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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 (NH₃), methanimine (CH₂NH₂), and hydrogen cyanide (HCN) has been shown to
84 yield aminoacetonitrile (NH₂CH₂CN); 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 (CH₃OH) ice at
90 20 K and the thermal processing of an ice mixture composed of water (H₂O) and sulphur
91 dioxide (SO₂) 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.

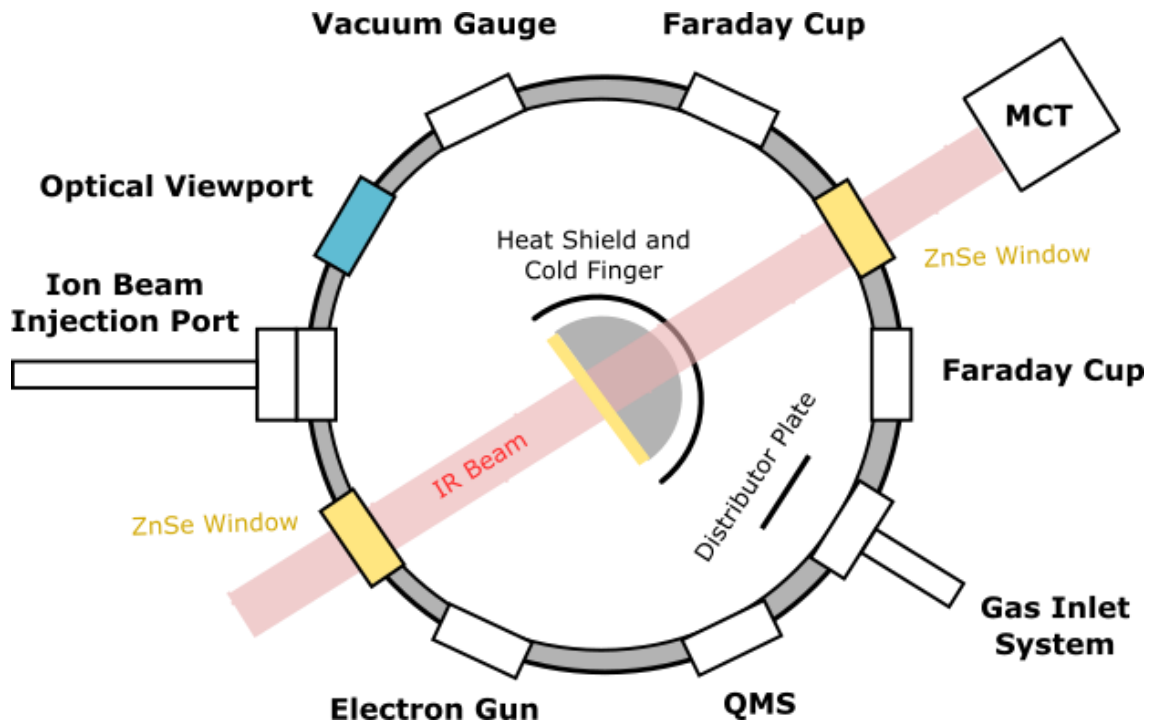
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94 **2 Description of the ICA facility**

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 10⁻⁷ mbar with the combined use of a
104 dry rough vacuum pump and a turbomolecular pump. Even lower pressures of a few 10⁻⁸ 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° .

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° 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 CH_3OH ice are presented in Sect. 4.

132 The port located at 72° 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)

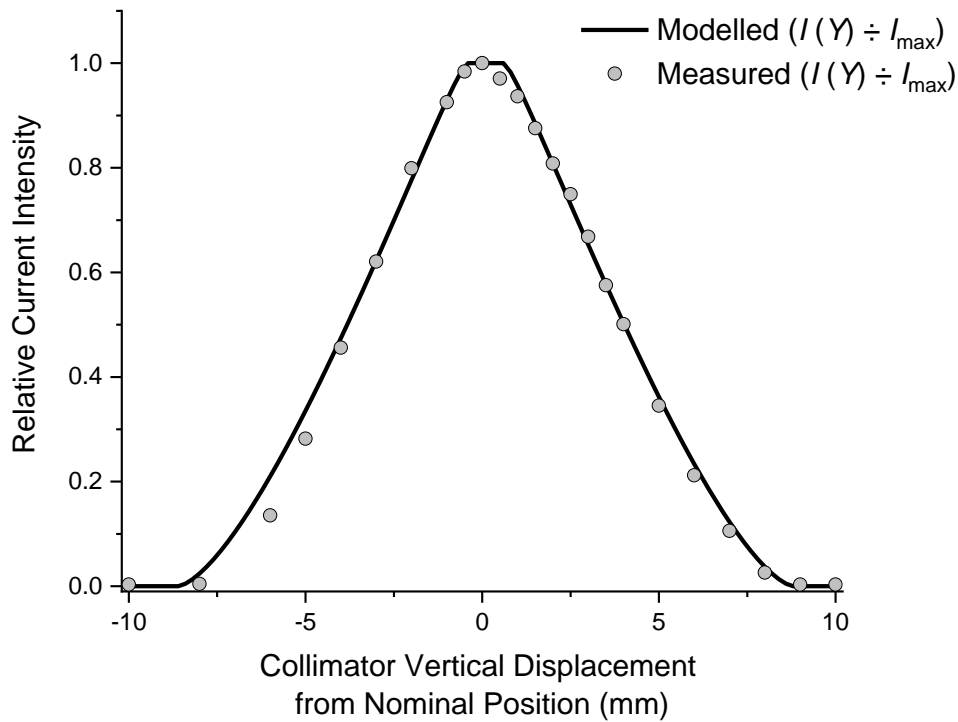
171 where R_c is the radius of the collimator and $i(x, y)$ is the hypothetical current density in the
172 plane of the ice sample surface. A unique solution for the model function current density i does
173 not exist when compared with measured values and so, in the strictest sense, this cannot be
174 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_{max} and the fundamental electric charge ($e = 1.602 \times 10^{-19}$ C) may be used to calculate
182 the electron flux Φ (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 φ (electrons 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 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 (cm^{-1}) and
219 A_v is the integrated band strength value for that particular band (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_{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 CH₃OH ice**

248 In this Sect., we provide some preliminary results from the 2 keV electron irradiation of
249 amorphous CH₃OH ice at 20 K in order to showcase some of the experimental capabilities of
250 ICA. Our choice of CH₃OH 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 CH₃OH may yield complex organic molecules, many of which are relevant to astrobiology (for
255 a detailed review on the radiochemical processing of CH₃OH, see [8]).

256 The experimental protocol followed for this irradiation was as follows: an aliquot of CH₃OH
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 μm ice
259 on zinc selenide substrates. The thickness d (μm) of the ice was determined using the measured
260 column density N at the 1027 cm^{-1} absorbance band and the known molecular mass m (u) and
261 density ρ (g cm^{-3}) of CH₃OH [17,18]:

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

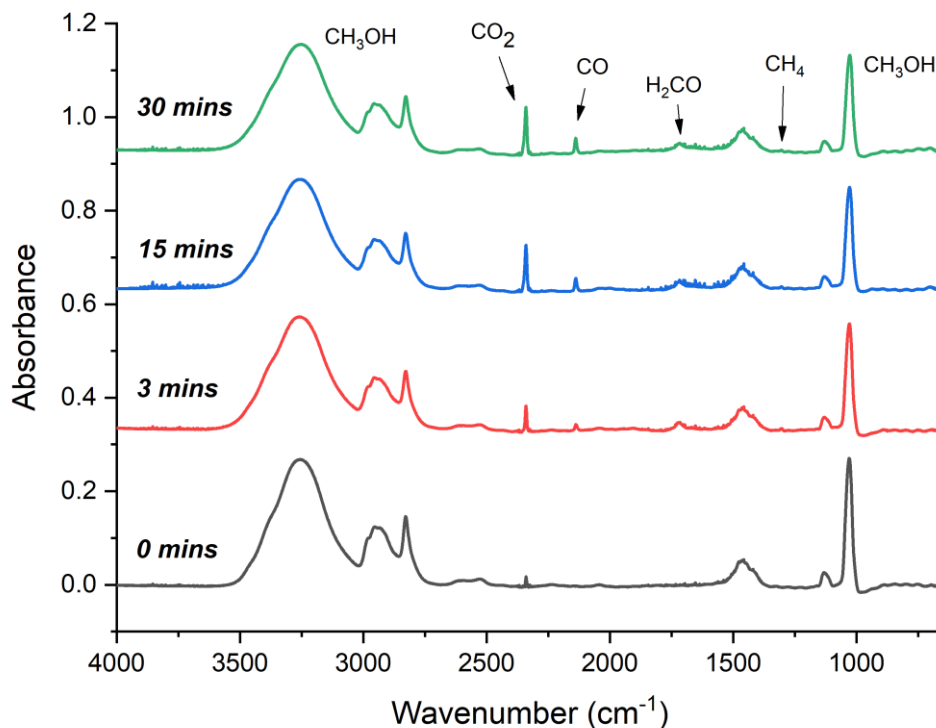
264 Once deposited, a pre-irradiation FTIR absorbance spectrum of the ice was collected. The ice
265 was then irradiated by 2 keV electrons for a total of 30 minutes, with spectra being collected at
266 three-minute intervals. FTIR absorbance spectra were collected over the 4000-650 cm^{-1} range
267 at a resolution of 1 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 μA) 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 4.21×10^{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 CH₃OH 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 (CO₂), formaldehyde (H₂CO),
 281 and methane (CH₄). The formation of these products is in line with the results reported by prior
 282 studies of electron irradiation of frozen CH₃OH [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 CH₃OH may occur via
 285 the loss of hydrogen (yielding the neutral radicals CH₃O and CH₂OH), the loss of oxygen
 286 (yielding CH₄), or the simultaneous (one-step) loss of two hydrogen atoms (yielding H₂CO).
 287 Abstraction of hydrogen from CH₃O or CH₂OH also affords H₂CO, 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 CO₂. Relevant rate constants for these processes
 290 were provided by Bennett *et al.* [21].



291

292 **Fig. 3** Spectral evolution of 1 μm CH₃OH ice after irradiation by 2 keV electrons for 3, 15, and 30 minutes ($\Phi =$
 293 4.21×10^{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.

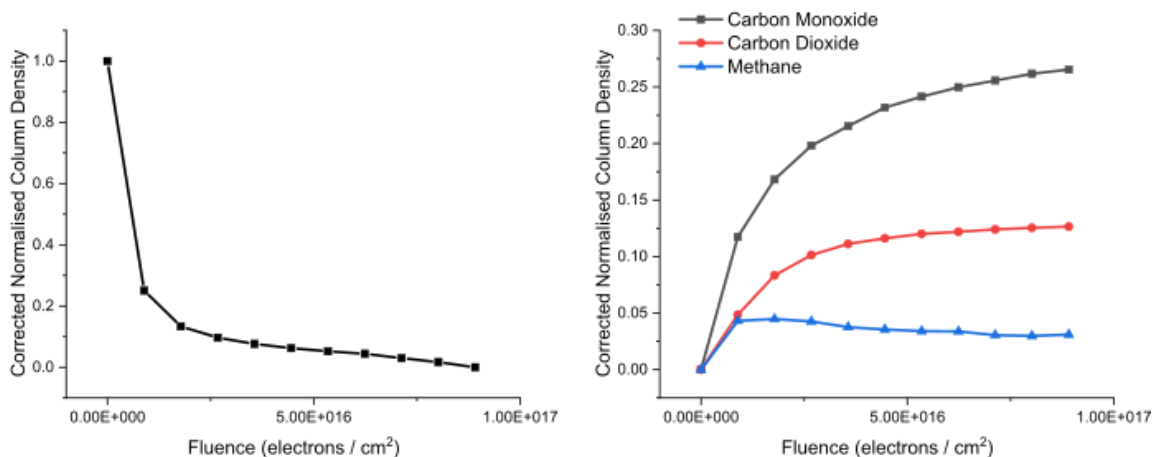
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296 **Table 1** List of FTIR absorbance bands used to identify the presence of molecular species in the CH₃OH ice after
 297 30 minutes irradiation with 2 keV electrons ($\Phi = 4.21 \times 10^{14}$ electrons $\text{cm}^{-2} \text{s}^{-1}$).

Peak Position [<i>integration limits</i>] (cm^{-1})	Vibrational Mode Assignment	Integrated Band Strength ($10^{-17} \text{ cm molecule}^{-1}$)	Reference
1027 [989-1096]	ν_8 CH ₃ OH	1.610	[18]
1300 [1294-1317]	ν_4 CH ₄	0.776	[23]
1725 [1689-1740]	ν_4 H ₂ CO	0.960	[24]
2138 [2117-2162]	ν_1 CO	1.100	[25]
2343 [2315-2363]	ν_3 CO ₂	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 CH₃OH reactant, as well as for the product molecules
300 CO, CO₂, and CH₄ (Fig. 4). Although the decay profile of the CH₃OH 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 CH₃OH is fairly rapid, and only begins to
304 slow down once a fluence of $\sim 2.50 \times 10^{16}$ electrons cm⁻² 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 CO₂. The production of CO₂
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⁻², most likely due to the establishment of an equilibrium between its formation
309 and conversion to other molecules such as CO or carbon trioxide (CO₃). Finally, the column
310 density evolution of CH₄ 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 CH₃OH (left) and product species (right)
314 corrected using Eqs. 5a and 5b.

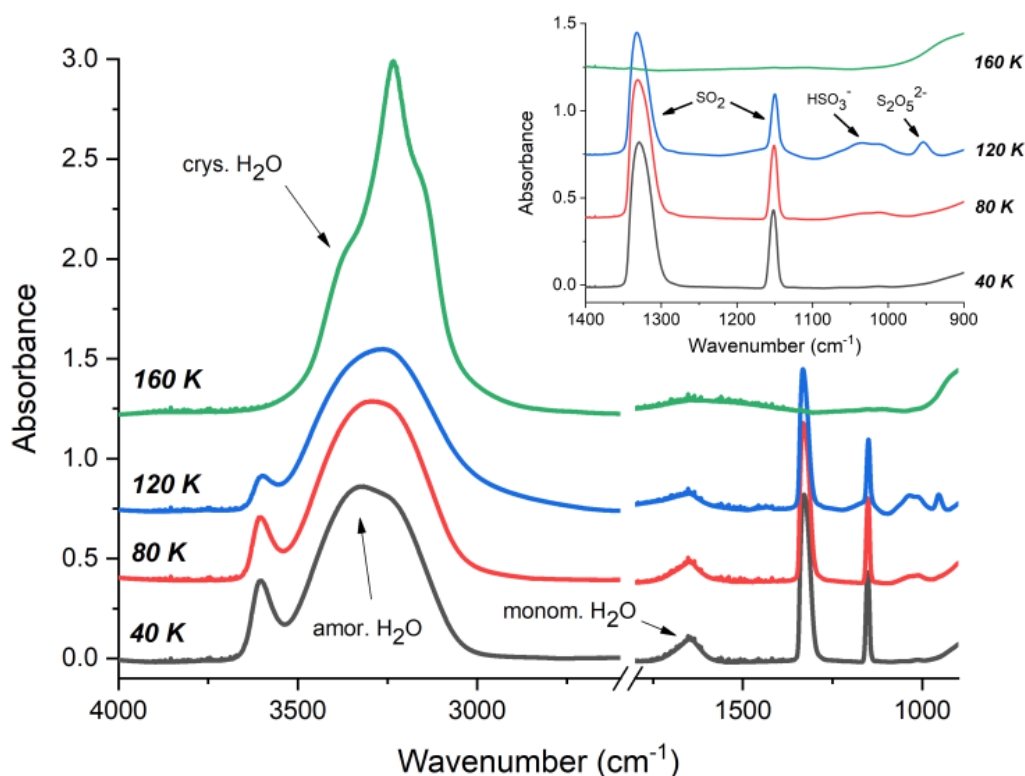
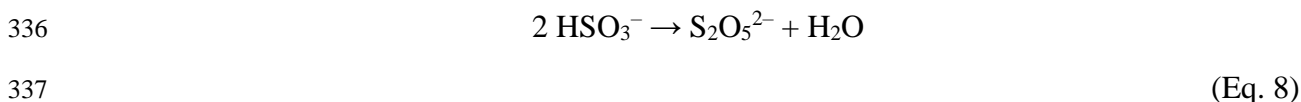
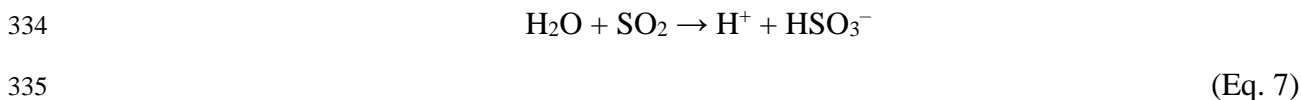
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316 **5 Thermal chemistry in a mixed ice containing H₂O and SO₂**

317 In this Sect., we outline the results of thermal reactions occurring in a mixed ice containing
318 H₂O and SO₂. Thermal reactions involving sulphur-bearing molecules (such as SO₂) 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 SO₂ and H₂O, with the primary product being bisulphite
322 (HSO₃⁻) alongside a smaller quantity of meta-bisulphite (S₂O₅²⁻) [28,29]. In the presence of
323 oxidant species, the SO₂ may be oxidised to bisulphate (HSO₄⁻) or sulphate (SO₄²⁻) [30-33].

324 A 3 μm thick mixed H₂O:SO₂ 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⁻¹ 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 H₂O:SO₂ ice mixture was warmed, new peaks appeared centred at
328 around 1040 cm⁻¹ and 956 cm⁻¹ (Fig. 5; Table 2). We ascribe the appearance of these peaks to

329 the formation of 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 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 SO_2 and H_2O result in the sequential formation of 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 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 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 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 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 SO_2 , HSO_3^- , or $\text{S}_2\text{O}_5^{2-}$ in the ice.

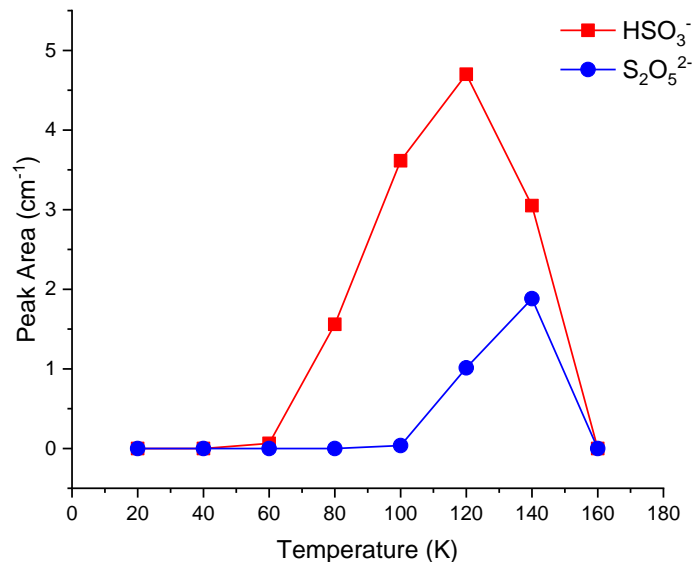
357

358 **Table 2** Vibrational mode assignments and characteristics for SO_2 and H_2O .

Peak Position [<i>integration limits</i>] (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 HSO_3^- and $\text{S}_2\text{O}_5^{2-}$ with temperature. As the ice is warmed, reactions between SO_2
 363 and H_2O initially yield 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_ν 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 CH₃OH ice at 20 K resulted in an initial rapid
374 decay of CH₃OH within the so-called active ice volume under consideration. Fragmentation of
375 CH₃OH led to the formation of new product molecules, including CO, CO₂, H₂CO, and CH₄,
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 CH₃OH, such as those by Bennett *et al.* [21] and Schmidt *et al.* [22].

379 Our thermal processing of a mixed H₂O:SO₂ 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 HSO₃⁻ and S₂O₅²⁻. The abundance of these products increased during
382 warming until temperatures of 120 K (HSO₃⁻) and 140 K (S₂O₅²⁻) 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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