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# Electron irradiation and thermal chemistry studies of interstellar and planetary ice analogues at the ICA astrochemistry facility

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## 34 **Abstract**

35 The modelling of molecular excitation and dissociation processes relevant to astrochemistry  
36 requires the validation of theories by comparison with data generated from laboratory  
37 experimentation. The newly commissioned Ice Chamber for Astrophysics-Astrochemistry  
38 (ICA) allows for the study of astrophysical ice analogues and their evolution when subjected  
39 to energetic processing, thus simulating the processes and alterations interstellar icy grain  
40 mantles and icy outer Solar System bodies undergo. ICA is an ultra-high vacuum compatible  
41 chamber containing a series of IR-transparent substrates upon which the ice analogues may be  
42 deposited at temperatures of down to 20 K. Processing of the ices may be performed in one of  
43 three ways: (i) ion impacts with projectiles delivered by a 2 MV Tandatron-type accelerator,  
44 (ii) electron irradiation from a gun fitted directly to the chamber, and (iii) thermal processing  
45 across a temperature range of 20-300 K. The physico-chemical evolution of the ices is studied  
46 *in situ* using FTIR absorbance spectroscopy and quadrupole mass spectrometry. In this paper,  
47 we present an overview of the ICA facility with a focus on characterising the electron beams  
48 used for electron impact studies, as well as reporting the preliminary results obtained during  
49 electron irradiation and thermal processing of selected ices.

50

## 51 **1 Introduction**

52 The modelling of intense excitation processes in low-temperature ices has found applications  
53 in a wide variety of fields [1], but particularly in molecular astrophysics where such processes  
54 may lead to novel chemistry within the ice structure [2-5]. Interstellar and planetary ices may  
55 be modelled as dense gases experiencing weak intermolecular forces of attraction and restricted  
56 degrees of freedom. Although astrochemical modelling on its own may greatly contribute to  
57 our knowledge of extra-terrestrial chemistry, it is often necessary to perform comparative  
58 laboratory experiments so as to serve as a benchmark against which multi-scale models and  
59 theories may be tested and validated.

60 Accordingly, the establishment of experimental facilities where solid-phase astrochemistry  
61 may be investigated is an important aspect of the development of astrochemistry research. The  
62 recently commissioned Ice Chamber for Astrophysics-Astrochemistry (ICA), hosted by the  
63 Institute for Nuclear Research (Atomki) in Debrecen, is one such facility which is able to  
64 simulate various astrophysical environments (e.g. the interstellar medium, icy planetary and  
65 lunar surfaces, etc.) and quantitatively analyse the physico-chemical changes occurring in  
66 deposited astrophysical ice analogues as a result of energetic processing.

67 Within the context of interstellar and Solar System ice astrochemistry, one of the more notable  
68 forms of energetic processing is electron irradiation. The study of electron-induced chemistry  
69 in astrophysical environments is important as it is thought that such chemistry is a major route  
70 to the synthesis of molecules [6,7]. Non-thermal low-energy (<20 eV) electrons are produced  
71 as a result of the interaction between ionising radiation and matter and are believed to drive  
72 most of the radiolytic chemistry in astrophysical ices via a combination of impact ionisations,  
73 electronic excitations, and dissociative electron attachments [8]. Higher energy electrons are a  
74 component of galactic cosmic rays, planetary magnetospheric plasmas, and the solar wind [8-  
75 12] and their impact into ices may also engender radiochemical reactions via the ionisation of  
76 the atomic and molecular constituents of the ice.

77 Another significant form of processing to which astrophysical ices are subjected is thermal  
78 processing. Thermally-induced chemical reactions may occur in all astrophysical settings  
79 where temperatures are high enough to overcome the relevant activation energy barriers [13].  
80 This is especially important in the contexts of comets and icy outer Solar System moons, where  
81 such chemistry is not only known to be prevalent, but also leads to the formation of complex  
82 molecules of astrobiological relevance. For instance, the thermal processing of ices containing  
83 ammonia (NH<sub>3</sub>), methanimine (CH<sub>2</sub>NH<sub>2</sub>), and hydrogen cyanide (HCN) has been shown to  
84 yield aminoacetonitrile (NH<sub>2</sub>CH<sub>2</sub>CN); an important precursor to amino acids [14].

85 The importance of characterising the electron irradiation and thermal processing leading to  
86 interstellar and outer Solar System ice chemistry is therefore apparent. In this paper, we present  
87 a brief introduction to ICA so as to highlight some of its experimental capabilities with a focus  
88 on characterising the electron beam profiles used for electron irradiation studies. Additionally,  
89 we also present the results of the electron irradiation of amorphous methanol (CH<sub>3</sub>OH) ice at  
90 20 K and the thermal processing of an ice mixture composed of water (H<sub>2</sub>O) and sulphur  
91 dioxide (SO<sub>2</sub>) in order to further demonstrate the ability of the set-up to provide data which  
92 may be useful to the astrophysical and astrochemical modelling communities.

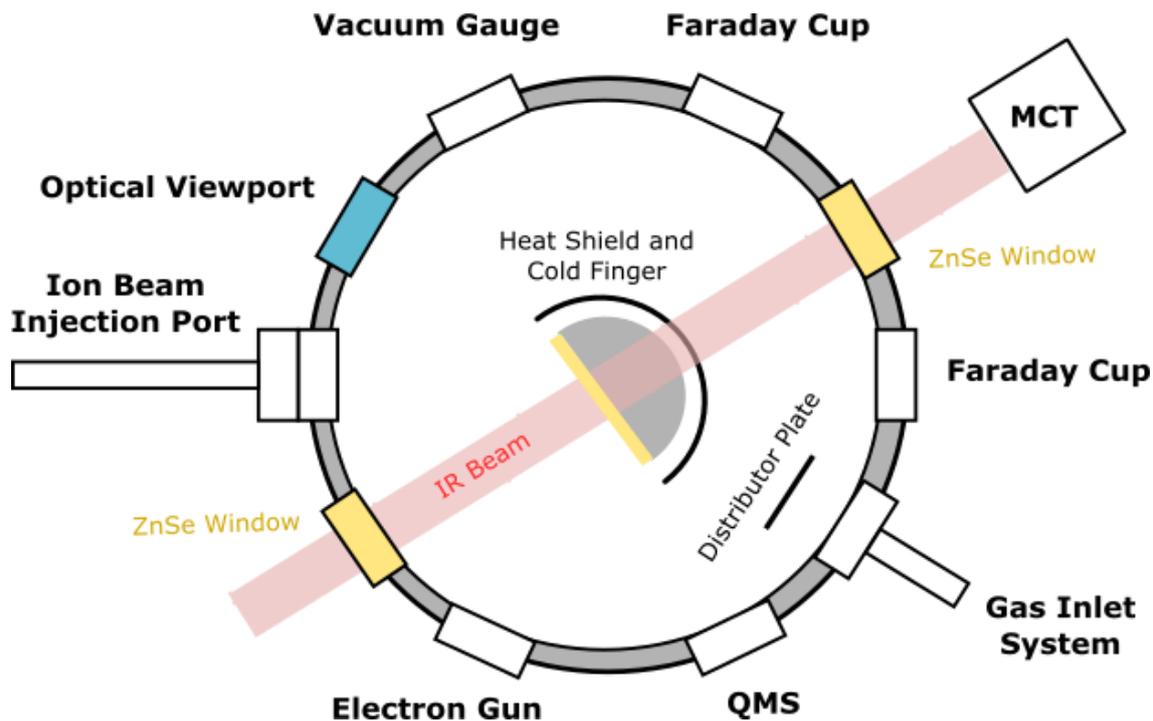
93

## 94 **2 Description of the ICA facility**

95 A complete technical description of ICA is provided in another publication [15], and thus in  
96 the present paper we limit ourselves to a brief overview. ICA is composed of an ultra-high  
97 vacuum compatible chamber of inner diameter 160 mm, within the centre of which is a heat-  
98 shielded copper sample holder (Fig. 1). This sample holder currently may hold up to four  
99 substrates onto which ice analogue replicates may be deposited under identical conditions.  
100 Thus, ICA has been purposefully designed to facilitate the performance of systematic ice  
101 processing studies where a number of experimental parameters (e.g. ice thickness, morphology,  
102 temperature, processing type, etc.) may be controlled and varied with ease.

103 Pressure within the chamber may be reduced to a few 10<sup>-7</sup> mbar with the combined use of a  
104 dry rough vacuum pump and a turbomolecular pump. Even lower pressures of a few 10<sup>-8</sup> mbar  
105 are attained upon cooling of the sample holder, which is performed using a closed-cycle helium  
106 cryostat able to offer a working temperature range of 20-300 K. Accurate temperature  
107 measurements are made using two silicon diodes connected to a Lake Shore temperature  
108 controller and a proportional integral-differential controller. The positioning of one diode at  
109 the top of the sample holder and the other at the bottom allows for the identification of any  
110 potential temperature gradients across the holder which may introduce uncertainties during  
111 experimentation.

112 The deposition of astrophysical ice analogues onto the substrates is conducted by introducing  
113 gases into the chamber via a fine needle valve. The presence of a distributor (scattering) plate  
114 in front of the inlet tube allows for a reduction in chamber pressure heterogeneity during this  
115 background deposition, thus ensuring that the ices produced are of roughly the same thickness  
116 on all deposition substrates. Both uni- and multi-component ices may be prepared by making  
117 use of a system of valves to introduce the gases into a mixing container, the partial pressures  
118 of which are monitored by a mass independent capacitive manometer gauge.



119

120 **Fig. 1** Top-view schematic diagram of the ICA chamber. Although the sample holder and heat shield are rotatable,  
 121 both ion beam and electron beam irradiations are typically performed as depicted, with the IR beam pathway  
 122 orthogonal to the sample surface and charged projectiles impacting at angles of  $36^\circ$ .

123

124 The chamber is equipped with ten DN-40 CF ports on its side walls separated from one another  
 125 by angles of  $36^\circ$  which are used for external connections (Fig. 1). One of these ports hosts a  
 126 Kimball ELG-2A electron gun for electron irradiation studies. The emitted electron energy  
 127 range of this gun is 5-2000 eV, and beam current stability and intensity can be monitored using  
 128 a Faraday cup mounted on the port directly opposite to the electron gun. For this monitoring to  
 129 take place, the sample holder includes a 9.6 mm diameter collimator in place of one of the  
 130 deposition substrates. The characterisation of the emitted electron beam is discussed in Sect. 3,  
 131 while results obtained from the radiolysis of  $\text{CH}_3\text{OH}$  ice are presented in Sect. 4.

132 The port located at  $72^\circ$  from the electron gun in a clockwise sense serves as the entrance for  
 133 projectile ion beams supplied by a 2 MV Tandatron-type accelerator; the stability and intensity  
 134 of these beams may be monitored using another Faraday cup mounted on the port directly  
 135 opposite to the ion beam entry port (Fig. 1). The accelerator facility, as well as preliminary  
 136 experimental results obtained by ion radiolysis of astrophysical ice analogues, are the focus of  
 137 separate publications [15,16]. Other ports on the chamber are used to house the gas inlet dosing  
 138 line, a vacuum gauge, and an optical viewport for direct observation of the sample holder and  
 139 substrates.

140 Another two ports on the chamber are used as the entrance and exit points for the IR beam used  
 141 to monitor the physico-chemical evolution of the interstellar and Solar System ice analogues  
 142 undergoing energetic processing (Fig. 1). The ice samples are analysed by FTIR absorbance  
 143 spectroscopy with IR analysis nominally set up in transmission mode using IR-transparent

144 deposition substrates (typically zinc selenide). These substrates are coated with a fine gold  
145 mesh to prevent charging of the surface during high-current (>100 nA) irradiation [15]. Prior  
146 to ice deposition, background spectra of the bare substrates are obtained at the appropriate  
147 temperature and pressure and subtracted from the spectra collected during processing. During  
148 irradiation, species may be sputtered or desorbed from the ice and these molecules may be  
149 analysed by means of a quadrupole mass spectrometer located on another port.

150

### 151 **3 Electron beam analysis**

#### 152 **3.1 Electron beam profiling and flux determination**

153 In order to qualitatively assess any chemical changes brought about by electron irradiation of  
154 deposited ice layers, it is necessary to have knowledge of both the current density distribution  
155 at the surface of the ice as well as the electron flux. Optimum conditions for studying the  
156 physico-chemical evolution of the ice are attained when the current density is constant over the  
157 entirety of the ice surface which is monitored by the IR spectroscopic beam. However, a nearly  
158 constant current density within a circular area which is smaller than that monitored by the IR  
159 beam may also be used, provided that appropriate measurement corrections are made (an  
160 example of which is discussed in more detail in Sect. 3.2).

161 To characterise the electron beam profile, a 9.6 mm diameter collimator is mounted onto the  
162 sample holder in place of one of the deposition substrates. The emitted electron beam is passed  
163 through this collimator and into the Faraday cup opposite the electron gun (Fig. 1), which is  
164 used to measure the current as a function of the vertical position of the collimator  $Y$  as it is  
165 displaced from its nominal position in fine steps. The zero-value for the  $x$ ,  $y$ , and  $Y$  coordinates  
166 at the surface of the ice is defined by the passage of the axis of the electron beam through the  
167 plane of the surface. The measured current values  $I(Y)$  may then be compared to model  
168 calculations:

$$169 \quad I_{\text{model}}(Y) = \iint_{x^2+y^2 \leq R_c^2} dx dy i(x, y - Y)$$

170 (Eq. 1)

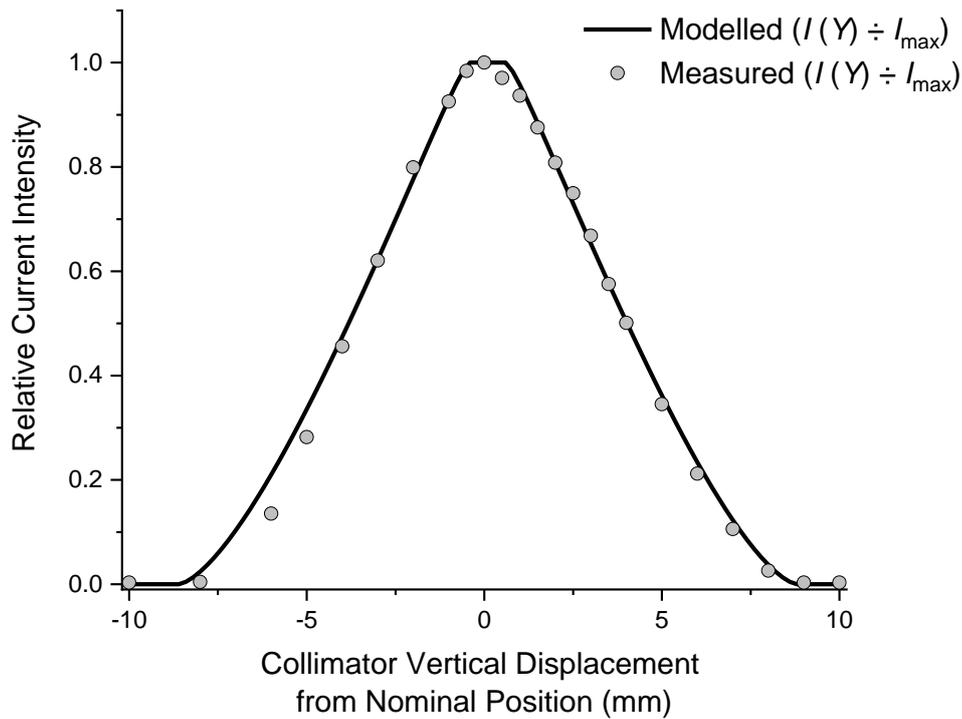
171 where  $R_c$  is the radius of the collimator and  $i(x, y)$  is the hypothetical current density in the  
172 plane of the ice sample surface. A unique solution for the model function current density  $i$  does  
173 not exist when compared with measured values and so, in the strictest sense, this cannot be  
174 considered a fit. However, given reasonable, few-parameter  $i$  functions, a reasonable estimation  
175 for the shape and uniformity of the beam may be obtained. An example of this for a 2 keV  
176 electron beam (as was used in Sect. 4) is given in Fig. 2 which shows that our measured data  
177 matches the current density function for a modelled cylindrical and homogeneous beam of  
178 diameter 8.4 mm quite well.

179 The characterisation of the electron beam profile allows for the determination of the beam spot  
180 area  $A$  incident on the sample ice during irradiation. This value, together with the measured  
181 current  $I_{\text{max}}$  and the fundamental electric charge ( $e = 1.602 \times 10^{-19}$  C) may be used to calculate  
182 the electron flux  $\Phi$  (electrons  $\text{cm}^{-2} \text{s}^{-1}$ ). In order to ensure that a constant flux is used throughout

183 an experiment, the beam current is measured on the Faraday cup opposite to the electron gun  
 184 prior to each irradiation and compared to the current emitted by the filament, which is displayed  
 185 on the digital power supply system. This displayed emitted current was continuously monitored  
 186 during irradiation and was observed to be stable. Our test runs showed that the ratio between  
 187 the measured and displayed currents did not change by more than 1% over five hours. By  
 188 integrating the flux over the time of irradiation  $t$ , the electron fluence  $\varphi$  (electrons  $\text{cm}^{-2}$ ) may  
 189 be determined:

$$\Phi = \frac{I_{\max}}{A \times e} \quad (\text{Eq. 2a})$$

$$\varphi = \int_{t=0}^t \Phi dt \quad (\text{Eq. 2b})$$



194

195 **Fig. 2** Plots of measured electron current  $I(Y)$  relative to maximum beam current  $I_{\max}$  as a function of the  
 196 displacement of the 9.6 mm diameter collimator from its nominal position along the vertical axis for a 2 keV  
 197 electron beam. In these plots, points represent measured values, while the plotted line is defined by Eq. 1 for a  
 198 simple, cylindrical, homogeneous electron beam with a diameter of 8.4 mm at the sample ice surface.

199

200 Fig. 2 represents a rather special electron beam focusing condition which cannot be performed  
 201 for all cases. Sharp focusing with a beam diameter  $< 3$  mm, however, can be set at all beam  
 202 energies and can be checked using Eq. 1. In general, we ensure a uniform electron beam density  
 203 by sweeping this focused electron beam in the  $x$  and  $y$  directions using sawtooth-shaped

204 voltages applied to the deflection electrodes of the electron gun. In such cases, the uniformity  
205 of the beam current density can also be determined from the measured profile and the sample  
206 geometry by using Eq. 1 with a straightforward algorithm. Making use of this sweeping mode  
207 is the preferred option if beam homogeneity is important and the beam current density is the  
208 relevant physical quantity. If an accurate value of the total flux is more important, a beam spot  
209 size <9.6 mm (as depicted in Fig. 2) is the optimum solution.

210

### 211 3.2 Corrections to measured molecular column densities

212 In circumstances where the surface area of the ice irradiated by electrons spans the entirety of  
213 the area scanned by the IR monitoring beam, the abundances of both reactant and product  
214 molecules may be determined spectroscopically by measuring the peak areas of their  
215 characteristic absorbance bands and calculating the column density  $N$  (molecules  $\text{cm}^{-2}$ ):

$$216 \quad N = \frac{\ln(10) \times P}{A_v}$$

217 (Eq. 3)

218 where  $P$  is the peak area of the characteristic band for the given molecular species ( $\text{cm}^{-1}$ ) and  
219  $A_v$  is the integrated band strength value for that particular band ( $\text{cm molecule}^{-1}$ ) [17]. These  
220 column densities may be normalised as a fraction of the initial (pre-irradiative) column density  
221 of the reactant species  $N_0$ :

$$222 \quad n = \frac{N}{N_0}$$

223 (Eq. 4)

224 However, it may be the case that the overall surface area irradiated by the electron beam is  
225 smaller than that monitored spectroscopically. Furthermore, the range (penetration depth) of  
226 the electrons may be smaller than the actual thickness of the target ice. In such scenarios, there  
227 exists an ‘active volume’ within the ice in which electron-induced chemistry is taking place.  
228 As such, it is preferable to correct for the ‘inactive volume’ when making measurements of the  
229 relative abundances of reactant and product molecules present. Under prolonged irradiation, it  
230 is possible to assume that the overwhelming majority of reactant molecules within the active  
231 volume are destroyed. Therefore, a working approximation of the ratio of this active volume  
232 to the volume monitored by the IR beam may be gleaned from the calculated final normalised  
233 column density  $n_{\text{fin}}$  at the end of irradiation. This allows for the following corrected column  
234 density relations to be proposed for reactant  $x$  and product  $y_i$  molecules:

$$235 \quad x = \frac{c}{c_0} = \frac{n - n_{\text{fin}}}{1 - n_{\text{fin}}}$$

236 (Eq. 5a)

$$237 \quad y_i = \frac{c_i}{c_0} = \frac{n_i}{1 - n_{\text{fin}}}$$

238 (Eq. 5b)

239 where  $n$  and  $n_i$  refer to the normalised column densities of the respective reactant and product  
240 species, and  $c$  and  $c_i$  refer to the molecular concentrations of the reactant and product species,  
241 while  $c_0$  refers to the initial molecular concentration of the reactant prior to irradiation. The  
242 extension of these corrections to mixed ices is relatively straightforward. The advantage of Eqs.  
243 5a and 5b is that they provide a model independent, one parameter correction which is  
244 reasonable under prolonged irradiation. The more complicated general formulae (based on the  
245 Beer-Lambert Law) are not given here.

246

#### 247 **4 High-energy electron irradiation of amorphous CH<sub>3</sub>OH ice**

248 In this Sect., we provide some preliminary results from the 2 keV electron irradiation of  
249 amorphous CH<sub>3</sub>OH ice at 20 K in order to showcase some of the experimental capabilities of  
250 ICA. Our choice of CH<sub>3</sub>OH as a target ice was motivated by the fact that this species is one of  
251 the more common extra-terrestrial molecules, having already been identified in several  
252 astrophysical environments including low- and high-mass protostars, comets, and centaur  
253 planetoids [6,8]. Furthermore, several studies have shown that the radiolytic processing of  
254 CH<sub>3</sub>OH may yield complex organic molecules, many of which are relevant to astrobiology (for  
255 a detailed review on the radiochemical processing of CH<sub>3</sub>OH, see [8]).

256 The experimental protocol followed for this irradiation was as follows: an aliquot of CH<sub>3</sub>OH  
257 was de-gassed in a glass vial via several freeze-thaw cycles using liquid nitrogen. Vapours  
258 from this aliquot were subsequently introduced into the chamber at 20 K to deposit a 1  $\mu\text{m}$  ice  
259 on zinc selenide substrates. The thickness  $d$  ( $\mu\text{m}$ ) of the ice was determined using the measured  
260 column density  $N$  at the 1027  $\text{cm}^{-1}$  absorbance band and the known molecular mass  $m$  (u) and  
261 density  $\rho$  ( $\text{g cm}^{-3}$ ) of CH<sub>3</sub>OH [17,18]:

$$262 \quad d = 10^4 \times \frac{Nm}{\rho \times 6.02 \times 10^{23}} \quad (\text{Eq. 6})$$

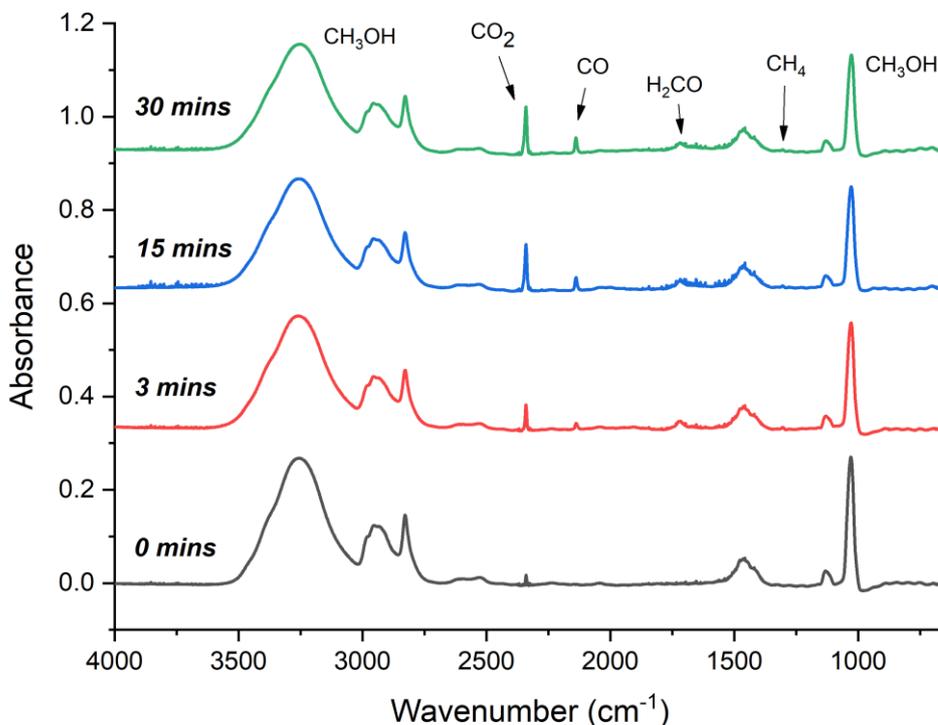
264 Once deposited, a pre-irradiation FTIR absorbance spectrum of the ice was collected. The ice  
265 was then irradiated by 2 keV electrons for a total of 30 minutes, with spectra being collected at  
266 three-minute intervals. FTIR absorbance spectra were collected over the 4000-650  $\text{cm}^{-1}$  range  
267 at a resolution of 1  $\text{cm}^{-1}$  using 128 scans each measured over an integration time of 1 s. During  
268 every spectral acquisition, the electron beam was switched off.

269 During irradiation, electrons impacted the surface of the ice at an angle of 36°, as depicted in  
270 Fig. 1, and the beam spot (diameter = 8.4 mm) covered approximately 50% of the area  
271 monitored by the IR beam (diameter = 12 mm). The beam current (4.5  $\mu\text{A}$ ) was measured by  
272 making use of the collimator on the sample holder and the Faraday cup mounted opposite the  
273 gun and was used to calculate a flux of  $4.21 \times 10^{14}$  electrons  $\text{cm}^{-2} \text{s}^{-1}$ , as described in Sect. 3.1.  
274 Under such conditions, the power deposition of the beam is on the order of a few mW, and so  
275 it is expected that any physico-chemical changes within the ice as a result of heating are likely  
276 to be insignificant.

277 Electron irradiation of the CH<sub>3</sub>OH ice resulted in a decrease in each peak area of its  
278 characteristic absorbance bands, as well as the appearance of several new spectral features

279 which were attributed to the formation of radiolytic products (Fig. 3; Table 1). These products  
 280 included the molecules carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), formaldehyde (H<sub>2</sub>CO),  
 281 and methane (CH<sub>4</sub>). The formation of these products is in line with the results reported by prior  
 282 studies of electron irradiation of frozen CH<sub>3</sub>OH [8,15,19-22].

283 Studies by Bennett *et al.* [21] and Schmidt *et al.* [22] have provided detailed information as to  
 284 the likely formation routes of these molecules. Initial fragmentation of CH<sub>3</sub>OH may occur via  
 285 the loss of hydrogen (yielding the neutral radicals CH<sub>3</sub>O and CH<sub>2</sub>OH), the loss of oxygen  
 286 (yielding CH<sub>4</sub>), or the simultaneous (one-step) loss of two hydrogen atoms (yielding H<sub>2</sub>CO).  
 287 Abstraction of hydrogen from CH<sub>3</sub>O or CH<sub>2</sub>OH also affords H<sub>2</sub>CO, which may itself undergo  
 288 either successive (two-step) or simultaneous loss of two hydrogen atoms to yield CO. Reaction  
 289 of CO with a hydroxide radical (OH) produces CO<sub>2</sub>. Relevant rate constants for these processes  
 290 were provided by Bennett *et al.* [21].



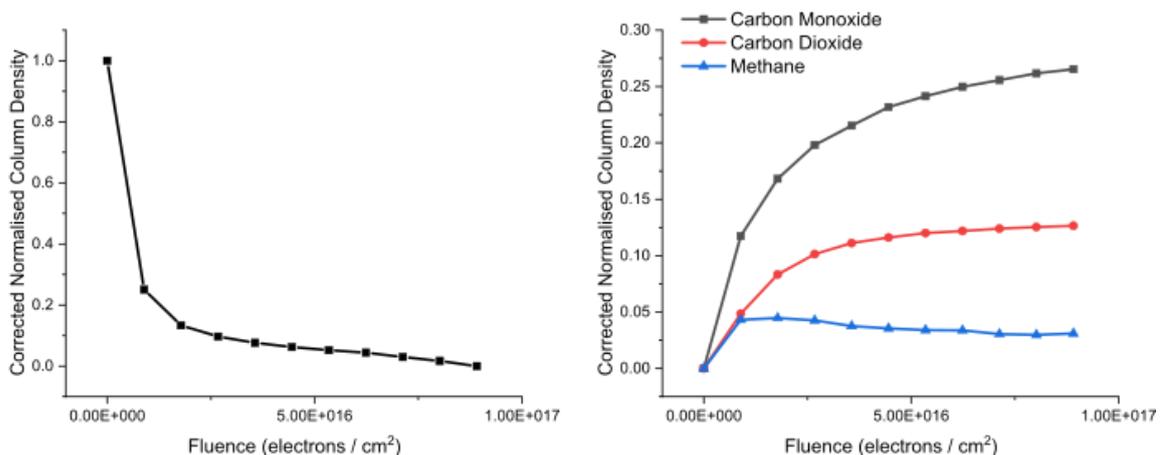
291  
 292 **Fig. 3** Spectral evolution of 1  $\mu\text{m}$  CH<sub>3</sub>OH ice after irradiation by 2 keV electrons for 3, 15, and 30 minutes ( $\Phi =$   
 293  $4.21 \times 10^{14}$  electrons  $\text{cm}^{-2} \text{s}^{-1}$ ). The formation of radiolytic product molecules has been highlighted. Spectra have  
 294 been offset vertically for clarity.

295  
 296 **Table 1** List of FTIR absorbance bands used to identify the presence of molecular species in the CH<sub>3</sub>OH ice after  
 297 30 minutes irradiation with 2 keV electrons ( $\Phi = 4.21 \times 10^{14}$  electrons  $\text{cm}^{-2} \text{s}^{-1}$ ).

Peak Position [ <i>integration limits</i> ] ( $\text{cm}^{-1}$ )	Vibrational Mode Assignment	Integrated Band Strength ( $10^{-17} \text{ cm molecule}^{-1}$ )	Reference
1027 [989-1096]	$\nu_8$ CH <sub>3</sub> OH	1.610	[18]
1300 [1294-1317]	$\nu_4$ CH <sub>4</sub>	0.776	[23]
1725 [1689-1740]	$\nu_4$ H <sub>2</sub> CO	0.960	[24]
2138 [2117-2162]	$\nu_1$ CO	1.100	[25]
2343 [2315-2363]	$\nu_3$ CO <sub>2</sub>	7.600	[26]

298 We have analysed the column density evolution (as per Eqs. 5a and 5b outlined in Sect. 3.2)  
299 with increasing electron fluence for the CH<sub>3</sub>OH reactant, as well as for the product molecules  
300 CO, CO<sub>2</sub>, and CH<sub>4</sub> (Fig. 4). Although the decay profile of the CH<sub>3</sub>OH column density does not  
301 reach an asymptotic limit at the end of irradiation, the irradiation period is nonetheless  
302 sufficiently long for Eqs. 5a and 5b to be considered a reasonable correction.

303 Our results show that the initial decay of amorphous CH<sub>3</sub>OH is fairly rapid, and only begins to  
304 slow down once a fluence of  $\sim 2.50 \times 10^{16}$  electrons cm<sup>-2</sup> is reached. The production of CO is  
305 also most efficient at the earlier stages of irradiation, and begins to slow down at higher  
306 fluences due to its own radiolytic destruction or conversion to CO<sub>2</sub>. The production of CO<sub>2</sub>  
307 follows a similar trend and its column density begins to plateau at a fluence of  $\sim 2.50 \times 10^{16}$   
308 electrons cm<sup>-2</sup>, most likely due to the establishment of an equilibrium between its formation  
309 and conversion to other molecules such as CO or carbon trioxide (CO<sub>3</sub>). Finally, the column  
310 density evolution of CH<sub>4</sub> follows a different pattern, with its abundance within the ice peaking  
311 fairly early on and subsequently diminishing under more prolonged irradiation.



312

313 **Fig. 4** Column density evolution with increasing electron fluence for CH<sub>3</sub>OH (left) and product species (right)  
314 corrected using Eqs. 5a and 5b.

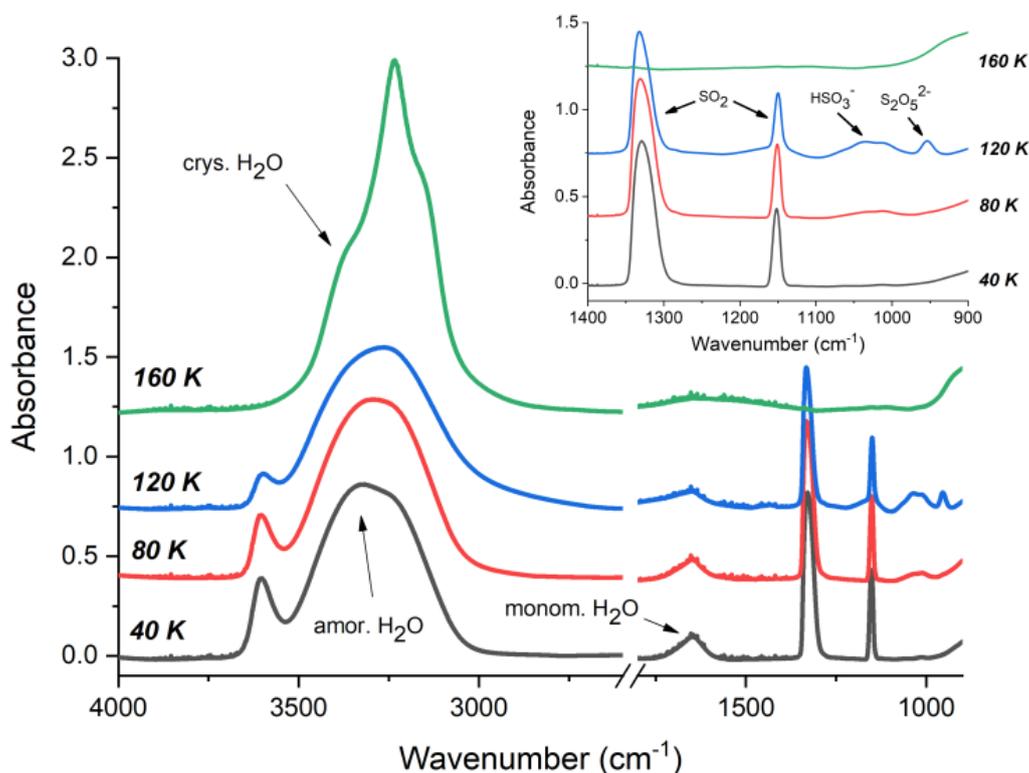
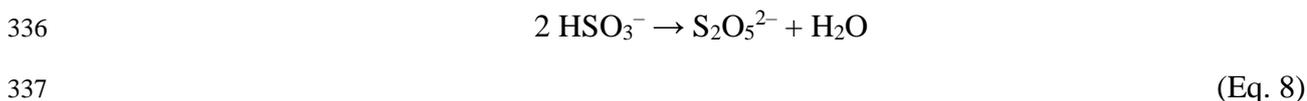
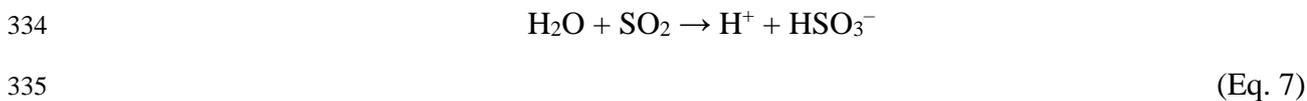
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## 316 5 Thermal chemistry in a mixed ice containing H<sub>2</sub>O and SO<sub>2</sub>

317 In this Sect., we outline the results of thermal reactions occurring in a mixed ice containing  
318 H<sub>2</sub>O and SO<sub>2</sub>. Thermal reactions involving sulphur-bearing molecules (such as SO<sub>2</sub>) are  
319 especially relevant to astrochemical and astrobiological studies of Solar System bodies such as  
320 Mars and the Galilean moons of Jupiter [27]. Previous studies have revealed that thermal  
321 reactions take place in mixed ices of SO<sub>2</sub> and H<sub>2</sub>O, with the primary product being bisulphite  
322 (HSO<sub>3</sub><sup>-</sup>) alongside a smaller quantity of meta-bisulphite (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>) [28,29]. In the presence of  
323 oxidant species, the SO<sub>2</sub> may be oxidised to bisulphate (HSO<sub>4</sub><sup>-</sup>) or sulphate (SO<sub>4</sub><sup>2-</sup>) [30-33].

324 A 3 μm thick mixed H<sub>2</sub>O:SO<sub>2</sub> ice (compositional ratio = 3:5) was deposited at 20 K onto a zinc  
325 selenide substrate, after which it was gradually warmed at a rate of 2 K min<sup>-1</sup> until a final  
326 temperature of 160 K was reached. FTIR absorbance spectra were collected at 20 K intervals.  
327 Results showed that, as the H<sub>2</sub>O:SO<sub>2</sub> ice mixture was warmed, new peaks appeared centred at  
328 around 1040 cm<sup>-1</sup> and 956 cm<sup>-1</sup> (Fig. 5; Table 2). We ascribe the appearance of these peaks to

329 the formation of  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_5^{2-}$ , respectively [34,35]. The identification of these bands is  
 330 only qualitative, as to the best of the authors' knowledge their integrated band strengths are not  
 331 known, and so an accurate quantitative assessment of the amount of  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_5^{2-}$   
 332 produced cannot be performed. The chemical equations for the formation of these products are  
 333 given below:



338  
 339 **Fig. 5** Spectral analysis of a thermally processed  $\text{H}_2\text{O}:\text{SO}_2$  (compositional ratio = 3:5) mixed ice. As the ice is  
 340 warmed, reactions between  $\text{SO}_2$  and  $\text{H}_2\text{O}$  result in the sequential formation of  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_5^{2-}$  (whose respective  
 341 absorbance peaks at  $\sim 1040 \text{ cm}^{-1}$  and  $\sim 956 \text{ cm}^{-1}$  are more clearly visible in the inset). The formation of these  
 342 products is most evident at 120 K, and further heating to 160 K causes a decline in the peaks attributable to the  
 343 sulphur-containing species due to their sublimation, as well as a structural rearrangement of the water ice from  
 344 the amorphous phase to the crystalline (hexagonal) one. In both the main figure and the inset, spectra are vertically  
 345 offset for clarity. Increases in the 160 K spectrum at wavenumbers  $< 1000 \text{ cm}^{-1}$  are due to changes in the high-  
 346 temperature background profile that are not taken into account by the background spectrum measured at 20 K.

347  
 348 The band area attributable to  $\text{HSO}_3^-$  was initially visible at 40 K, and continued to grow in peak  
 349 area with increasing temperature, representing a build-up in the concentration of this molecule  
 350 within the ice structure (Figs. 5 and 6). The first diagnostic traces of  $\text{S}_2\text{O}_5^{2-}$  were observed only  
 351 later at 80 K. This is logical, as the formation of  $\text{S}_2\text{O}_5^{2-}$  first requires sufficient accumulation

352 of  $\text{HSO}_3^-$  as per Eqs. 7 and 8. Further increases in temperature were accompanied by increases  
 353 in the peak areas of both product molecules up until 120 K in the case of  $\text{HSO}_3^-$  and 140 K in  
 354 the case of  $\text{S}_2\text{O}_5^{2-}$ . At higher temperatures, peak areas for these molecules, as well as for  $\text{SO}_2$ ,  
 355 began to decrease due to sublimation [38]. By the time a temperature of 160 K was reached,  
 356 there were no detectable traces of  $\text{SO}_2$ ,  $\text{HSO}_3^-$ , or  $\text{S}_2\text{O}_5^{2-}$  in the ice.

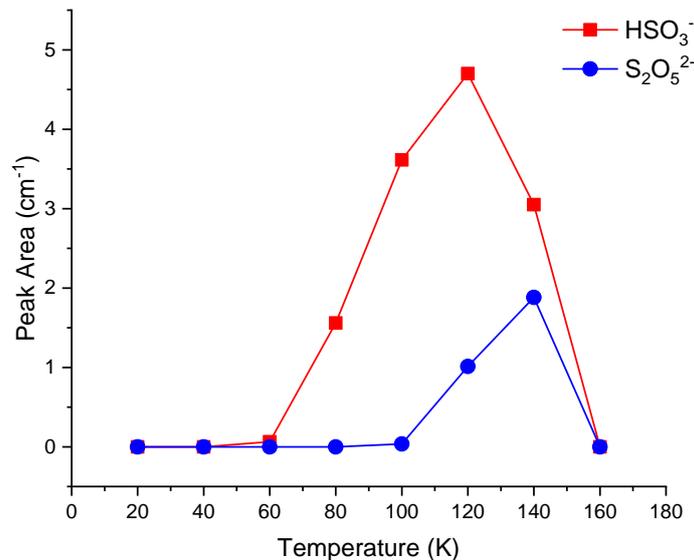
357

358 **Table 2** Vibrational mode assignments and characteristics for  $\text{SO}_2$  and  $\text{H}_2\text{O}$ .

Peak Position [ <i>integration limits</i> ] ( $\text{cm}^{-1}$ )	Vibrational Mode Assignment	Integrated Band Strength ( $10^{-17} \text{ cm molecule}^{-1}$ )	Reference
1149 [1136-1167]	$\nu_1 \text{ SO}_2$	0.22	[36]
1335 [1274-1361]	$\nu_3 \text{ SO}_2$	1.47	[36]
1660 [1586-1731]	$\nu_2 \text{ H}_2\text{O}$	1.20	[26]
3280 [2964-3709]	$\nu_1, \nu_3 \text{ H}_2\text{O}$	14.00	[37]

359

360



361

362 **Fig. 6** Peak area evolution of  $\text{HSO}_3^-$  and  $\text{S}_2\text{O}_5^{2-}$  with temperature. As the ice is warmed, reactions between  $\text{SO}_2$   
 363 and  $\text{H}_2\text{O}$  initially yield  $\text{HSO}_3^-$ , which then reacts to form  $\text{S}_2\text{O}_5^{2-}$  as per Eqs. 7 and 8. Sublimation of all sulphur-  
 364 containing molecules is achieved by 160 K. Conversion of the peak areas to molecular column densities as per  
 365 Eq. 3 is not possible as the integrated band strengths  $A_\nu$  for these molecules are not known.

366

## 367 6 Conclusions and future work

368 In this paper we have presented a technical and operational overview of the ICA facility located  
 369 at the Institute for Nuclear Research (Atomki) in Debrecen with a particular emphasis on the  
 370 characterisation of electron beams used for electron impact studies of astrophysical ice  
 371 analogues. We have also validated results obtained by the facility through comparison of our  
 372 preliminary experimental results with those obtained by other research groups.

373 The 2 keV electron irradiation of amorphous CH<sub>3</sub>OH ice at 20 K resulted in an initial rapid  
374 decay of CH<sub>3</sub>OH within the so-called active ice volume under consideration. Fragmentation of  
375 CH<sub>3</sub>OH led to the formation of new product molecules, including CO, CO<sub>2</sub>, H<sub>2</sub>CO, and CH<sub>4</sub>,  
376 which could all be observed in the FTIR absorbance spectra. These results are in good  
377 agreement with the findings of several other studies considering the electron irradiation of  
378 CH<sub>3</sub>OH, such as those by Bennett *et al.* [21] and Schmidt *et al.* [22].

379 Our thermal processing of a mixed H<sub>2</sub>O:SO<sub>2</sub> ice of compositional ratio 3:5 demonstrated that,  
380 as the ice mixture was warmed from 20 K, molecular reactions resulted in the formation of new  
381 products, namely HSO<sub>3</sub><sup>-</sup> and S<sub>2</sub>O<sub>5</sub><sup>2-</sup>. The abundance of these products increased during  
382 warming until temperatures of 120 K (HSO<sub>3</sub><sup>-</sup>) and 140 K (S<sub>2</sub>O<sub>5</sub><sup>2-</sup>) were reached, after which  
383 the sulphur-containing molecular components of the ice began to sublime. These results  
384 mirror the findings of previous studies, particularly those by Moore *et al.* [28] and Kaňuchová  
385 *et al.* [29], who also considered such thermochemical reactions.

386 Further expansion of the capabilities of ICA is a core element of future planned work. At  
387 present, a viewport equipped with a laser interferometer for more accurate determination of the  
388 deposited ice layer thickness is under construction. An effusive evaporator will also be installed  
389 in the future to allow for the deposition and study of more refractory materials such as  
390 polycyclic aromatic hydrocarbons, biomolecules, and ionic compounds. We are also planning  
391 to increase the selection of spectrophotometers available for molecule identification, so as to  
392 bolster our current mid-IR capabilities with UV-vis measurements.

393 Finally, we note that at the time of writing ICA is a designated transnational access distributed  
394 planetary laboratory facility within the Europlanet Society consortium. As such, there are  
395 currently regular calls for research project proposals which are open to academic groups from  
396 around the world. Successful applications are funded by the European Union Horizon 2020  
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398

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412

## 413 **Author Contributions**

414 All authors contributed to the design, installation, and initial testing of ICA. DVM and BS wrote the manuscript,  
415 performed the experimental work, and performed the data analysis. ZJ, PH, and STSK performed the experimental

416 work and participated in result interpretation. BP assisted with installation and usage of the electron gun and  
417 participated in the experimental work. SI, ZK, PAH, ATM, NJM, and RWM all assisted with the discussion and  
418 interpretation of results.

419

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