sup> and Rubin *et al.*<sup>22</sup>

Comet	Abundance relative to H <sub>2</sub> O							
	CH <sub>3</sub> OH	H <sub>2</sub> S	SO <sub>2</sub>	OCS	CS <sub>2</sub>	S <sub>2</sub>	CH <sub>3</sub> SH	CH <sub>3</sub> CH <sub>2</sub> 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  $\text{CH}_3\text{OH}$ , although there is some ambiguity as to whether the allotropic sulfur reacts directly with  $\text{CH}_3\text{OH}$  itself or with the  $\text{H}_2\text{O}$  produced as a result of its radiolysis. In any case, the presence of  $\text{CH}_3\text{OH}$  (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  $\text{CH}_3\text{OH}$  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  $\text{CH}_3\text{OH}$  ice on top of elemental sulfur at 25 K using 1 MeV  $\text{He}^+$  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  $\text{CH}_3\text{OH}$  ice (including several complex organic molecules), as well as various sulfur-bearing species. These sulfur-bearing molecules include  $\text{SO}_2$ ,  $\text{CS}_2$ ,  $\text{H}_2\text{SO}_4$ , and the sulfur oxyanions  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{HSO}_3^-$ , and  $\text{S}_2\text{O}_5^{2-}$ . Tentative evidence for the formation of  $\text{H}_2\text{S}$  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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