

# JWST Observations of Young protoStars (JOYS+): Detection of icy complex organic molecules and ions

## I. CH<sub>4</sub>, SO<sub>2</sub>, HCOO<sup>-</sup>, OCN<sup>-</sup>, H<sub>2</sub>CO, HCOOH, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CHO, CH<sub>3</sub>OCHO, CH<sub>3</sub>COOH

W. R. M. Rocha<sup>1,2</sup>, E. F. van Dishoeck<sup>2,3</sup>, M. E. Ressler<sup>4</sup>, M. L. van Gelder<sup>2</sup>, K. Slavicinska<sup>1,2</sup>, N. G. C. Brunken<sup>2</sup>, H. Linnartz<sup>1</sup>, T. P. Ray<sup>5</sup>, H. Beuther<sup>6</sup>, A. Caratti o Garatti<sup>7</sup>, V. Geers<sup>8</sup>, P. J. Kavanagh<sup>9</sup>, P. D. Klaassen<sup>8</sup>, K. Justannont<sup>10</sup>, Y. Chen<sup>2</sup>, L. Francis<sup>2</sup>, C. Gieser<sup>3</sup>, G. Perotti<sup>6</sup>, Ł. Tychoniec<sup>11</sup>, M. Barsony<sup>12</sup>, L. Majumdar<sup>13,14</sup>, V. J. M. le Gouellec<sup>15</sup>, L. E. U. Chu<sup>15</sup>, B. W. P. Lew<sup>16</sup>, Th. Henning<sup>6</sup>, and G. Wright<sup>8</sup>

(Affiliations can be found after the references)

Received xxxx; accepted yyyy

### ABSTRACT

**Context.** Complex organic molecules (COMs) are ubiquitously detected in the gas phase and are thought to be mostly formed on icy grains. Nevertheless, no unambiguous detection of COMs larger than CH<sub>3</sub>OH in ices has been reported so far, but exploring this matter in more detail has become possible with the unprecedented possibilities offered by the *James Webb* Space Telescope (JWST) within the infrared (IR) spectral range with its very high sensitivity and spectral resolution in the critical 5–10 μm range, the fingerprint region of oxygen-bearing COMs.

**Aims.** In the program JWST Observations of Young protoStars (JOYS+), more than 30 protostars are being observed with the Medium Resolution Spectrograph (MRS) of the Mid-IR Instrument (MIRI). The goal of this study is to comprehensively explore the COMs ice signatures in one low- and one high-mass protostar, NGC 1333 IRAS 2A and IRAS 23385+6053, respectively.

**Methods.** We perform global continuum and silicate subtractions of the MIRI-MRS spectra, followed by a local continuum subtraction in optical depth scale in the range around 6.8 and 8.6 μm, the ice COM fingerprint region. Different choices of local continuum and silicate subtraction were explored. Next, we fit observational data with a large sample of available IR laboratory ice spectra. We use the ENIGMA fitting tool, a genetic algorithm-based code that not only finds the best fit between the lab data and the observations but also performs statistical analysis of the solutions, such as deriving the confidence intervals and quantifying fit degeneracy.

**Results.** We report the best fits for the spectral ranges between 6.8 and 8.6 μm in NGC 1333 IRAS 2A and IRAS 23385+6053, originating from simple molecules and COMs, as well as negative ions. In total, 10 chemical species are needed to reproduce the astronomical data. The strongest feature in this range (7.7 μm) is dominated by CH<sub>4</sub> and has contributions of SO<sub>2</sub> and OCN<sup>-</sup>. Our results indicate that the 7.2 and 7.4 μm bands are mostly dominated by HCOO<sup>-</sup>. We also find statistically robust detections of COMs based on multiple bands, most notably CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>OH, and CH<sub>3</sub>OCHO. The likely detection of CH<sub>3</sub>COOH is also reported. Based on the ice column density ratios between CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CHO of NGC 1333 IRAS 2A and IRAS 23385+6053, we find compelling evidence that these COMs are formed on icy grains. Finally, the derived ice abundances for NGC 1333 IRAS 2A correlate well with those in comet 67P/GC within a factor of 5.

**Conclusions.** Based on the high-quality JWST (MIRI-MRS) spectra, we conclude that COMs are present in interstellar ices, thus providing additional proof for a solid-state origin of these species in star-forming regions. In addition, the good correlation between the ice abundances in comet 67P and NGC 1333 IRAS 2A is fully in line with the idea that cometary COMs can be significantly inherited from the early protostellar phases.

**Key words.** Astrochemistry – ISM: molecules – solid state: volatile

## 1. Introduction

Complex organic molecules (COMs) are molecules with 6 atoms or more and have at least one atom of Carbon (Herbst & van Dishoeck 2009). They are intrinsically important to comprehend the chemical complexity developed in star-forming regions since these materials are the feedstock for future exoplanetary systems. Once available in primitive planetary systems, this material can potentially promote the habitability of planets. An important question for delivering organic material to new solar systems is whether the molecules are in the gas phase or in ices as part of icy dust grains. Only in the latter case water and organic molecules are expected to be effectively delivered to terrestrial planets as discussed by Morbidelli et al. (2012); van Dishoeck et al. (2014); Morbidelli et al. (2018); O’Brien et al. (2018); van Dishoeck

et al. (2021) and the lower UV photodestruction cross-section of those molecules in the solid-phase (e.g., Öberg 2016). Yet, very little information is available about these organic molecules in ices. The *James Webb* Space Telescope (JWST) provides a tool to change the situation by observing ice features during the early protostellar phases with higher resolution and sensitivity than before.

Gas-phase observations have been exceptionally successful in probing the chemical complexity towards low-mass and massive young stellar objects (LYSOs and MYSOs, respectively) as shown in the literature (e.g., Blake et al. 1987; Cazaux et al. 2003; Bergner et al. 2017; Manigand et al. 2020; Belloche et al. 2020; van Gelder et al. 2020; Jørgensen et al. 2020; Nazari et al. 2021; Gieser et al. 2021), and the observations and abundances of many COMs are summarized in the review by Jørgensen

et al. (2020). The current consensus is that COMs are efficiently formed in the solid phase, and desorb into the gas phase by thermal and non-thermal mechanisms. Nevertheless, methanol ( $\text{CH}_3\text{OH}$ ) is the only COM securely identified in the solid phase based on the infrared (IR) spectra from the United Kingdom Infrared Telescope (UKIRT; Grim et al. 1991; Skinner et al. 1992; Dartois et al. 1999), Infrared Space Observatory (*ISO*, e.g., Gibb et al. 2004), Very Large Telescope (Pontoppidan et al. 2004; Dartois et al. 2003; Thi et al. 2006), Infrared Telescopic Facility (Chu et al. 2020), *Spitzer* Space Telescope (Boogert et al. 2008; Bottinelli et al. 2010), AKARI (Shimonishi et al. 2010; Perotti et al. 2021), and recently with JWST (e.g., Yang et al. 2022; McClure et al. 2023). Larger COMs compared to  $\text{CH}_3\text{OH}$  have been tentatively identified based on only a single infrared (IR) vibrational mode or were proposed as possible carriers for yet unidentified features, such as ethanol -  $\text{CH}_3\text{CH}_2\text{OH}$  and acetaldehyde -  $\text{CH}_3\text{CHO}$  (Schutte et al. 1999; Öberg et al. 2011; Terwisscha van Scheltinga et al. 2018). These two COMs were also tentatively identified in the JWST high spectral resolution and sensitivity spectrum of IRAS 15398–3359 (Yang et al. 2022) and towards two background stars (McClure et al. 2023), although at lower spectral resolution. Other upper limits have been determined for methyl formate ( $\text{CH}_3\text{OCHO}$ ; Terwisscha van Scheltinga et al. 2021), methylamine ( $\text{CH}_3\text{NH}_2$ ; Rachid et al. 2021), methyl cyanide ( $\text{CH}_3\text{CN}$ ; Rachid et al. 2022), and formamide ( $\text{NH}_2\text{CHO}$ ; Schutte et al. 1999; Slavicinska et al. 2023). Boudin et al. (1998) also estimated upper limits for molecules such as ethane ( $\text{C}_2\text{H}_6$ ), acetylene ( $\text{C}_2\text{H}_2$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and the hydrozonium ion ( $\text{N}_2\text{H}_5^+$ ).

In parallel, gas phase formation of COMs through ion-molecule reactions has been proposed as well (e.g., Balucani et al. 2015; Skouteris et al. 2018; Vazart et al. 2022). The recent detection in a protoplanetary disk of gas phase  $\text{CH}_3^+$  (Berné et al. 2023), an important intermediate in such reactions, supports the idea that COM formation is not exclusively realized on icy grains. This study focuses on the latter.

In the mid-IR spectral range, icy COMs have multiple absorption features, at for example,  $\sim 5.8 \mu\text{m}$ ,  $6.8\text{--}7.0 \mu\text{m}$ ,  $7.2 \mu\text{m}$ ,  $7.4 \mu\text{m}$ ,  $\sim 8 \mu\text{m}$ , and  $\sim 9.5\text{--}9.8 \mu\text{m}$ . However, due to the spectral overlap with the features of other molecules (including dust grain species), the bands at  $7.2$  and  $7.4 \mu\text{m}$  bands have been considered the main fingerprint of COMs (e.g., Schutte et al. 1999; Öberg et al. 2011; Terwisscha van Scheltinga et al. 2018), which is also emphasized in this work. For example, Schutte et al. (1999) proposed that the  $7.2 \mu\text{m}$  band can be due to  $\text{HCOOH}$  (formic acid) ice, notably, the O–H bending mode of the carboxylic functional group and the C–H bending mode. In particular, Bisschop et al. (2007) finds a good match between the  $7.2 \mu\text{m}$  band of the high-mass protostar W33A and the tertiary mixture  $\text{HCOOH}:\text{CH}_3\text{OH}:\text{H}_2\text{O}$ . The assumption that  $\text{HCOOH}$  would be the only carrier of the  $7.2 \mu\text{m}$  band would lead to an unrealistic high solid-state abundance which is not in line with gas-phase observations (Bisschop et al. 2007). Nevertheless, this is not an argument for excluding  $\text{HCOOH}$  as a component of the interstellar ice, because it is also visible at other wavelengths (e.g.,  $5.8 \mu\text{m}$ ). Instead, this indicates that  $\text{HCOOH}$  is not the main carrier of the  $7.2 \mu\text{m}$  band. As an alternative, Boudin et al. (1998) and Öberg et al. (2011) propose that the deformation mode in the methyl functional group ( $\text{CH}_3$ ) of ethanol can be the carrier for the  $7.2 \mu\text{m}$  band. In the case of the  $7.4 \mu\text{m}$  absorption feature, Schutte et al. (1999) propose that the formate ion ( $\text{HCOO}^-$ ) and acetaldehyde can be the carriers of this band. In all cases, these tentative assignments need a convincing profile fit with laboratory data to confirm these chemical species as carriers of

those bands. These fits must also consider a larger spectral range around the  $7\text{--}8 \mu\text{m}$  range where other typical vibrational modes of COMs are also detectable.

In addition to COMs, ions such as  $\text{OCN}^-$  (cyanate ion),  $\text{HCOO}^-$  and  $\text{NH}_4^+$  have been proposed to be present in interstellar ices mostly as part of salts produced by acid-base reactions (e.g., Geballe 1984; Grim & Greenberg 1987; Schutte et al. 1999; Schutte & Khanna 2003; Gálvez et al. 2010; Maté et al. 2012; Moreno et al. 2013; Bergner et al. 2016; Kruczkiewicz et al. 2021). The presence of  $\text{OCN}^-$  in ice mantles can be considered a secure detection based on comprehensive laboratory experiments and extensive analysis towards several protostars (e.g., Geballe 1984; van Broekhuizen et al. 2004) and towards background stars (McClure et al. 2023), and the good correlation between gas-phase abundances of  $\text{HNCO}$  and  $\text{OCN}^-$  ice (Öberg et al. 2009a). In the case of  $\text{HCOO}^-$  and  $\text{NH}_4^+$ , Boogert et al. (2015) argue that a convincing profile fit is still needed to firmly confirm the presence of these ions in ice mantles. If present in interstellar ices, these ions are likely part of refractory salts such as ammonium formate ( $\text{NH}_4^+\text{HCOO}^-$ ) studied in the laboratory and found in comet 67P/G-C (e.g., Poch et al. 2020). In addition, the presence of  $\text{OCN}^-$  and  $\text{HNCO}$  in ices has a strong astrobiological appeal:  $\text{HNCO}$  participates as a peptide bond between two single amino acids (e.g., Fedoseev et al. 2015; Quénard et al. 2018; Colzi et al. 2021; Ligterink et al. 2022).

In this work, we address the presence of simple molecules, COMs, and ions in protostellar ices using newly observed JWST spectra of two protostars with the Medium Resolution Spectrograph (MRS) of the Mid-Infrared Instrument (MIRI) under the JOYS+ program<sup>1</sup> (JWST Observations of Young protoStars; van Dishoeck et al. 2023). The first source is a high-mass ( $\sim 220 M_\odot$ ;  $d = 4.9$  kpc; Molinari et al. 1998, 2008) star-forming region called IRAS 23885+6053 (hereafter IRAS 23385). This cluster is highly embedded in its natal molecular cloud and shows maser emissions of  $\text{H}_2\text{O}$  (Casoli et al. 1986) and  $\text{CH}_3\text{OH}$  (Kurtz et al. 2004), characteristic of shocks. *Spitzer* observations of this source reveal extended emission of polycyclic aromatic hydrocarbons (PAHs) that are excited in this region by surrounding sources with spectral types between B1.5 and B5 (Molinari et al. 2008). NOEMA (Northern Extended Millimeter Array) observations of this source show a variety of gas-phase molecules, such as  $\text{OCS}$ ,  $\text{H}_2\text{CO}$ ,  $\text{HNCO}$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CN}$  (Cesaroni et al. 2019). No other gas-phase COM have been detected in this region apart from  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CN}$  (Gieser et al. 2021). Recently, Beuther et al. (2023) present the rich MIRI-MRS spectrum of IRAS 23885, with focus on the outflow tracers  $\text{H}_2(0\text{--}0) S(7)$ ,  $[\text{Fe II}] (^4F_{9/2} - ^6D_{9/2})$  and  $[\text{Ne II}] (^2P_{1/2} - ^2P_{3/2})$ , and an accretion tracer, the Humphreys  $\alpha$   $\text{HI}(7\text{--}6)$  emission line detected at a  $3\text{--}4\sigma$  level. A multiwavelength analysis using MIRI and NOEMA data provides information about the hot, warm and cold molecular components in IRAS 23385 (Gieser et al. 2023). In addition, Francis et al. (submitted) analyse the compact gaseous molecular emission in IRAS 23385.

The second source targeted in this work is the low-mass Class 0 protostar NGC 1333 IRAS 2A (hereafter IRAS 2A) (e.g., Jørgensen et al. 2005; Brinch et al. 2009), a well-studied hot-corino located in the Perseus complex, specifically in the NGC 1333 molecular cloud, at a distance of  $299 \pm 3$  pc (Ortiz-León et al. 2018; Zucker et al. 2018). This is a protobinary system (Looney et al. 2000; Reipurth et al. 2002), hosting two collimated jets (Sandell et al. 1994; Tobin et al. 2015). IRAS 2A is also a source where several gas-phase COMs are identified (e.g.,

<sup>1</sup> <https://miri.strw.leidenuniv.nl/>

156 Bottinelli et al. 2007), including glycolaldehyde (HCOCH<sub>2</sub>OH; 216  
157 Coutens et al. 2015; Taquet et al. 2015; De Simone et al. 2017), 217  
158 an important sugar molecule that participates in the formation of 218  
159 ribose, a component of the ribonucleic acid (RNA). 219

160 Compared to the *Spitzer* Space Telescope, which had enough 220  
161 sensitivity to observe the brighter low-mass protostars but low 221  
162 spectral resolution, the JWST (MIRI/MRS) observations are 222  
163 qualitatively superior. The MIRI-MRS resolving power ( $R$ ) 223  
164 around the 7–8  $\mu\text{m}$  region, where COMs signatures are present, 224  
165 is  $R = 3500\text{--}4000$  (Labiano et al. 2021), whereas the *Spitzer* In- 225  
166 frared Spectrograph (IRS) offered a resolving power of only  $R =$  226  
167 60. Yang et al. (2022) demonstrate for IRAS 15398–3359 that 227  
168 the ice absorption features around the 7–8  $\mu\text{m}$  are significantly 228  
169 stronger with much higher S/N profiles due to better resolution 229  
170 and sensitivity in the MIRI/MRS compared with *Spitzer*/IRS. 230

171 An important disclaimer to make is that although this pa- 231  
172 per presents JWST/MIRI spectra of a high- and low-mass proto- 232  
173 star, this is not a comparative work of ices in those objects. In- 233  
174 stead, we show data from two sources that were observed first in 234  
175 our programs. A suitable comparison of ice features in different 235  
176 sources needs a more extended list of protostars and will be per- 236  
177 formed in future work. This paper is structured as follows: Sec- 237  
178 tion 2 introduces the JWST/MIRI observations of IRAS 23385 238  
179 and IRAS 2A, the method for the data reduction, and the back- 239  
180 ground subtraction. In Section 3 we describe how the ice bands 240  
181 are isolated, the fitting procedure, the method for quantifying 241  
182 the fitting degeneracy, and which criteria we use for a firm de- 242  
183 tection. We focus in this paper on the 6.8–8.6  $\mu\text{m}$  range, and 243  
184 therefore molecules with vibrational modes outside this interval 244  
185 are not discussed (e.g., H<sub>2</sub>O, CO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>). The results are shown 245  
186 in Section 4, which includes the spectral fits, degeneracy analy- 246  
187 sis and ice column densities. The discussions of these results are 247  
188 presented in Section 5, outlining the important insights from the 248  
189 JWST observations, and how the ice COMs abundances corre- 249  
190 late between the low- and high-mass protostar, as well as with the 250  
191 comet 67P/G-C. The conclusions are summarized in Section 6. 251

192 Below we provide some guidelines for a selective reading of 252  
193 this paper: 253

- 194 – JWST data treatment and subtractions performed on the 254  
195 data: Sections 2.1, 2.2, 3.1, 3.2, 3.3. Appendices A and B. 255
- 196 256
- 197 – Fitting methodology and results: Sections 3.4 and 4.1. 257  
198 Appendices C and G. 258
- 199 259
- 200 – Statistical analysis and degeneracy: Sections 3.5 and 4.2. 260  
201 Appendices H, I and J. 261
- 202 262
- 203 – Identification criteria and suggestions for future works: 263  
204 Sections 3.6 and 3.7. Appendices E and F. 264
- 205 265
- 206 – Ice column densities, abundances, and correlations: Sec- 266  
207 tions 4.3, 4.4, 4.5, 5.1.3, and 5.3. Appendix D and K. 267
- 208 268
- 209 – Ice chemical complexity discussions: Sections 4.1, 5.1 and 269  
210 5.2. Appendix L. 270

## 211 2. Observations 272

### 212 2.1. Data reduction 273

213 IRAS 23385+6053 (R.A. 23<sup>h</sup>40<sup>m</sup>54.5<sup>s</sup>, Dec. +61<sup>d</sup>10<sup>m</sup>28<sup>s</sup>) and 274  
214 NGC 1333 IRAS 2A (R.A. 03<sup>h</sup>28<sup>m</sup>55.57<sup>s</sup>, Dec. +31<sup>d</sup>14<sup>m</sup>36.97<sup>s</sup>) 275  
215 were observed with JWST as part of the guaranteed observation 276

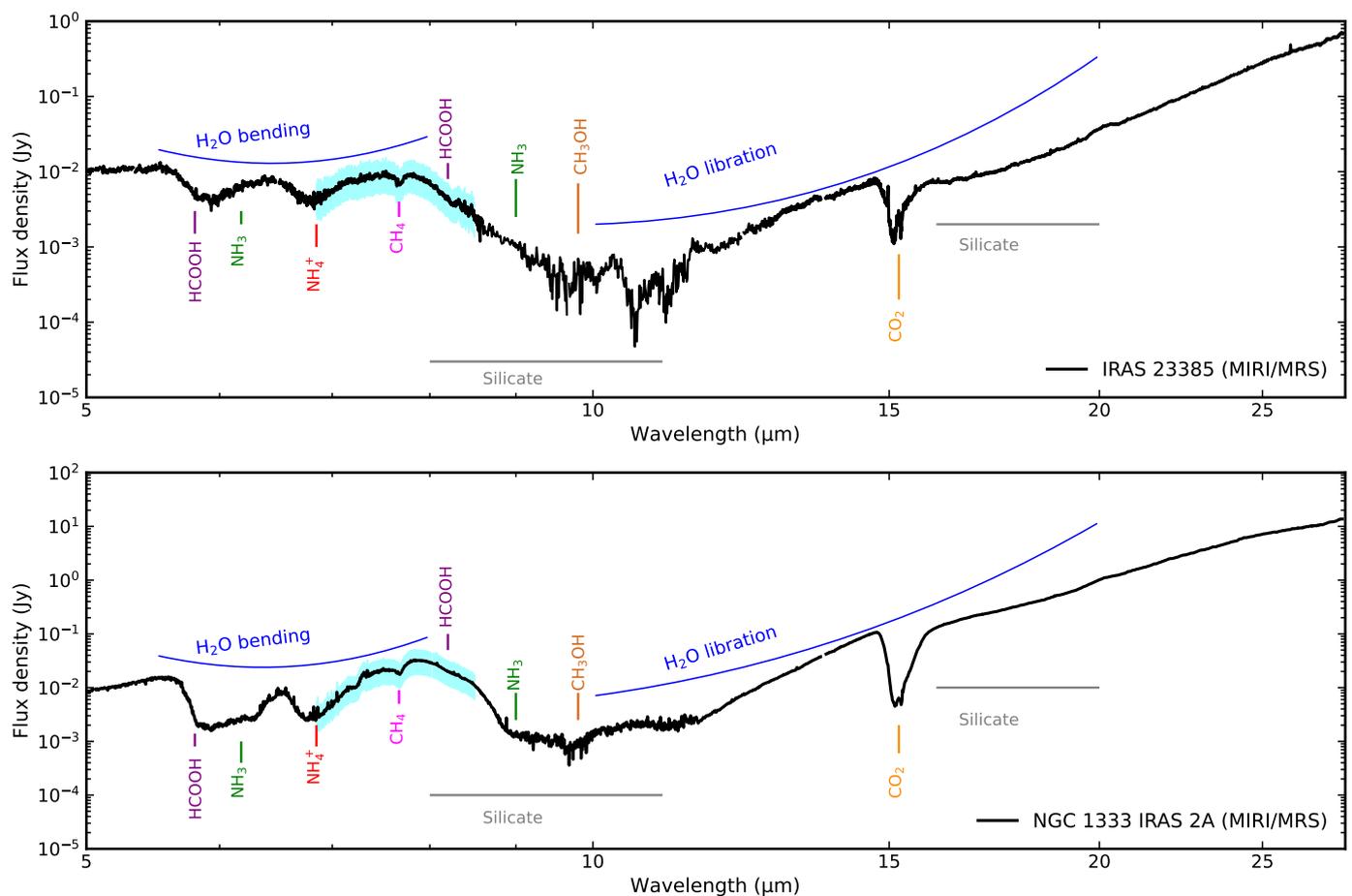
216 time (GTO) 1290 (P.I. E. F. van Dishoeck) and 1236 (P.I. M. 217  
218 Ressler), respectively. 219

220 All data presented in this paper were taken with the Mid- 221  
222 InfraRed Instrument (MIRI; Rieke et al. 2015; Wright et al. 223  
224 2015, 2023) in the Medium Resolution Mode (MRS; Wells 225  
226 et al. 2015; Labiano et al. 2021; Argyriou et al. 2023). For 227  
228 IRAS 23385, the observation was done in 2-point dither mode 229  
230 in a 4-point mosaic surrounding the central protostellar cluster. 231  
232 For IRAS2A, the observation consists of a single pointing on the 233  
234 protostellar binary in 2-point dither mode. For both targets, also 235  
236 dedicated background observations were performed (no dither 237  
238 for IRAS 23385, 2-point dither for IRAS 2A). For both targets, 239  
240 all three gratings (A, B, C) were used, providing the full wave- 241  
242 length coverage of MIRI (4.9–28  $\mu\text{m}$ ). All data were taken using 243  
244 the FASTR1 readout mode. The integration time in each grating 245  
246 was 200 s and 111 s for IRAS 23385 (per pointing in the mosaic) 247  
248 and IRAS 2A, respectively. 249

250 The data were processed through all three stages of 251  
252 the JWST calibration pipeline (Bushouse et al. 2022), using 253  
254 the reference context `jwst_1017.pmap` (IRAS 23385) 255  
256 and `jwst_0994.pmap` (IRAS2A) of the JWST Calibra- 257  
258 tion Reference Data System (CRDS; Greenfield & Miller 259  
260 2016). The raw `uncal` data were first processed through 261  
262 the `Detector1Pipeline` of the pipeline, followed by the 263  
264 `Spec2Pipeline`. In the latter step, the data are corrected for 265  
266 fringes using the fringe flat for extended sources (Mueller et al. 266  
267 in prep.), followed by applying a residual fringe correction (Ka- 267  
268 vanagh et al. in prep.). Moreover, in the case of IRAS2A, the 268  
269 telescope background was subtracted in this step using the dedi- 269  
270 cated background observation. However, the background obser- 270  
271 vation of IRAS 23385 includes significant astronomical back- 271  
272 ground emission across all wavelengths, as well as strong emis- 272  
273 sion of PAHs, and could thus not be used to subtract the tele- 273  
274 scope background. The background estimation and subtraction 274  
275 procedure for IRAS 23385 is further discussed in Sect. 2.2. 275  
276 As mentioned in Beuther et al. (2023), an astrometric correc- 276  
277 tion was applied for IRAS 23385, i.e., 1.6077'' in Right As- 277  
278 cension and 0.3485'' in Declination based on identified GAIA- 278  
279 DR3 stars in the parallel images. No such correction was neces- 279  
sary for IRAS2A. The data were further processed with the 280  
`Spec3Pipeline` of the pipeline which produces cubes of all 12 281  
subbands. In this step, both the master background and outlier 282  
rejection routines were switched off. 283

284 The observation of IRAS 23385+6053 reveals two mid- 285  
286 infrared continuum sources (Beuther et al. 2023) that are re- 286  
287 solved at shorter wavelengths (channels 1 and 2,  $\lambda < 12 \mu\text{m}$ ), 287  
288 but which start to become marginally resolved at longer wave- 288  
289 lengths (channel 3,  $12 \mu\text{m} < \lambda < 17 \mu\text{m}$ ) and are completely 289  
290 unresolved at the longest wavelengths (channel 4,  $\lambda > 17 \mu\text{m}$ ). 290  
291 The spectrum is therefore extracted from a large aperture of 2.5'' 291  
292 in diameter (which does not increase with wavelength) centred 292  
293 in between the two sources (R.A. (J2000) 23<sup>h</sup>40<sup>m</sup>54.49<sup>s</sup>, Dec 293  
(J2000) 61<sup>d</sup>10<sup>m</sup>27.40<sup>s</sup>) to encompass the flux of both sources 294  
295 across the full wavelength range. The estimated  $1\sigma$  rms increases 294  
296 from about 0.4 mJy below 20  $\mu\text{m}$  to a few mJy at the longest 295  
297 wavelengths. 296

298 In the observation of IRAS2A, only continuum emission re- 299  
299 lated to the primary component of the binary is detected. The 299  
300 spectrum is therefore extracted from the peak of the continuum 300  
301 emission at 5.5  $\mu\text{m}$  (R.A. (J2000) 03<sup>h</sup>28<sup>m</sup>55.57<sup>s</sup>, Dec (J2000) 301  
302 31<sup>d</sup>14<sup>m</sup>36.76<sup>s</sup>). We assume that any contribution of the sec- 302  
303 ondary component to the spectrum is negligible. The diameter 303  
304 of the aperture was set to  $4 \times 1.22\lambda/D$  to capture as much of the 304  
305 source flux as possible without including too much noise. The 305



**Fig. 1.** MIRI MRS spectrum of the high-mass protostar IRAS 23385+6053 (top) and the low-mass protostar NGC 1333 IRAS 2A (bottom). Strong gas-phase emission lines are masked in both spectra. The assignments for the absorption bands are given and differentiated by the colours. The shaded cyan area indicates the “COMs region” that is studied in this work.

280 estimated  $1\sigma$  rms is about 0.4 mJy below 15  $\mu$ m and increases  
 281 to a few mJy at 19  $\mu$ m and > 10 mJy longwards of 22  $\mu$ m.

282 Figure 1 (top) shows the MIRI/MRS spectra of  
 283 IRAS 23385+6053 (Beuther et al. 2023) and Figure 1 (bottom)  
 284 shows IRAS 2A covering the range between 5 and 28  $\mu$ m, and  
 285 with a resolving power of 4000–1500 (Labiano et al. 2021).  
 286 The spectral absorption features are associated with different  
 287 ice molecules where the principal molecules are labelled in this  
 288 figure, and those in the cyan region will be further discussed in  
 289 Section 4. We highlight the broad feature of H<sub>2</sub>O covering the  
 290 range between 5.5 and 8  $\mu$ m (bending mode) and between 10  
 291 and 20  $\mu$ m (libration mode). HCOOH shows prominent features  
 292 at 5.8 and 8.2  $\mu$ m which can be distinguished in these sources.  
 293 Small features attributed to NH<sub>3</sub> (ammonia), CH<sub>4</sub> (methane) and  
 294 NH<sub>4</sub><sup>+</sup> (ammonium) are also seen in this spectrum. Silicates are  
 295 the other main solid-state species contributing to the absorption  
 296 bands around 9.8 and 18  $\mu$ m. In addition to the absorption  
 297 features, the spectra of IRAS 23385 and IRAS 2A have various  
 298 narrow emission lines which are masked in this work since it is  
 299 focused on ice absorption features. We also point out that the  
 300 IRAS 23385 spectrum is binned by a factor of four between 8.6  
 301 and 12  $\mu$ m because of the saturated silicate band, and IRAS 2A  
 302 spectrum is binned by a factor of two in the entire MIRI-MRS  
 303 range.

## 2.2. Background subtraction for IRAS 23385+6053

304

In the case of IRAS 23385+6053, the telescope and other back- 305  
 grounds could not be subtracted in either the Spec2Pipeline 306  
 or Spec3Pipeline since this results in negative fluxes due to 307  
 significant astronomical emission in the dedicated background 308  
 observation. It is, however, crucial to remove the telescope back- 309  
 ground from our observations to derive accurate ice column den- 310  
 sities. The background was therefore estimated by extracting a 311  
 spectrum from the science observation off-source from the main 312  
 infrared continuum sources at the position within the IFU (In- 313  
 tegral Field Unit) where the background flux was the lowest 314  
 (R.A. (J2000) 23<sup>h</sup>40<sup>m</sup>54.15<sup>s</sup>, Dec (J2000) 61<sup>d</sup>10<sup>m</sup>26.96<sup>s</sup>) using 315  
 the same aperture size as used for extracting the science data 316  
 (2.5’). The background subtraction also results in the subtrac- 317  
 tion of the 8.6  $\mu$ m and 11.3  $\mu$ m PAH features, the emission 318  
 of which was about equally strong in the background-position 319  
 as at the source position. However, a possible under- or over- 320  
 subtraction of PAH emission does not alter the results in this 321  
 work since the PAH bands are broader than the ice bands at the 322  
 wavelengths targeted in this paper. The background subtracted 323  
 spectrum of IRAS 23385+6053 is shown in the top panel of 324  
 Fig. 1. The numerous strong gas-phase emission lines have been 325  
 masked in this version of the spectrum. The unmasked version 326  
 is available in Beuther et al. (2023) and van Gelder et al. (2023) 327  
 for IRAS 23385 and IRAS 2A, respectively. 328

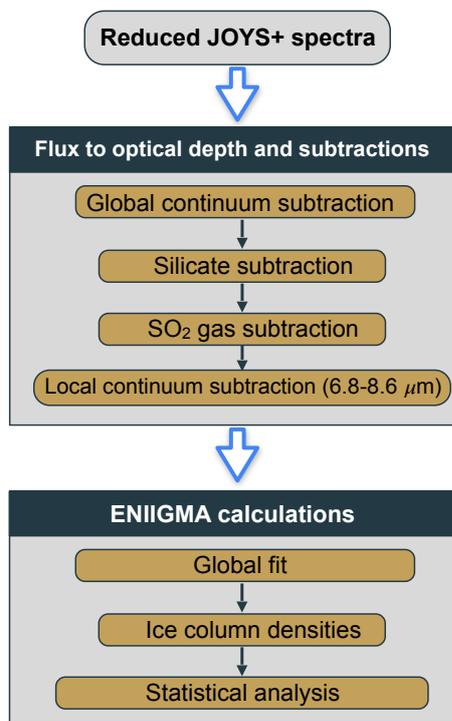


Fig. 2. Summary of the methodology used in this paper.

### 3. Methodology

In this section, we provide information about the methods used to trace and subtract the dust continuum profile, the procedure to remove the silicate bands, and finally, the technique used to fit and identify the ice absorption bands. The focus of this paper is on the 6.8–8.6  $\mu\text{m}$  range as indicated in Figure 1, but the entire MIRI spectrum has to be taken into account for the continuum fitting. For clarity reasons, we summarize the methodology steps in a flowchart shown in Figure 2.

#### 3.1. Continuum subtraction and silicate removal

The spectral energy distributions (SEDs) of IRAS 23385+6053 and IRAS 2A show an increasing slope towards long wavelengths which is typical of embedded protostars. Such SED shapes are also observed towards many high-mass protostars (e.g., Orion BN, Orion IRC2; Gibb et al. 2004) and low-mass protostars (e.g., CrA IRAS32, IRAS 03301+311 and L1448 IRS1 Boogert et al. 2008). The shorter wavelength SED is composed of contributions by warm dust at a range of temperatures, whereas the increase in flux beyond 20  $\mu\text{m}$  is due to the coldest envelope material (Adams et al. 1987). Determining the continuum of these protostars in the mid-IR range is not trivial because of the broad absorption bands in this spectral region. Often, a guided polynomial function is used (e.g., Boogert et al. 2008) to trace the continuum SED. In this work, a third-order polynomial function is used to fit selected points between 5.3–5.5 and 27–28.5  $\mu\text{m}$  where there is little or no overlap exists with ice absorption bands. An additional point was added at 7.5  $\mu\text{m}$  **slightly above the observational data to avoid unrealistic inflexions in the low-order polynomial that would lead to an unphysical continuum. The reason for using this point is to account for known broad absorption features in this range**, for example, the blue wing of the 9.8  $\mu\text{m}$  silicate feature, the H<sub>2</sub>O ice broad bending mode, part of the C5 component proposed in Boogert

et al. (2008), and some of the complex molecules targeted in this paper. In this case, the observed flux itself at 7.5  $\mu\text{m}$  is not suitable to be used as an anchor point. Uncertainties in the position of this guiding point do not affect the conclusions of this work. Figures 3a and 3b, show the polynomial fits used for IRAS 23385 and IRAS 2A, respectively, and the emission lines are masked. Note that there is significant absorption with respect to this continuum over the entire wavelength range in both sources.

Once the continuum SED is determined, we convert the MIRI-MRS spectra of the two protostars to an optical depth scale, as shown in Figures 3c and 3d by using the equation below:

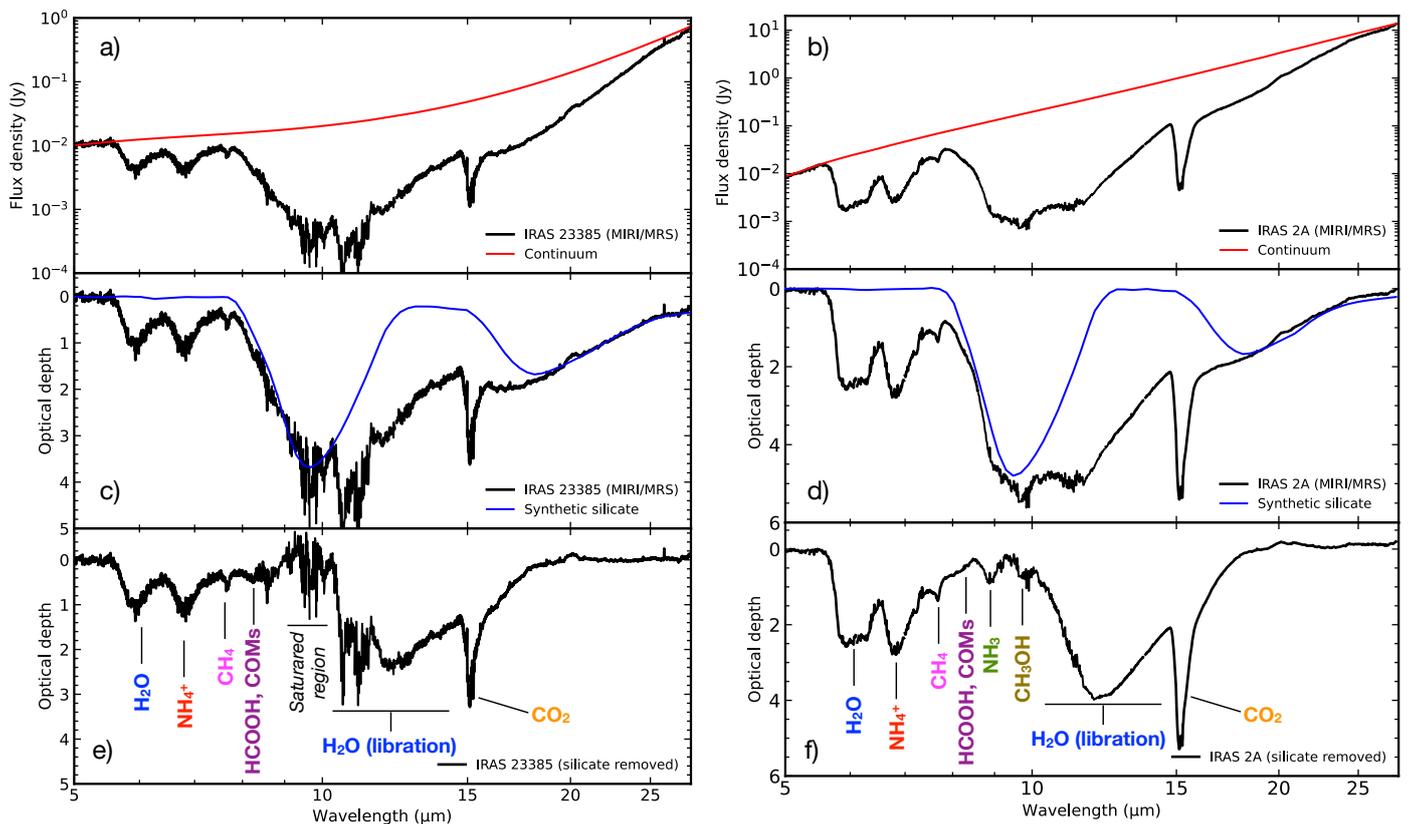
$$\tau_{\lambda} = -\ln\left(\frac{F_{\lambda}^{\text{source}}}{F_{\lambda}^{\text{cont}}}\right), \quad (1)$$

where  $F_{\lambda}^{\text{source}}$  is the source spectrum and  $F_{\lambda}^{\text{cont}}$  is the continuum SED.

Among the absorption bands seen in both spectra, silicates significantly contribute to the bands around 9.8  $\mu\text{m}$  and 18  $\mu\text{m}$ . Since the profile at 9.8  $\mu\text{m}$  is positioned on top of a few ice bands, we perform a silicate removal to analyse the absorption features related to icy molecules. Often, the silicate profile observed towards the galactic centre source, GCS 3, is used to remove the silicate profile of other protostars (Boogert et al. 2008; Bottinelli et al. 2010). However, this method is not used in this work because the shape of the silicate features towards IRAS 23385+6053 and IRAS 2A are broader than GCS 3 as shown in Figures A.1 and A.2 (Appendix A), and would lead to a spurious absorption profile around 8.6  $\mu\text{m}$  after removing the silicate. As an alternative method, we combine two types of silicate to match the band at 9.8  $\mu\text{m}$  following the approach described in Boogert et al. (2011); Poteet et al. (2015); Do-Duy et al. (2020) and McClure et al. (2023). Specifically, we use a mixture of amorphous pyroxene ( $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{SiO}_3$ ) and olivine ( $\text{MgFeSiO}_4$ ) from Dorschner et al. (1995).

We use the `optool` code (Dominik et al. 2021) to generate optical depth spectra of the two silicate types. Briefly, we assume a mixture of silicate and carbon, typical chemical species of interstellar grains, with volume fractions of 87% and 13%, for IRAS 23385 and 82% and 18% for IRAS 2A, as typically used in protostar models. The variation in the fraction of carbon in the models allows us to fit the 9.8  $\mu\text{m}$  and 18  $\mu\text{m}$  bands simultaneously because a higher volume fraction of amorphous carbon reduces the intensities of the silicate bands. Different carbon fractions have been used in the literature to create dust models, for example, 30% (Weingartner & Draine 2001), and 15% (Pontoppidan et al. 2005; Woitke et al. 2016). For the dust models, we assume a power-law size distribution with an exponent of -3.5 and grain sizes ranging from 0.1 to 1  $\mu\text{m}$ . We adopt a distribution of hollow spheres (DHS; Min et al. 2005) to model the silicate band, as this approach mimics irregular geometries of the dust grains. The generated silicates are combined linearly to match the 18  $\mu\text{m}$  band without exceeding the absorption at 9.8  $\mu\text{m}$  and the blue silicate wing around 8.5  $\mu\text{m}$  as shown in Figure 3c and 3d.

The optical depth ratio between the 9.8 and 18  $\mu\text{m}$  silicate features is equal to 2.7 for IRAS 23385 and 2.95 for IRAS 2A. These values are higher compared to the silicates found in the diffuse interstellar medium, which ranges from 1.4 to 2.0 (Chiar & Tielens 2006). It is likely that grain growth plays a role in this case, but a detailed study of this process is beyond the scope of this work. The silicate-removed spectra of IRAS 23385



**Fig. 3.** Continuum (a, b) and silicate subtraction (c, d) steps in IRAS 23385 (left) and IRAS 2A (right). The spectrum of IRAS 23385 is binned by a factor of two between 9 and 11  $\mu\text{m}$  due to the saturated silicate profile. A third-order polynomial function is used to trace the continuum, and the silicate profile is a combination of two laboratory silicate spectra (olivine and pyroxene). Panels e and f show the silicate subtracted spectra of both protostars, with major features labelled.

422 and IRAS 2A are presented in Figures 3e and 3f. By removing  
 423 the silicate bands, the  $\text{H}_2\text{O}$  ice libration band is revealed  
 424 around 12  $\mu\text{m}$ . One can also see the ammonia umbrella mode at  
 425 9.0  $\mu\text{m}$  and the methanol C-O stretch mode at 9.8  $\mu\text{m}$  in IRAS 2A  
 426 (Fig. 3f), but not in IRAS 23385 because of the saturation due to  
 427 the silicate feature, as well as the higher noise level.

428 For completeness, we show in Appendix B the silicate sub-  
 429 traction using different silicates for IRAS 2A, the source with  
 430 high signal-to-noise ratio (S/N). Those spectra are scaled to an  
 431 optical depth of  $\tau = 4.9$ , which is the same as in the synthetic  
 432 silicate fit (top panel of Figure B.1). The subtracted spectra are  
 433 shown in the bottom panel. It is clear that the synthetic silicate  
 434 and the  $\text{MgSiO}_3$  model taken from Poteet et al. (2015) show very  
 435 similar profiles. On the other hand, the use of the GCS 3 sili-  
 436 cate leads to an unrealistic absorption excess. Finally, it is worth  
 437 mentioning that silica ( $\text{SiO}_2$ ) has a blue shoulder at 8.6  $\mu\text{m}$  and a  
 438 peak at 9  $\mu\text{m}$ . However, the presence of silica is associated with  
 439 other materials such as enstatite and forsterite whose spectral  
 440 features are not seen in the sources addressed in this paper. For  
 441 the different silicates considered in this paper, there are no rele-  
 442 vant differences in the spectral shapes between 7.8 and 8.5  $\mu\text{m}$ .

### 443 3.2. $\text{SO}_2$ gas emission subtraction

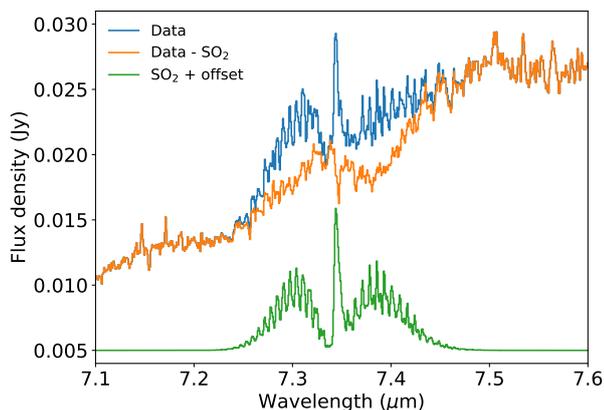
444 In the spectrum of IRAS 2A, clear molecular emission is su-  
 445 perimposed on the ice absorption features between  $\sim 7.25$   $\mu\text{m}$   
 446 and  $\sim 7.45$   $\mu\text{m}$ , see Fig. 4. This emission was recently found  
 447 to originate from warm gas-phase  $\text{SO}_2$  (van Gelder et al. 2023).  
 448 In order to accurately determine the contribution of ices in this

wavelength range, the gas-phase emission lines of  $\text{SO}_2$  ( $\nu_3$ ) have  
 449 to be subtracted from the spectrum. This was achieved by sub-  
 450 tracting the best-fit gas-phase emission line model of  $\text{SO}_2$ , which  
 451 was recently derived by van Gelder et al. (2023). This model is  
 452 very well constrained by the R branch lines at 7.3  $\mu\text{m}$ .  
 453

The  $\text{SO}_2$  emission subtracted spectrum is also presented in  
 454 Figure 4 as the orange line and clearly reveals an ice absorption  
 455 feature around 7.4  $\mu\text{m}$  that was hidden by the  $\text{SO}_2$  emission. The  
 456  $\text{SO}_2$  emission is slightly over-subtracted around 7.35  $\mu\text{m}$  (i.e. at  
 457 the Q-branch) but this does not hamper the analysis of the ice  
 458 bands since this residual is much more narrow than typical ice  
 459 absorption bands.  
 460

### 461 3.3. Isolating ice features between 6.85 and 8.6 $\mu\text{m}$

Weak absorption features have been measured in the laboratory  
 462 covering the range between 6.85 and 8.6  $\mu\text{m}$  (e.g., Lacy et al.  
 463 1991; Schutte et al. 1999; Öberg et al. 2011), and Terwisscha  
 464 van Scheltinga et al. (2018), which are compared with observa-  
 465 tional spectra of massive protostars, by Boogert et al. (2008);  
 466 Öberg et al. (2011), low-mass protostars (e.g., Zasowski et al.  
 467 2009; Yang et al. 2022) and background stars (McClure et al.  
 468 2023). Most notable are the absorption features around 7.2 and  
 469 7.4  $\mu\text{m}$ . To isolate these bands, previous works used a polynomi-  
 470 al fit on the flux scale data to trace a local continuum start-  
 471 ing around 7.0–7.14  $\mu\text{m}$  and finishing around 7.8–8.0  $\mu\text{m}$  (e.g.,  
 472 Schutte et al. 1999). This approach isolates the 7.2 and 7.4  $\mu\text{m}$   
 473 features but excludes potential absorption features around 7  $\mu\text{m}$   
 474



**Fig. 4.** The observed spectrum of IRAS 2A (blue) surrounding the 7.2  $\mu\text{m}$  and 7.4  $\mu\text{m}$  ice absorption features with  $\text{SO}_2$  ( $\nu_3$ ) emission. The best-fit  $\text{SO}_2$  model of van Gelder et al. (2023) is presented in green and the  $\text{SO}_2$  subtracted spectrum of IRAS2A is shown in orange. Subtracting the  $\text{SO}_2$  emission clearly reveals the 7.4  $\mu\text{m}$  absorption feature.

475 and at wavelengths long-wards of 7.8  $\mu\text{m}$  where C–H and C–O  
476 absorption features of many possible molecules contribute.

477 In this work, we isolate the 7.2 and 7.4  $\mu\text{m}$  features using  
478 a third-order polynomial function, and following a slightly dif-  
479 ferent approach. First, instead of using the spectrum on the flux  
480 scale, we perform the polynomial fit on the optical depth scale  
481 after removing the silicate absorption. The strong silicate band  
482 makes it difficult to observe small features such as those due  
483 to COMs. Second, we use guiding points fitted by a third-order  
484 polynomial function, as shown in the left panels of Figure 5.  
485 This additional continuum represents blended absorption pro-  
486 files from the broad  $\text{H}_2\text{O}$  ice bending mode, the red wing of the  
487  $\text{NH}_4^+$  cation, and the C5 component proposed by Boogert  
488 et al. (2008). Another small contribution from the O–H bending  
489 mode of  $\text{CH}_3\text{OH}$  ice is also considered in this step. The points  
490 used for IRAS 23385 are at 6.8, 7.2, 7.7 and 8.5  $\mu\text{m}$  and at 6.8,  
491 7.3, 7.5, 9.4 and 10  $\mu\text{m}$  for IRAS 2A. The positions of the guid-  
492 ing points are distinct because of the differences in the absorp-  
493 tion profiles of the two sources. In order to account for possible  
494 C–H absorption bands, the first point at 6.8  $\mu\text{m}$  is chosen to be  
495 marginally above the wing of the strong 6.85  $\mu\text{m}$  feature. The  
496 points long-wards of 7.8  $\mu\text{m}$  are selected where we expect no  
497 or weak ice absorption, to account for the C–O features. In the  
498 case of IRAS 2A, we use points at 9.4 and 10.0  $\mu\text{m}$  because of  
499 the clear absorption profiles at 9 and 9.8  $\mu\text{m}$ .

500 After subtracting the local continuum fit, we isolate the ice  
501 features in the range between 6.8 and 8.5  $\mu\text{m}$  as shown in the  
502 right panels of Figure 5. In these figures, one can see absorp-  
503 tion bands at 7, 7.2, 7.4, 7.5–7.8 and 8.2  $\mu\text{m}$  that are fitted and  
504 discussed in Sections 4 and 5, respectively. Notably, the 8.2  $\mu\text{m}$   
505 band of IRAS 23385 seems broad and asymmetric, whereas in  
506 IRAS 2A the same band seems broad, weaker and symmetric.  
507 The band around 7.7  $\mu\text{m}$  has a prominent blue shoulder in both  
508 sources, reflecting the interaction with other neighbouring chem-  
509 ical species.

### 510 3.4. Fits and laboratory data

511 Since molecules have multiple functional groups, performing si-  
512 multaneous fits at different wavelengths supports secure detec-  
513 tion. Additionally, some molecules are expected to absorb in  
514 the wavelength range targeted in this paper, such as  $\text{CH}_4$ ,  $\text{SO}_2$ ,

$\text{HCOOH}$ ,  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CH}_2\text{OH}$  (e.g., Schutte et al. 1999; 515  
Bisschop et al. 2007; Öberg et al. 2008), which are used as start- 516  
ing point in the MIRI spectral ice decomposition. We fit the re- 517  
gion between 6.8 and 8.6  $\mu\text{m}$  of IRAS 2A and IRAS 23385 using 518  
the ENIIGMA fitting tool (Rocha et al. 2021). This code searches 519  
for the global minimum solution that fits the observations by 520  
performing a linear combination of laboratory ice data. The ge- 521  
netic algorithm approach benefits from a simple fitness function 522  
(Baek et al. 2000), and here we use the root-mean-square error 523  
(RMSE) given by the equation below: 524

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=0}^{n-1} \left( \tau_{\nu,i}^{\text{obs}} - \sum_{j=0}^{m-1} w_j \tau_{\nu,j}^{\text{lab}} \right)^2} \quad (2)$$

525 where both experimental ( $\tau_{\nu,j}^{\text{lab}}$ ) and observational ( $\tau_{\nu,i}^{\text{obs}}$ ) spectrum 526  
are converted to wavenumber space ( $\nu$ ),  $w_j$  is the scale factor, 527  
and  $m$  and  $n$  are the  $m$ th and  $n$ th data point. The absorbance lab- 528  
oratory data ( $Abs$ ) are converted to an optical depth scale by the 529  
equation  $\tau_{\nu}^{\text{lab}} = 2.3Abs_{\nu}$ . In the degeneracy analysis shown in 530  
Section 3.5, the error of the data is taken into account. 531

532 In a nutshell, ENIIGMA uses genetic modelling algorithms for 533  
searching the optimal coefficients of the linear combination ( $w$ ). 534  
Genetic algorithms are robust optimization techniques based on 535  
the processes of natural selection that aim to find the global mini- 536  
mum solution for complex problems (Holland 1975; Koza 1992). 537  
Once the best fit is found, ENIIGMA calculates the ice column 538

$$N_{\text{ice}} = \frac{1}{A} \int_{\nu_1}^{\nu_2} \tau_{\nu}^{\text{lab}} d\nu, \quad (3)$$

539 where  $A$  is the vibrational mode band strength of the molecule, 540  
which is listed in Table 1. The band strengths of molecules 541  
change depending on the chemical environment. For this reason, 542  
we adopt values of corrected band strengths, when available, to 543  
derive the ice column densities. The derivation of band strengths 544  
is not straightforward because it depends on the ice density. The 545  
typical band strength uncertainties are around 15% and 30% for 546  
pure and mixed ices, respectively (Rachid et al. 2022; Slavcin- 547

548 ska et al. 2023). 549  
The laboratory data considered in this paper are listed in Ap- 550  
pendix C. These data were taken mainly from the Leiden Ice 551  
Database for Astrochemistry<sup>2</sup> (LIDA; Rocha et al. 2022) and 552  
from the Goddard NASA database<sup>3</sup>. The methodology used by 553  
ENIIGMA to test the data available is detailed in Rocha et al. 554  
(2021). Here, we provide a brief description of the method. In 555  
the first stage ENIIGMA combines IR spectra of pure ice at low 556  
temperature with pure ice at high temperature. The best group 557  
of solutions is passed to the second step. In the second stage, 558  
ENIIGMA combines the previous best solution with pure ice, with 559  
all ice mixtures in the ENIIGMA database in a sequential way. At 560  
this stage, all data that has an IR feature in the range fitted was 561  
tested. Finally, ENIIGMA passes the best-ranked groups of solu- 562  
tions to a final stage, where species from one group of solutions 563  
are mixed and combined with species from another group. This 564  
allows the code to diversify the number of combinations and in- 565  
creases the possibility for the code to find the global minimum 566  
solution not only among the coefficients but also among the lab- 567  
oratory data available. In total, the code tested 3173 different 568

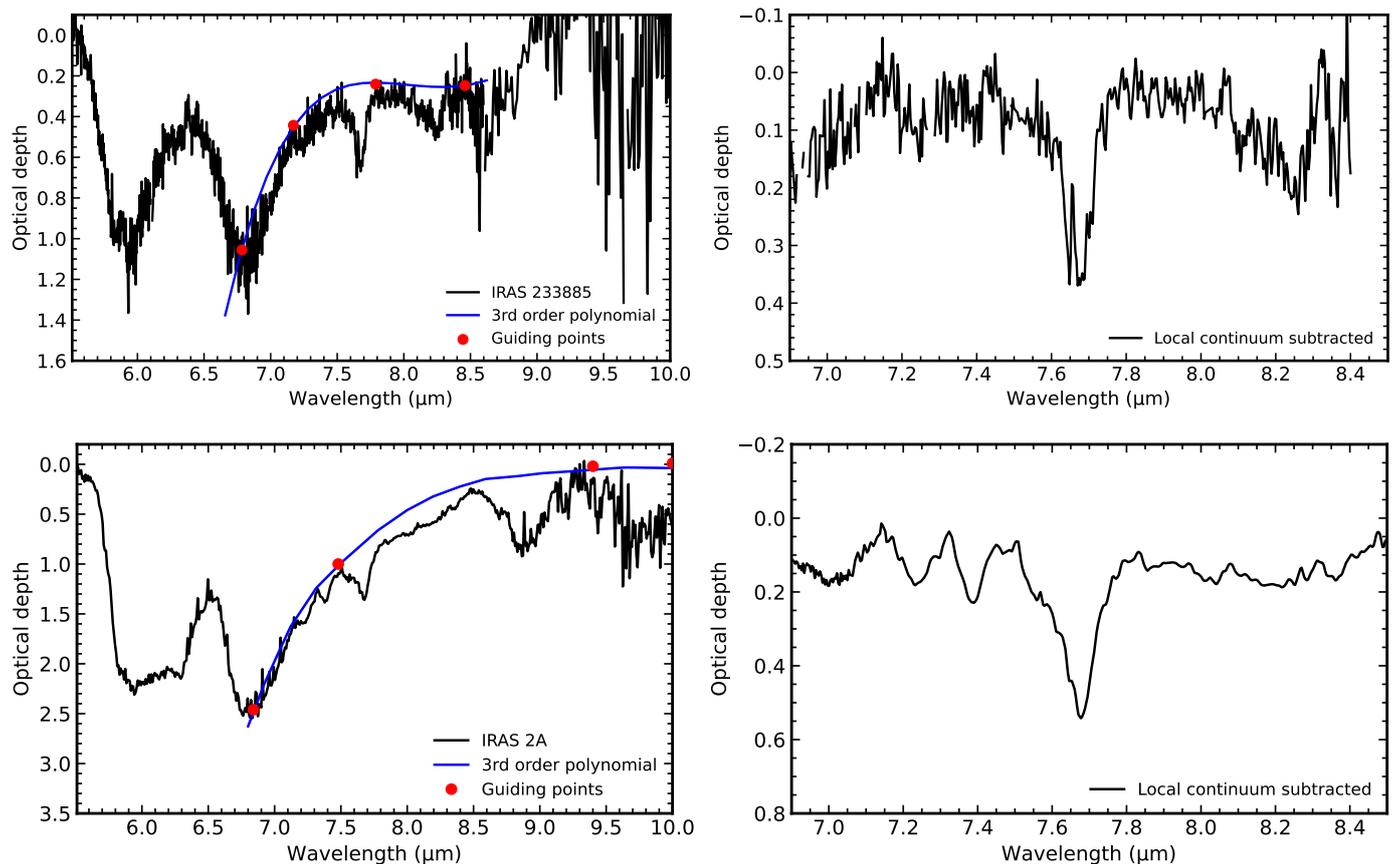
<sup>2</sup> <https://icedb.strw.leidenuniv.nl/>

<sup>3</sup> <https://science.gsfc.nasa.gov/691/cosmicice/spectra.html>

**Table 1.** List of vibrational transitions and band strengths of molecules considered in this paper.

Structure	Chemical formula	Name	$\lambda$ [ $\mu\text{m}$ ]	$\nu$ [ $\text{cm}^{-1}$ ]	Identification	$\mathcal{A}$ [ $\text{cm molec}^{-1}$ ]	References
	H <sub>2</sub> O	Water	13.20	760	libration	$3.2 \times 10^{-17}$	[1]
	CH <sub>4</sub>	Methane	7.67	1303	CH <sub>4</sub> def.	$8.4 \times 10^{-18}$	[1]
	SO <sub>2</sub>	Sulfur dioxide	7.60	1320	SO <sub>2</sub> stretch	$3.4 \times 10^{-17}$	[2]
	H <sub>2</sub> CO	Formaldehyde	8.04	1244	CH <sub>2</sub> rock	$1.0 \times 10^{-18}$	[1]
	CH <sub>3</sub> OH	Methanol	9.74	1026	C–O stretch	$1.8 \times 10^{-17}$	[1]
	HCOOH	Formic acid	8.22	1216	C–O stretch	$2.9 \times 10^{-17}$	[1]
	CH <sub>3</sub> CHO	Acetaldehyde	7.41	1349	CH <sub>3</sub> s-def./CH wag.	$4.1 \times 10^{-18,a}$	[3]
	CH <sub>3</sub> CH <sub>2</sub> OH	Ethanol	7.23	1383	CH <sub>3</sub> s-def.	$2.4 \times 10^{-18,a}$	[4]
	CH <sub>3</sub> OCHO	Methyl formate	8.25	1211	C–O stretch	$2.52 \times 10^{-17,a}$	[5]
						$2.28 \times 10^{-17,b}$	[5]
	CH <sub>3</sub> COOH	Acetic acid	7.82	1278	OH bend	$4.57 \times 10^{-17}$	[6]
	HCOO <sup>-</sup> (B1)	Formate ion	7.23	1383	C–O stretch	$8.0 \times 10^{-18}$	[3]
	HCOO <sup>-</sup> (B2)	Formate ion	7.38	1355	C–O stretch	$1.7 \times 10^{-17}$	[3]
	OCN <sup>-</sup>	Cyanate ion	7.62	1312	Comb. ( $2\nu_2$ )	$7.45 \times 10^{-18}$	[6]
	CH <sub>3</sub> OCH <sub>3</sub>	Dimethyl ether	8.59	1163	COC str. + CH <sub>3</sub> rock.	$4.9 \times 10^{-18,a}$	[5]
	CH <sub>3</sub> CN	Methyl cyanide	7.27	1374	CH <sub>3</sub> sym. def.	$1.2 \times 10^{-18,a}$	[5]
	CH <sub>3</sub> COCH <sub>3</sub>	Acetone	7.33	1363	CCC asym. str.	$1.2 \times 10^{-17,a}$	[7]
	CH <sub>3</sub> NH <sub>2</sub>	Methylamine	8.5	1176	CH <sub>3</sub> rock	$1.3 \times 10^{-18,a}$	[8]
	NH <sub>2</sub> CHO	Formamide	7.2	1388	CH bend	$1.4 \times 10^{-17,a}$	[9]
	HCOCH <sub>2</sub> OH	Glycolaldehyde	7.3	1372	CH bend	$7.7 \times 10^{-18}$	[10]

**Notes.** [1] Bouilloud et al. (2015), [2] Boogert et al. (1997), [3] Hudson & Ferrante (2020), [4] Boudin et al. (1998), [5] Terwisscha van Scheltinga et al. (2021), [6] This work - see Appendix D. <sup>a</sup>Mixture with H<sub>2</sub>O. <sup>b</sup>Mixture with CH<sub>3</sub>OH, [7] Rachid et al. (2020), [8] Rachid et al. (2021), [9] Slavicinska et al. (2023), [10] Hudson et al. (2005)



**Fig. 5.** Left: Local continuum in the 6.8–8.6 spectral range using a fourth-order polynomial function. Right: Isolated 6.8–8.6 optical depth spectrum in both protostars.

566 combinations, where the best solution is the best-ranked group  
567 of components based on the RMSE value.

568 We note that for the purpose of this paper, we subtract the  
569 absorption profiles of  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  around  $6.8 \mu\text{m}$  from the  
570 ice mixtures using a local subtraction with a polynomial function  
571 (see Appendix E). This enables fitting the observational data after  
572 local subtraction. As previously mentioned, the contribution  
573 of these two molecules is taken into account in the polynomial fit  
574 used to trace the local continuum between  $6.8$  and  $8.6 \mu\text{m}$ . Most  
575 of the COM laboratory data have a spectral resolving power of  
576  $R = 5000$ , which is degraded to the nominal spectral resolution  
577 of the two sources ( $R \sim 3500$ ) around  $7\text{--}8 \mu\text{m}$ . In the case of  
578  $\text{HCOO}^-$  and  $\text{OCN}^-$ , we isolated the ice bands of these ions using  
579 a local baseline subtraction. These two species are formed  
580 from molecules engaged in an acid-base reaction, also known as  
581 Bronsted-Lowry acid-base theory (Brönsted 1923; Lowry 1923),  
582 and also seen in interstellar ices (e.g., Grim & Greenberg 1987;  
583 Schutte & Khanna 2003; van Broekhuizen et al. 2004). The  
584 amount of ions formed depends on the initial abundances of the  
585 parent molecules. By isolating these bands, one can mimic at  
586 first order, different initial conditions of parent species. It is also  
587 worth mentioning that the baselines of  $\text{HCOOH}$  ice mixture are  
588 checked before the analysis. Öberg et al. (2011) comments that  
589 one should be careful when deriving the formic acid and formate  
590 ion column densities because of baseline issues in some  
591 experimental data measured further in the past. In addition, it  
592 is important to note that  $\text{HCOO}^-$  and  $\text{HCOOH}$  share a band at  
593  $7.2 \mu\text{m}$ . For that reason, we would recommend using the  $7.4 \mu\text{m}$   
594 to quantify  $\text{HCOO}^-$ .

### 3.5. Degeneracy analysis

595 The ENIIGMA fitting tool performs a degeneracy analysis of the  
596 coefficients in the linear combination that results in the best fit.  
597 Briefly, the code performs a Gaussian variation around each coeffi-  
598 cient by using the numpy function `numpy.random.normal`  
599 (Harris et al. 2020), and is given by:  
600

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \quad (4)$$

601 where  $\mu$  values are the optimal coefficients, and  $\sigma$  is the standard  
602 deviation around  $\mu$ . This analysis allows us to calculate  $\chi^2$  values  
603 for each new linear combination, and derive confidence intervals  
604 based on a  $\Delta\chi^2$  map (Avni & Bahcall 1980), which is formulated  
605 as:

$$\chi^2 = \frac{1}{dof} \sum_{i=0}^{n-1} \left( \frac{\tau_{v,i}^{\text{obs}} - \sum_{j=0}^{m-1} w_j \tau_{v,j}^{\text{lab}}}{\gamma_{v,i}^{\text{obs}}} \right)^2 \quad (5a)$$

$$\Delta\chi^2(\alpha, \epsilon) = \chi^2 - \chi_{\min}^2 \quad (5b)$$

606 where *dof* is the number of degrees of freedom,  $\gamma$  is the error  
607 in the observational optical depth spectrum propagated from  
608 the flux error assumed to be 10%,  $\alpha$  and  $\epsilon$  are the statistical sig-  
609 nificance and the number of free parameters, respectively.  $\chi_{\min}^2$   
610 corresponds to the goodness-of-fit in the global minimum solu-  
611 tion.

612 ENIIGMA also quantifies the statistical significance of a given  
613 IR spectrum based on its recurrence, which is defined as:

$$\mathcal{R} = \frac{f_i}{S}, \quad (6)$$

614 where  $f_i$  is the absolute frequency of sample  $i$  (i.e. how many  
615 times a specific laboratory data participates in the fit) and  $S$  is  
616 the total number of solutions. If  $\mathcal{R} = 100\%$ , the chemical species  
617 cannot be excluded from the fit. On the other hand, lower per-  
618 centages mean that the spectrum can be replaced by another one  
619 with a similar spectral shape without going outside of the confi-  
620 dence intervals. While the confidence interval analysis evaluates  
621 the degeneracy among the components in the best fit, the recur-  
622 rence analysis quantifies the degeneracy among different spectral  
623 data.

### 624 3.6. Criteria for firm COM ice detections

625 Boogert et al. (2015) classify three types of detection in ices:

- 626 1. Secure: multiple bands or bands of isotopologues are de-  
627 tected in high-quality spectra;
- 628 2. Likely: A single band is detected and the profile matches the  
629 laboratory spectra;
- 630 3. Possibly: A single band is detected and there is no exact  
631 match between the profile and the laboratory spectra;

632 COMs bands are naturally weak, and therefore the isotopo-  
633 logues criteria in (1) will be hardly satisfied for solid-phase  
634 detections. In addition, to these three criteria, Jørgensen et al.  
635 (2020) discuss gauges for the detection of exotic chemical  
636 species in the context of gas-phase observations. They mention  
637 that a firm identification needs a complete spectral survey with a  
638 synthetic spectrum that accounts for all the bands of the identi-  
639 fied molecules instead of using independent analytical functions  
640 (e.g., Gaussian fits) of individual lines. These criteria can also  
641 be applied in the context of COMs in ice, and it is strongly rec-  
642 ommended to use IR laboratory data for comparison instead of  
643 analytical functions (e.g., Gaussian, Lorentzian).

644 We note that different from gas-phase observations, where  
645 the emission profiles are narrow and isolated, solid-phase ab-  
646 sorption profiles are often blended because of the common func-  
647 tional groups and broader spectral features. In addition, because  
648 of the ice matrix in which the molecules are embedded, the shape  
649 of the absorption bands change, with mixing ratio and tempera-  
650 ture (e.g., Öberg et al. 2007; Bouwman et al. 2007). While ice  
651 COMs show peculiar band shapes at high temperatures ( $> 70$  K),  
652 they are very similar at lower temperatures (see Terwisscha van  
653 Scheltinga et al. (2018); Rachid et al. (2020, 2021); Terwisscha  
654 van Scheltinga et al. (2021); Rachid et al. (2022); Slavicska  
655 et al. (2023)). In this sense, we add to the criteria presented by  
656 Boogert et al. (2015) and Jørgensen et al. (2020) that a degen-  
657 eracy analysis of molecules sharing similar functional groups is  
658 needed in order to claim a firm ice COM detection.

### 659 3.7. Remarks for future works

660 In this section, we point out some aspects important to guide  
661 future works on the analysis of COMs fingerprints in protostellar  
662 ices:

- 663 – The intensities of COM bands in observational data are  
664 weaker compared to the major ice components. In this case,  
665 special attention must be paid to the baseline correction of  
666 COM IR laboratory spectra. Any minor inflexion can mimic  
667 a spurious feature and lead to misinterpretation of the obser-  
668 vational spectrum. An example is presented in Appendix F.  
669 The example is given for  $\text{H}_2\text{O}:\text{CH}_3\text{CH}_2\text{OH}$  ice spectrum  
670 where a 7th-order polynomial is used to baseline correct the  
671 spectrum. We show that if a lower number of data points is

672 considered around  $8\ \mu\text{m}$ , the polynomial function can fluctu-  
673 ate and originate spurious features in the final data. Instead  
674 cubic spline functions can be used to mitigate those fluc-  
675 tuations. Another issue, not shown here, is that some weak  
676 bands can be removed unintentionally if the user is not fam-  
677 iliar with a particular dataset and source details.

- Tracing the local continuum on the observed spectrum is as  
678 critical as the spectral fitting. In the COMs fingerprint region,  
679 where broad bands are present, one should be careful when  
680 attributing zero absorption for tracing the local continuum  
681 between  $6.8\text{--}8.6\ \mu\text{m}$ .  
682
- Analysis of observational spectra in the range between  $6.8$   
683 and  $8.6\ \mu\text{m}$  using laboratory data of  $\text{H}_2\text{O}$ - or  $\text{CH}_3\text{OH}$ -  
684 containing ices must have the features of these two molecules  
685 subtracted to allow direct comparison with observational  
686 data after local continuum removal. Appendix E shows an  
687 example of how the  $\text{CH}_3\text{CH}_2\text{OH}$  bands in the mixture with  
688  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  were isolated. While a single 4th-order  
689 polynomial was used in the case of  $\text{H}_2\text{O}:\text{CH}_3\text{CH}_2\text{OH}$ , three  
690 polynomial functions with different orders were needed in  
691 the case of  $\text{CH}_3\text{OH}:\text{CH}_3\text{CH}_2\text{OH}$ , which increases the risk of  
692 creating spurious features.  
693

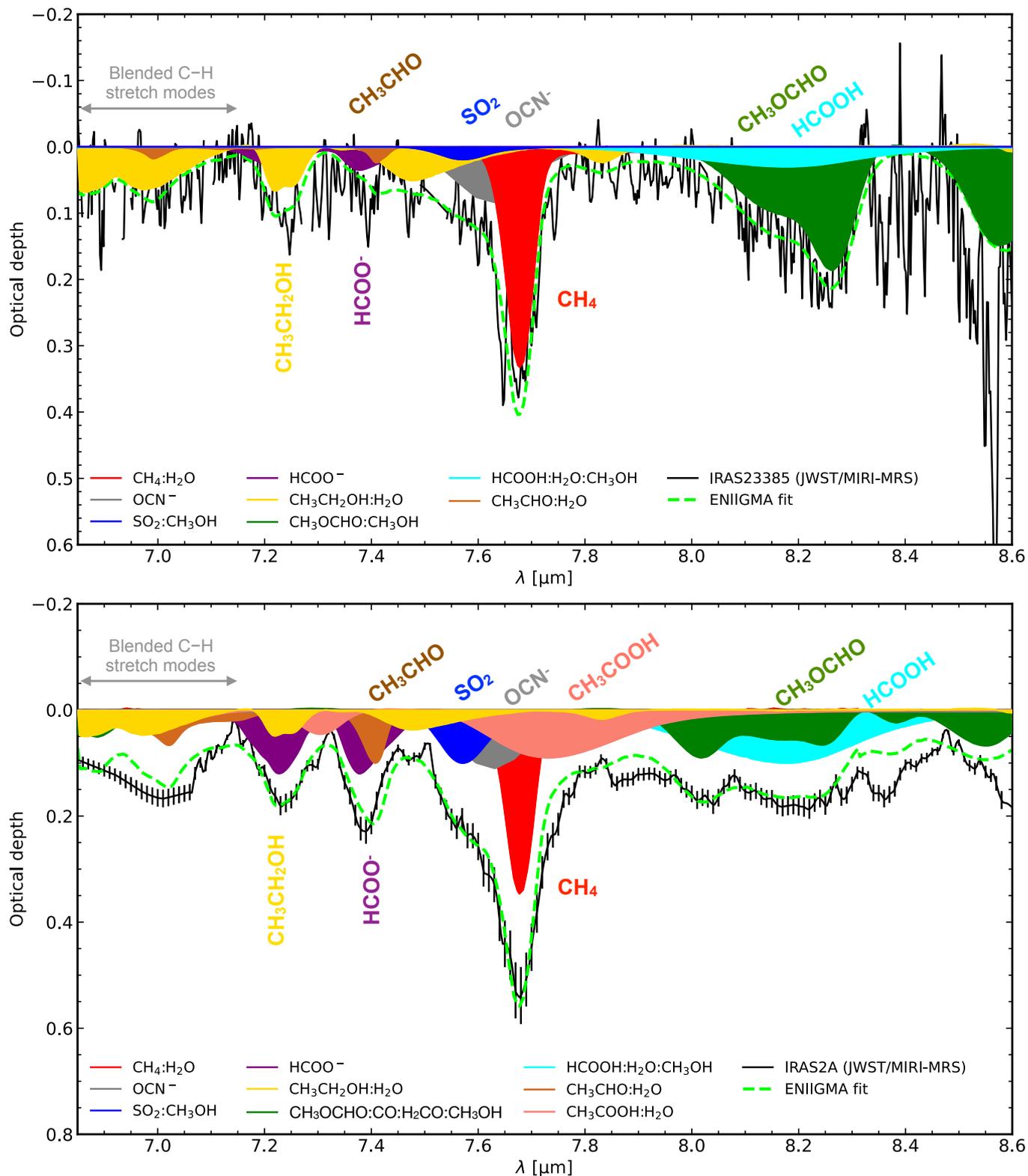
## 694 4. Results

695 In this section, we show the fitting results of the protostars  
696 IRAS 23385+6053 and IRAS 2A in the range between  $6.8$  and  
697  $8.4\ \mu\text{m}$ , as well as the confidence interval analysis.

### 698 4.1. Spectral decomposition and feature analysis

699 The fits of the IRAS23385 and IRAS 2A spectra are shown  
700 in Figure 6 top and bottom, respectively (see Appendix G for  
701 an incremental version of these figures, following the individ-  
702 ual fitting steps). These two MIRI/MRS spectra are decom-  
703 posed using nine laboratory spectra which were selected by  
704 ENIGMA and they provide the global minimum solution. Among  
705 the COMs fitted in this work are,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  
706  $\text{CH}_3\text{OCHO}$  (methyl formate) and  $\text{CH}_3\text{COOH}$  (acetic acid), with  
707 the first three robustly detected (see §3.6 and §4.2). The simple  
708 molecules identified are  $\text{CH}_4$ ,  $\text{SO}_2$ , and  $\text{HCOOH}$ . Additionally,  
709 we found a good match of two ions,  $\text{HCOO}^-$  and  $\text{OCN}^-$ . Be-  
710 cause of the contribution of  $\text{HCOO}^-$  with similar intensities at  
711  $7.2$  and  $7.4\ \mu\text{m}$ , we stress that these two bands are not only asso-  
712 ciated with COMs.

713 The band around  $7.68\ \mu\text{m}$  was clearly visible in previous ice  
714 observations (e.g., Gibb et al. 2004; Öberg et al. 2008), and is  
715 now seen in JWST spectra with unprecedented S/N and spec-  
716 tral resolution.  $\text{CH}_4$  ice is the main carrier of this feature, and  
717 Öberg et al. (2008) suggests that  $\text{SO}_2$  can contribute to the blue  
718 wing of this band based on a Gaussian decomposition of the  
719  $7.68\ \mu\text{m}$  feature. In the present work, this band is decomposed  
720 into four components, with  $\text{CH}_4$  mixed with  $\text{H}_2\text{O}$  the dominant  
721 carrier. This is in line with laboratory experiments suggesting  
722 a common formation pathway for  $\text{CH}_4$  and  $\text{H}_2\text{O}$  ices (Qasim  
723 et al. 2020). The blue wing has contributions of  $\text{SO}_2$  mixed with  
724  $\text{CH}_3\text{OH}$ , and the negative cyanate ion ( $\text{OCN}^-$ ) for both sources.  
725 The red wing of this band can be fitted with  $\text{CH}_3\text{COOH}$  in the  
726 case of IRAS 2A but is not present in IRAS 23385. A good cor-  
727 relation in ice column density between sulfur-bearing molecules  
728 and methanol was observed before by Boogert et al. (1997) and  
729 Boogert et al. (2022).  $\text{OCN}^-$  is one of the ions formed from  
730 molecules engaged in acid-base reactions, and it has a band at



**Fig. 6.** ENIIGMA fits of IRAS 23385 (top) and IRAS 2A (bottom). Gas-phase lines are masked. The figure labels show the ice mixture used in the fits, and a simplified version with the names of the chemical species names is shown close to the bands. The corresponding temperature of these laboratory spectra ranges between 10 K and 15 K.

731 7.63  $\mu\text{m}$ , in addition to its well-known feature at 4.61  $\mu\text{m}$ , commonly seen towards protostars. In fact, recent observations of  
 732 IRAS 2A with the JWST/Near-Infrared Spectrometer (NIRSpec)  
 733 detect the 4.61  $\mu\text{m}$  band, thus confirming the presence of  $\text{OCN}^-$   
 734 in the ices towards IRAS 2A as part of the JOYS program. The  
 735

analysis of the NIRSpec data of this source will be presented in  
 a future paper, but we calculate the ice column density of  $\text{OCN}^-$   
 at 4.61  $\mu\text{m}$  to check the consistency of the fit in the mid-IR (see  
 Section 4.3). As a result, the blue wing of the 7.68  $\mu\text{m}$  feature is  
 composed both by  $\text{SO}_2$  and  $\text{OCN}^-$ . We also note that  $\text{OCN}^-$  in  
 736  
 737  
 738  
 739  
 740

741 both sources has a similar intensity, whereas SO<sub>2</sub> is stronger in  
742 IRAS 2A.

743 Protostar observations in the mid-IR show the 7.2 and 7.4 μm  
744 features with similar strengths across a number of sources,  
745 which suggests the dominance of a single species. In fact, we  
746 find that the formate ion, initially proposed by Schutte et al.  
747 (1999), matches well the 7.2 and 7.4 μm bands of IRAS 2A and  
748 IRAS 23385. This ion is formed by the acid-base reaction of  
749 H<sub>2</sub>O:NH<sub>3</sub>:HCOOH (100:2.6:2) ice mixture at 14 K (Gálvez et al.  
750 2010). The intensity of the formate ion in IRAS 2A is a factor of  
751 three stronger than in IRAS 23385. In Appendix H, we compare  
752 the 7.2 and 7.4 μm band with the formate ion at other tempera-  
753 tures. The formate ion spectrum at 150 K has a broader profile at  
754 7.4 μm, whereas laboratory data at 210 K shows a strong feature  
755 at 7.3 μm that is not observed in either source. Thus, the 7.2 and  
756 7.4 μm features are a signature of ices dominated by ions in cold  
757 regions. Our results also show that despite HCOO<sup>-</sup> being the  
758 main carrier of the 7.2 and 7.4 μm bands, other components can  
759 contribute to these two features separately as discussed below.

760 The presence of HCOO<sup>-</sup> in the ice is supported by the de-  
761 tection of HCOOH at 8.2 μm, in addition to its band at 5.8 μm.  
762 The best fit is found when formic acid is mixed with CH<sub>3</sub>OH and  
763 H<sub>2</sub>O as suggested by Bisschop et al. (2007). The lower intensity  
764 of formic acid in IRAS 23385 can be related to the nature of the  
765 source. At warmer temperatures (>50 K), HCOOH is more ef-  
766 ficiently destroyed via an acid-base reaction (e.g., Schutte et al.  
767 1999; Gálvez et al. 2010). Another possibility is that HCOOH  
768 was not efficiently formed in this high-mass source because  
769 of the lower amount of CO ice available in a high-mass star-  
770 forming region.

771 CH<sub>3</sub>CH<sub>2</sub>OH is detected in both protostars through the ab-  
772 sorption of four vibrational modes at 6.8–7.15 μm (C–H  
773 stretch), 7.25 μm (CH<sub>3</sub> s-deformation), 7.4–7.7 μm (OH de-  
774 formation) and at 7.85 μm (CH<sub>2</sub> torsion). Among the ethanol  
775 data tested, the mixture with H<sub>2</sub>O provides the best fit. Ethanol  
776 is stronger and contributes significantly to the 7.2 μm band in  
777 IRAS 23385, whereas it is less prominent in IRAS 2A.

778 CH<sub>3</sub>CHO shows weak absorption around 7.03 μm (C–H  
779 stretch), and at 7.41 μm (CH<sub>3</sub> s-deformation/CH wagging).  
780 These bands are stronger in IRAS 2A than in IRAS 23385. Ex-  
781 perimental characterization of the CH<sub>3</sub> s-deformation/CH wag-  
782 ging shows a strong dependence on the chemical environment  
783 and temperature (Terwisscha van Scheltinga et al. 2018). The  
784 closer match with both protostars is for acetaldehyde mixed with  
785 H<sub>2</sub>O ice, which has a peak at 7.41 μm. The observed band, how-  
786 ever, has a peak at 7.38 μm, indicating other carriers for this band  
787 (e.g., HCOO<sup>-</sup>).

788 CH<sub>3</sub>OCHO is observed in both sources around 8.2 and  
789 8.6 μm, but with different spectral shapes and intensities. In  
790 IRAS 23385, the methyl formate band is better fitted by a mix-  
791 ture with methanol at 15 K, although the data at 30 and 80 K are  
792 also statistically likely (see Section 4.2.3). Other methyl formate  
793 mixtures do not exhibit such an asymmetric profile, which makes  
794 them unlikely to be the carrier of this band (see Section 5.1.1).  
795 While the shape of the 8.2 μm is well defined, this is not the  
796 case for the 8.6 μm band, which is affected by saturation due  
797 to the strong silicate feature. In IRAS 2A the bands at 8.2 and  
798 8.6 μm are consistent with a mixture containing CO, H<sub>2</sub>CO, and  
799 CH<sub>3</sub>OH. This ice mixture of CH<sub>3</sub>OCHO also fits well the 8.0 μm  
800 band associated with H<sub>2</sub>CO.

801 CH<sub>3</sub>COOH is found to fit well to the IRAS 2A spectrum, but  
802 not that of IRAS 23385. In addition, a better match with the ob-  
803 servations is found for acetic acid mixed with H<sub>2</sub>O ice. The two  
804 identified bands are located at 7.3 and 7.7 μm (salmon colour in

Figure 6, bottom). Specifically, the 7.7 μm band in IRAS 2A has  
805 a broad profile that is more than just CH<sub>4</sub> and it is necessary to fit  
806 the absorption excess around this region without strong overlap  
807 between 7.7 and 7.85 μm. The 7.3 μm is slightly over-estimated  
808 in the fits, because of the amount of absorption needed to fit the  
809 7.7 μm band. This can be because of the SO<sub>2</sub> emission lines sub-  
810 traction around 7.3 μm or the uncertainties involved in the local  
811 continuum choice around the 7.7 μm band.

812 The robustness of these detections based on the difference  
813 in local continuum choice is discussed in Section 4.2.4 for  
814 IRAS 2A, the higher S/N source.  
815

## 816 4.2. Statistical analysis

### 817 4.2.1. Confidence intervals

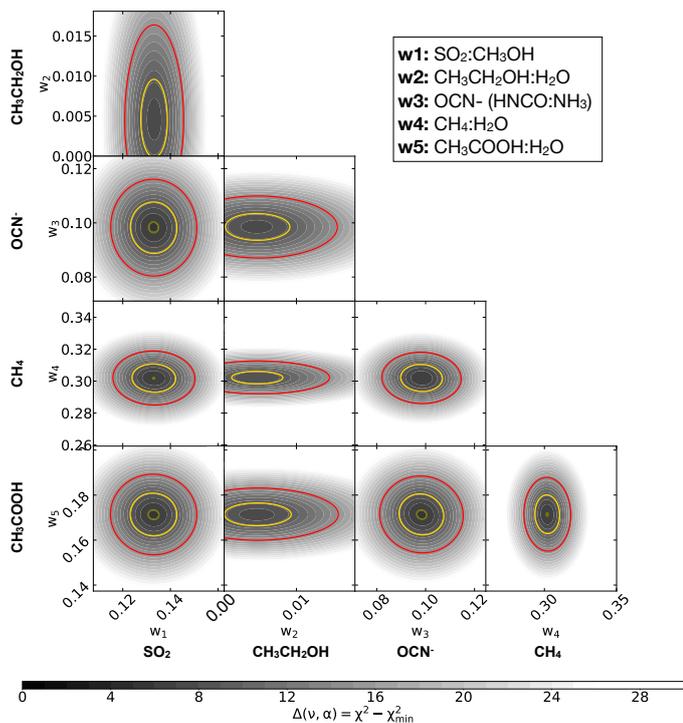
818 We derive the confidence intervals (see Section 3.5) of the fits  
819 for IRAS 23385 and IRAS 2A in three different ranges sepa-  
820 rately: (i) 6.85–7.5 μm, (ii) 7.5–7.8 μm and (iii) 7.8–8.6 μm.  
821 The components in these three ranges are relatively isolated, and  
822 therefore their contribution in one given interval is kept constant  
823 when analysing other ranges.

824 In Figure 7, we show the confidence intervals for the fit  
825 of IRAS 2A in the range between 7.5 and 7.8 μm. The yel-  
826 low and red contours indicate 2σ and 3σ confidence intervals.  
827 Based on these contours, one can note that all components, but  
828 CH<sub>3</sub>CH<sub>2</sub>OH, are required to fit IRAS 2A. In this particular spec-  
829 tral range (7.5 and 7.8 μm), only a small portion of CH<sub>3</sub>CH<sub>2</sub>OH  
830 spectrum at 7.5 μm contributes to the absorption. Therefore, the  
831 confidence interval analysis shows that CH<sub>3</sub>CH<sub>2</sub>OH is not cru-  
832 cial to fit the 7.5 and 7.8 μm. The contribution of CH<sub>3</sub>CH<sub>2</sub>OH  
833 in IRAS 2A is better evaluated using the range between 6.86  
834 and 7.5 μm, which is shown in Appendix I. In Figure I.1 (top),  
835 the CH<sub>3</sub>CH<sub>2</sub>OH:H<sub>2</sub>O is not zero, which reinforces the idea that  
836 CH<sub>3</sub>CH<sub>2</sub>OH is robustly found in IRAS 2A. Another impor-  
837 tant result from Figure 7 is that SO<sub>2</sub> (w1) and OCN<sup>-</sup> (w3)  
838 are both required to fit IRAS 2A since their coefficients can-  
839 not be zero. Finally, CH<sub>3</sub>COOH:H<sub>2</sub>O cannot be excluded as a  
840 solution based on this statistical analysis. Further analysis of  
841 the 6.86–7.5 μm range allows us to conclude that CH<sub>3</sub>CHO,  
842 HCOO<sup>-</sup>, and HCOOH are also robust detections. In addition  
843 to these chemical species, Figure I.1 (bottom) also shows that  
844 CH<sub>3</sub>COOH cannot be excluded from the fit obtained with one  
845 specific continuum subtraction. More details for CH<sub>3</sub>COOH are  
846 presented in Section 4.2.4. The analysis of the spectral range be-  
847 tween 7.8 and 8.6 μm, shows that another COM, CH<sub>3</sub>OCHO is  
848 also a robust detection in IRAS 2A spectrum.

849 A similar analysis is performed for IRAS 23385 (Figures I.2  
850 and I.3). For the range between 7.5 and 7.8 μm, CH<sub>4</sub> and  
851 OCN<sup>-</sup> are essential, whereas SO<sub>2</sub> can be statistically not re-  
852 quired due to the low S/N in IRAS 23385 spectrum. Likewise,  
853 the analysis of the 6.86–7.5 μm range shows that CH<sub>3</sub>CH<sub>2</sub>OH,  
854 CH<sub>3</sub>CHO and HCOOH are robust detections, whereas the for-  
855 mate ion (HCOO<sup>-</sup>) absorption may be explained by CH<sub>3</sub>CH<sub>2</sub>OH  
856 or HCOOH ice features. For the 7.8–8.6 μm interval, both  
857 HCOOH and methyl formate (CH<sub>3</sub>OCHO) are robust detections.

### 858 4.2.2. Recurrence of the ice components

859 A complementary statistical analysis is performed on the recur-  
860 rence of all solutions within a given confidence interval. The  
861 difference in this method is that we do not vary the coefficient  
862 values of each solution, but the laboratory data instead. Figure 8  
863 (top) shows the recurrence of the IRAS 2A fit of 15 chemical



**Fig. 7.** Corner plots showing the IRAS 2A coefficient confidence intervals for the range between 7.5 and 7.8  $\mu\text{m}$ . The grey scale colour is the  $\Delta\chi^2$  map derived from a total of 5000 values. Yellow and red contours represent 2 and 3 $\sigma$  significance, respectively.

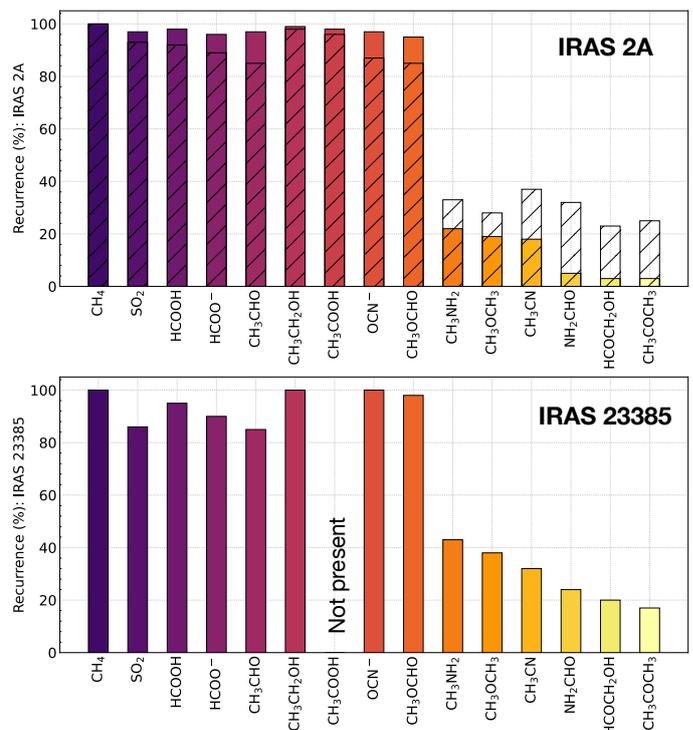
864 species inside 3 $\sigma$  confidence interval and considering several  
 865 solutions. This analysis indicates that the COMs providing the  
 866 best fits (see Figure 6), are the most recurrent in the bar chart  
 867 (87.5%  $\leq R \leq 100\%$ ), and therefore cannot be excluded as a  
 868 solution. Other chemical species, such as  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{OCH}_3$ ,  
 869  $\text{NH}_2\text{CHO}$ ,  $\text{HCOCH}_2\text{OH}$  and  $\text{CH}_3\text{COCH}_3$ , some of which have  
 870 been suggested previously to contribute in this range, have a recur-  
 871 recurrence lower than 50%. This is not sufficient to claim a firm  
 872 detection and at best upper limits can be derived.

873 The reason that formamide and acetone are not part of the  
 874 global fit is that the formate ion band shape dominates the absorp-  
 875 tion profile at 7.2 and 7.4  $\mu\text{m}$ . In addition, acetic acid and  
 876 ethanol also contribute to these two absorption profiles. In the  
 877 cases of methylamine and dimethyl ether, the fits indicate that  
 878 methyl formate contributes more to the 8.5–8.6  $\mu\text{m}$  range.

879 The same analysis is done for IRAS 23385, shown in Fig-  
 880 ure 8 (bottom). Since the MIRI data for this source have a  
 881 lower S/N compared to IRAS 2A, there exist slightly more varia-  
 882 tions among the recurrence values. The components found in the  
 883 global fit have a recurrence above 85%, whereas other COMs  
 884 are recurrent by  $\sim 40\%$  or less. Interestingly,  $\text{CH}_3\text{COOH}$  does  
 885 not participate in any of the solutions tested because  $\text{OCN}^-$  and  
 886  $\text{CH}_3\text{CH}_2\text{OH}$  account for all the absorption around 7.7  $\mu\text{m}$ .

#### 887 4.2.3. Temperature degeneracy

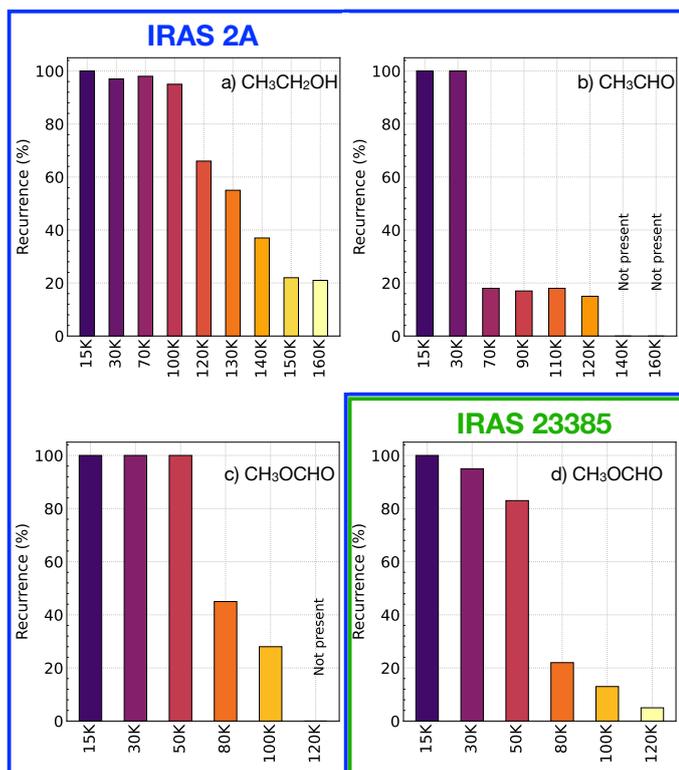
888 Despite the well-known changes in the band profiles of astro-  
 889 physical ices with temperature, there are some absorption fea-  
 890 tures that barely vary with temperature. Consequently, the fitting  
 891 routine is not able to distinguish between these data. Rocha et al.  
 892 (2021) show that when data that is known to provide a good fit is  
 893 arbitrarily removed from the database, the ENIIGMA fitting tool  
 894 uses another data of the same species, but with similar temper-



**Fig. 8.** Bar plot showing the recurrence of the difference chemical species to the fit in IRAS 2A (top) and IRAS 23385 (bottom). Recurrences above 50% are considered essential to the fit and robust detection.  $\text{CH}_3\text{COOH}$  in IRAS 23385 does not occur in any of the solutions. In the case of IRAS 2A (top panel) we present hatched bars that show the recurrence of the solutions if the errors in optical depth are increased by a factor of three.

895 ature when possible. This slightly increases the fitness function  
 896 value, but the fit is still good within the confidence intervals. In  
 897 this section, we perform a statistical analysis to evaluate which  
 898 temperature ranges are degenerate and provide a good fit, from  
 899 those temperature ranges that can be excluded as a solution.

900 Figure 9 shows the recurrence plots for  $\text{CH}_3\text{CH}_2\text{OH}$ ,  
 901  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{OCHO}$  in IRAS 2A and  $\text{CH}_3\text{OCHO}$   
 902 in IRAS 23385 for different temperatures settings available. The  
 903 analysis of  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CHO}$  is not performed for  
 904 IRAS 23385 because of the low S/N in the spectral range consid-  
 905 ered for the fits. To calculate the recurrence plot for these COMs,  
 906 we selected the solutions that are ranked inside a 3 $\sigma$  confidence  
 907 interval. For example, in the case of  $\text{CH}_3\text{CH}_2\text{OH}$ , we found 352  
 908 solutions where ethanol is present. The ethanol mixture at 15 K  
 909 is present in all of these solutions, and therefore it has a recur-  
 910 rence of 100%. There are solutions that combine the low tem-  
 911 perature (15%) ethanol mixture with other temperatures (e.g.,  
 912 30, 70, 100 K). Because of the similarity of the ethanol bands  
 913 in the fitted range, the recurrence of these additional ethanol  
 914 data is slightly reduced, but still high. For the data at 150 and  
 915 160 K, there are around 70 solutions using one of these data,  
 916 which gives a recurrence of  $\sim 20\%$ . Another way to perform the  
 917 same analysis is by using the best global solution as the initial  
 918 guess and running new fits by replacing the IR spectra of spe-  
 919 cific COMs at different temperatures. This forces ENIIGMA to  
 920 use only one  $\text{CH}_3\text{CH}_2\text{OH}$  data at a time, and prevents overlaps  
 921 of data with similar spectral shapes. For ethanol, we obtain a total  
 922 of 9 solutions if the presence of the other components is fixed.  
 923 In this case, the temperature range between 15 and 100 K has a  
 924 recurrence of 100%, and the higher temperatures, have a recur-



**Fig. 9.** Bar plot showing the recurrence of the same ice mixture, but at different temperatures. Plots inside the blue and green polygons refer to IRAS 2A and IRAS 23385, respectively.

925 recurrence of 0%. In the case of ethanol, IR spectra with temperatures  
 926 below 100 K are degenerate, and all  $\text{CH}_3\text{CH}_2\text{OH}:\text{H}_2\text{O}$  mixtures  
 927 fit IRAS 2A in that temperature range. Above 120 K, the ethanol  
 928 ice mixture no longer fits the IRAS 2A spectrum well because of  
 929 band broadening and shift.

930 Repeating the same procedure for the other species, we  
 931 notice a similar behaviour. The fits with acetaldehyde in  
 932 IRAS 2A are degenerate below 30 K. Above this temperature,  
 933  $\text{CH}_3\text{CHO}:\text{H}_2\text{O}$  ice mixtures do not offer likely solutions mostly  
 934 because of band shift. The fits with methyl formate are degener-  
 935 ated below 50 K in IRAS 2A. At higher temperatures, some sub-  
 936 structures arise in the  $\text{CH}_3\text{OCHO}$  spectrum that deviates from  
 937 the observational data. Similarly, in IRAS 23385, methyl for-  
 938 mate is degenerated below 50 K, whereas solutions at 80 K and  
 939 above are less recurrent because of changes in the band profile.  
 940 In conclusion, it is likely that most of the ices towards IRAS 2A  
 941 and IRAS 23385 are located in regions with temperatures below  
 942 50 K.

#### 943 4.2.4. Robustness of detection based on different local 944 continuum choices

945 Other local continuum fits for IRAS 2A (higher S/N) in the 6.8-  
 946  $8.6 \mu\text{m}$  region are also investigated and presented in Appendix J.  
 947 The first three panels of Figure J.1 display different continuum  
 948 profiles, where the top panel is the version adopted for the analy-  
 949 sis in this paper that traced a third-order polynomial to the guid-  
 950 ing points. The second panel displays the fourth-order polynomi-  
 951 al where the red dot is added to the guiding points. In this  
 952 case, the continuum is slightly elevated at shorter wavelengths  
 953 to accommodate the fit to the extra point at  $8.5 \mu\text{m}$ . The third  
 954 panel presents the continuum when two extra points are added

( $\lambda = 7.8 \mu\text{m}$  and  $8.5 \mu\text{m}$ ), and a sixth-order polynomial is used. 955  
 All subtracted spectra using these three approaches are shown 956  
 in the bottom panel of Figure J.1. The major difference is seen 957  
 in the last case (orange continuum), which completely removes 958  
 any absorption excess at  $7.8 \mu\text{m}$ , thus excluding any band at this 959  
 wavelength. 960

961 Given the variability of the optical depth spectra of IRAS 2A  
 962 between  $6.8\text{--}8.6 \mu\text{m}$  with the choice of the local continuum, it is  
 963 worth accessing the robustness of the detections reported in the  
 964 previous sections considering other continuum profiles. This is  
 965 shown in Figure J.2. Figure J.2 top presents the new fit assuming  
 966 the red continuum profile (inset panel) from Fig J.1. This spectral  
 967 fit remains good and all components found in the best fit are still  
 968 present. The only issue is found at  $8.5 \mu\text{m}$  (added guiding point) 969  
 where the  $\text{CH}_3\text{OCHO}$  band is slightly over-predicted. This situ- 970  
 ation changes when the orange continuum is used to isolate the 971  
 absorption features in IRAS 2A. The bottom panel of Figure J.2 972  
 depicts a fit where  $\text{CH}_3\text{COOH}$  is no longer needed because of 973  
 the guiding point at  $7.8 \mu\text{m}$  to trace the local continuum. In this 974  
 version of the fit, the  $\text{HCOO}^-$  and  $\text{OCN}^-$  components become 975  
 much stronger than in the other cases, and the COMs bands are 976  
 reduced by a factor between 1.5–2.0. A clear mismatch is seen 977  
 around  $7 \mu\text{m}$  because of the reduction of the COM bands. Also, 978  
 there is more excess around  $7.3 \mu\text{m}$  that is not fitted with the 979  
 other COMs tentatively detected in this work (see Section 4.4).

980 This analysis reinforces that the detections of  $\text{CH}_3\text{CHO}$ ,  
 981  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{OCHO}$ , as well as the ions and the simple  
 982 molecules, are robust and do not depend on the local continuum  
 983 choice. Clearly, the only exception is for  $\text{CH}_3\text{COOH}$ . However, a  
 984 valid question is what other chemical species would create an ab-  
 985 sorption profile similar to the orange continuum. There is no triv-  
 986 ial answer to this question. A tentative explanation comes from  
 987 the five components decomposition from Boogert et al. (2008),  
 988 in which only the C5 broad feature contributes to the  $7.8 \mu\text{m}$ .  
 989 The nature of the C5 component is not well understood and can  
 990 be related to a flat profile of high-temperature  $\text{H}_2\text{O}$  ice bending  
 991 mode, the overlap of other negative ions ( $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ )  
 992 or organic refractory residue produced by energetic processing.  
 993 The flatter bending mode would have little absorption at  $7.8 \mu\text{m}$   
 994 and therefore is less likely, but the other two options are strong  
 995 candidates.

#### 996 4.3. Ice column densities and abundances

997 The column densities of the molecules fitting the  $6.8\text{--}8.6 \mu\text{m}$   
 998 range are presented in Table 2. To derive their abundances with  
 999 respect to  $\text{H}_2\text{O}$  ice, we use the libration band around  $12 \mu\text{m}$  to  
 1000 calculate the water ice column density as shown in Appendix K.  
 1001 These abundances are compared to literature values for low- and  
 1002 high-mass protostars. In Section 5.3 we also show abundances  
 1003 with respect to  $\text{CH}_3\text{OH}$  ice, in which the method to derive the  
 1004 column density is demonstrated in Appendix K.

1005 The ice abundances of  $\text{CH}_4$ ,  $\text{SO}_2$ ,  $\text{OCN}^-$ ,  $\text{HCOO}^-$  and  
 1006  $\text{HCOOH}$  are within or close to the range expected for LYSOs  
 1007 and MYSOs. From the analysis in this paper,  $\text{CH}_4$ ,  $\text{SO}_2$ ,  $\text{OCN}^-$   
 1008 compose the band around  $7.67 \mu\text{m}$ , whereas previous works as-  
 1009 signed this band to only  $\text{CH}_4$ , with a possible contribution of  $\text{SO}_2$   
 1010 (Öberg et al. 2008). Additionally, instead of using Gaussian pro-  
 1011 files to derive the column densities, this paper uses laboratory  
 1012 data of  $\text{CH}_4:\text{H}_2\text{O}$  and  $\text{SO}_2:\text{CH}_3\text{OH}$ . Gaussian profiles provide  
 1013 first-order approach analysis of the profile of the ice bands, but  
 1014 they can under or overestimate the FWHM of real  $\text{CH}_4$  and  $\text{SO}_2$   
 1015 bands.

**Table 2.** Ice column densities and abundances with respect to H<sub>2</sub>O ice towards IRAS 2A and IRAS 23385. These values are compared to literature values for other objects.

Specie	$N_{\text{ice}}$ ( $10^{17}$ cm <sup>-2</sup> )		$X_{\text{H}_2\text{O}}$ (%)		Literature (% H <sub>2</sub> O)		
	IRAS 2A	IRAS 23385	IRAS 2A	IRAS 23385	LYSOs	MYSOs	Comet 67P/C-G <sup>m</sup>
H <sub>2</sub> O*	300±12	158±36	100	100	100	100	100
CH <sub>4</sub> *	4.9 <sup>7.5</sup> <sub>3.2</sub>	5.2 <sup>6.8</sup> <sub>4.3</sub>	1.6	3.3	<3 <sup>a</sup>	1–11 <sup>b</sup>	0.340±0.07
SO <sub>2</sub> *	0.6 <sup>1.9</sup> <sub>0.4</sub>	0.2 <sup>0.7</sup> <sub>0.0</sub>	0.2	0.1	0.08–0.76 <sup>a</sup>	< 0.9–1.4 <sup>b</sup>	0.127±0.100
HCOOH*	3.0 <sup>5.3</sup> <sub>1.7</sub>	1.8 <sup>2.7</sup> <sub>1.3</sub>	1.0	1.1	< 0.5–4 <sup>c</sup>	< 0.5–6 <sup>d</sup>	0.013±0.008
CH <sub>3</sub> OH*	15, 23 <sup>†</sup>	...	5.0, 7.6	...	< 1–25 <sup>d</sup>	< 3–31 <sup>d</sup>	0.21±0.06
CH <sub>3</sub> CHO*	2.2 <sup>2.8</sup> <sub>1.4</sub>	0.7 <sup>1.1</sup> <sub>0.4</sub>	0.7	0.4	...	<2.3 <sup>e</sup>	0.047±0.017
CH <sub>3</sub> CH <sub>2</sub> OH*	3.7 <sup>4.5</sup> <sub>0.5</sub>	2.9 <sup>4.1</sup> <sub>1.9</sub>	1.2	1.8	...	<1.9 <sup>e</sup>	0.039±0.023
CH <sub>3</sub> OCHO*	0.2 <sup>0.4</sup> <sub>0.1</sub>	1.1 <sup>1.3</sup> <sub>1.0</sub>	0.1	0.7	<2.3 <sup>f</sup>	...	0.0034±0.002
CH <sub>3</sub> COOH <sup>‡</sup>	0.9 <sup>1.3</sup> <sub>0.6</sub>	0.0	0.3	0	...	...	0.0034±0.002
HCOO <sup>-</sup> * (7.4 μm)	1.4 <sup>2.4</sup> <sub>0.4</sub>	0.3 <sup>0.5</sup> <sub>0.1</sub>	0.4	0.2	~0.4 <sup>g</sup>	<0.3–2.3 <sup>b</sup>	...
OCN <sup>-</sup> *	3.7 <sup>6.6</sup> <sub>3.3</sub>	0.9 <sup>1.7</sup> <sub>0.6</sub>	1.2	0.6	< 0.1–1.1 <sup>h</sup>	0.04–4.7 <sup>i</sup>	...
H <sub>2</sub> CO <sup>‡</sup>	12.4 <sup>19.7</sup> <sub>6.6</sub>	...	4.1	...	~6 <sup>g</sup>	~2–7 <sup>b</sup>	0.32±0.1
Upper limits							
CH <sub>3</sub> NH <sub>2</sub>	< 4.1	...	< 1.4	...	< 16 <sup>j</sup>	< 3.4 <sup>j</sup>	...
CH <sub>3</sub> OCH <sub>3</sub>	< 2.5	...	< 0.8	...	...	...	0.039±0.023
CH <sub>3</sub> COCH <sub>3</sub>	< 1.1	...	< 0.4	...	...	...	0.0047±0.0024
HCOCH <sub>2</sub> OH	< 0.9	...	< 0.3	...	...	...	0.0034±0.002
CH <sub>3</sub> CN	< 5.0	...	< 1.6	...	< 4.1 <sup>k</sup>	< 3.4 <sup>k</sup>	0.0059±0.0034
NH <sub>2</sub> CHO	< 1.3	...	< 0.4	...	< 3.7 <sup>l</sup>	< 2.1 <sup>l</sup>	0.0040±0.0023
Glycine	< 0.1–0.6	...	< 0.03–0.2	...	...	~0.3 <sup>b</sup>	...

**Notes.** <sup>a</sup>Öberg et al. (2008), <sup>b</sup>Gibb et al. (2004), <sup>c</sup>Öberg et al. (2011), <sup>d</sup>Schutte et al. (1999), <sup>e</sup>Terwisscha van Scheltinga et al. (2018), <sup>f</sup>Terwisscha van Scheltinga et al. (2021), <sup>g</sup>Boogert et al. (2008), <sup>h</sup>van Broekhuizen et al. (2005), <sup>i</sup>Boogert et al. (2022), <sup>j</sup>Rachid et al. (2021), <sup>k</sup>Rachid et al. (2022), <sup>l</sup>Slavicinska et al. (2023), <sup>m</sup>Rubin et al. (2019). <sup>†</sup> The CH<sub>3</sub>OH ice column density is considered a factor of 2 and 3 higher than the Gaussian fit shown in Figure K.2 because of the band saturation. \*Chemical species with secure detection. <sup>‡</sup>Tentative detections. CH<sub>3</sub>COOH depends on the local continuum choice. H<sub>2</sub>CO is based on a single band of this molecule mixed in the ice with other CO, CH<sub>3</sub>OH and CH<sub>3</sub>OCHO.

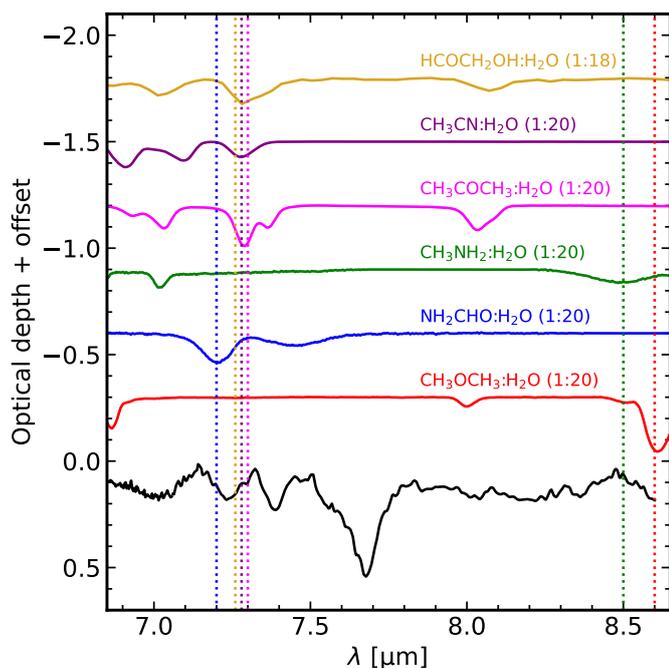
In the case of OCN<sup>-</sup>, we derived ice column densities and abundances from the band at 7.62 μm for IRAS 2A. For consistency, we also calculated the ice column from the NIRSPEC feature at 4.61 μm, which is 2.5×10<sup>17</sup> cm<sup>-2</sup>. Both values are consistent within the errors, and they result in OCN<sup>-</sup> abundances in agreement with the range estimated in the literature for low-mass protostars (van Broekhuizen et al. 2005). For IRAS 23385, the OCN<sup>-</sup> abundance calculated from the MIRI data is within the range found in MYSOs taken from Boogert et al. (2022).

Finally, the formic acid (HCOOH) and the formate ion (HCOO<sup>-</sup>) abundances are closely aligned with the literature values for both LYSOs and MYSOs. In the case of the formate ion in LYSOs, there is only one estimate in the literature for the low-mass protostar HH 46 IRS, which is similar to the abundance calculated for IRAS 2A. The ratios between HCOO<sup>-</sup> and HCOOH are 0.46 and 0.16 for IRAS 2A and IRAS23385, respectively.

For the COMs, we derive ice column densities and abundances for CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OCHO and CH<sub>3</sub>COOH. In terms of ice abundance with respect to H<sub>2</sub>O ice, IRAS 2A is more abundant in CH<sub>3</sub>CHO by a factor of 1.75 compared to IRAS 23385. CH<sub>3</sub>COOH is not detected in IRAS 23385, but has

an estimated abundance of 0.3% in IRAS 2A. CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>OCHO are more abundant in IRAS 23385 by a factor of 1.5 and 7, respectively, compared to IRAS 2A. We note that the CH<sub>3</sub>CH<sub>2</sub>OH abundance for IRAS 23385 is in line with the upper limit derived from the high-mass protostar W33A (Terwisscha van Scheltinga et al. 2018). The other ice abundances are consistent with the upper limits derived in the literature, illustrating that JWST can now probe deeper than previous instruments.

With respect to CH<sub>3</sub>OH ice, the abundances are between 9.3–14.6% for CH<sub>3</sub>CHO, 16.1–24.6% for CH<sub>3</sub>CH<sub>2</sub>OH, 0.9–1.3% for CH<sub>3</sub>OCHO and 3.9–6.0% for CH<sub>3</sub>COOH, depending on the lower and higher CH<sub>3</sub>OH listed in Table 2. The values are much lower than the upper limits derived in the literature (Terwisscha van Scheltinga et al. 2018) for CH<sub>3</sub>CHO (52%) and for CH<sub>3</sub>CH<sub>2</sub>OH (42%).

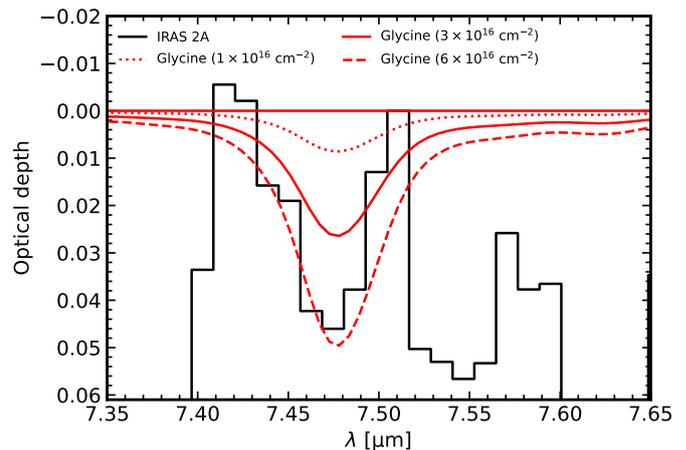


**Fig. 10.** IR spectra of COMs not contributing to the global fit, but with absorption features in the range between 6.8 and 8.6  $\mu\text{m}$ . These spectra are scaled to the IRAS 2A spectrum (black) to derive upper limit column densities. The vertical dotted lines are colour-coded and indicate the features used to derive the ice column densities. A small horizontal shift in the vertical lines is used to distinguish the bands at 7.3  $\mu\text{m}$ .

#### 4.4. Tentative detections and upper limits on column densities

A few COMs were not part of the global solution shown in Figure 6. In this case, we perform a separate comparison of these data to check for tentative detections and derive upper limit column densities in IRAS 2A. This procedure is not applied to IRAS 23385 due to the low signal-to-noise ratio. For this step, we scale laboratory spectra of COMs at specific wavelengths to the MIRI spectrum. This allows us to take into account both the intensity and width of the IR ice band. We performed separate scaling for COMs that have overlaps of the IR features. The molecules used in this step are  $\text{CH}_3\text{OCH}_3$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{HCOCH}_2\text{OH}$ ,  $\text{NH}_2\text{CHO}$ ,  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{CN}$  mixed with  $\text{H}_2\text{O}$  ice. Figure 10 shows the COMs spectra superposed to the IRAS 2A MIRI data, with upper limit column densities also listed in Table 2. To scale  $\text{CH}_3\text{OCH}_3$ , we use the  $\text{CH}_3$ -rock mode at 8.6  $\mu\text{m}$  as a reference. This band has also contributions of ammonia and methyl formate.  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{CN}$  have a  $\text{CH}_3$  symmetric deformation mode at  $\sim 7.3 \mu\text{m}$ , and  $\text{HCOCH}_2\text{OH}$  a  $\text{CH}_2$  deformation mode at the same position. Both  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{OCH}_3$  may contribute to the band at 8.1  $\mu\text{m}$  due to the CCC asymmetric stretch. In the case of  $\text{CH}_3\text{NH}_2$ , we use the  $\text{CH}_3$ -rock mode at 8.5  $\mu\text{m}$  as a reference, whereas the C–H bend at 7.2  $\mu\text{m}$  is considered for  $\text{NH}_2\text{CHO}$ .

Finally, we also check the potential presence of solid-phase glycine, the simplest amino acid, in the spectrum of IRAS 2A. In Ioppolo et al. (2021), the solid-state formation of this simplest amino acid was proven. Glycine has many absorptions features in the IR, and the  $\omega\text{CH}_2$  mode at 7.46  $\mu\text{m}$  is the strongest band of  $\beta$ -glycine. Depending on the glycine structure (e.g., neutral -  $\text{NH}_2\text{CH}_2\text{COOH}$  or zwitterion -  $\text{NH}_3^+\text{CH}_2\text{COO}^-$ ), the position of this band may shift (Potapov et al. 2022) or be nar-



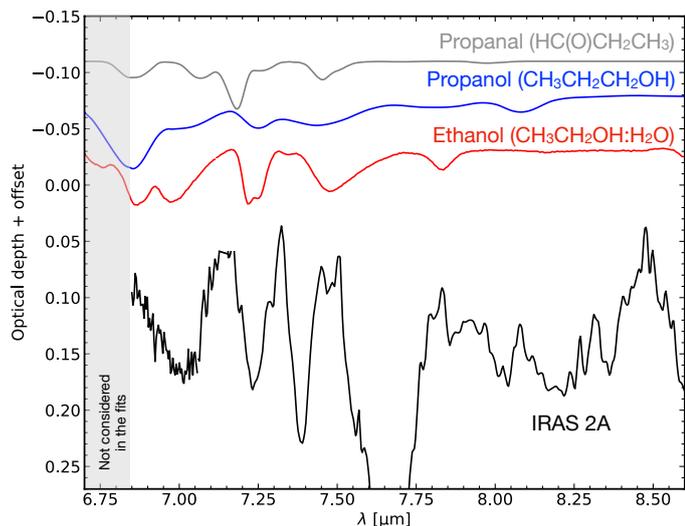
**Fig. 11.** Comparison of the  $\omega\text{CH}$  mode of glycine IR spectrum (red) with local subtracted spectrum of IRAS 2A (black). The intensities of the glycine band are given for three ice column densities.

rowed if the molecule is mixed in an argon sample (Ehrenfreund et al. 2001). In this paper, we use the zwitterionic form ( $\text{NH}_3^+\text{CH}_2\text{COO}^-$ ; Pilling et al. 2011), which is available in the UNIVAP database<sup>4</sup>. In Figure 11, we compare the local subtracted spectrum around the 7.46  $\mu\text{m}$  band with the  $\beta$ -glycine data at three different column densities. We use the band strength from Holtom et al. (2005) of the 7.46  $\mu\text{m}$  band, calculated as  $1.16 \times 10^{-17} \text{ cm molecule}^{-1}$ . This range of column densities is compatible with Gibb et al. (2004) who estimated an upper limit glycine column density of  $3 \times 10^{16} \text{ cm}^{-2}$ , based on the absorption feature around 5.8  $\mu\text{m}$  band. With respect to  $\text{H}_2\text{O}$  ice, we find an upper limit of between 0.03–0.2% (See Section 4.3 and Table 2). This is close to the upper limit derived for W33A (<0.3; Gibb et al. 2004), and in agreement with the theoretical models (0.03–0.7%; Ioppolo et al. 2021).

#### 4.5. Testing more complex alcohols and other molecules

In this section, we compare the IRAS 2A spectrum with two other alcohols more complex than  $\text{CH}_3\text{CH}_2\text{OH}$ , for instance, propanal ( $\text{CH}(\text{O})\text{CH}_2\text{CH}_3$ ) and 1-propanol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ). The goal is to check for similarities and differences between the functional groups of these alcohols with ethanol since these more complex alcohols are expected to have features at similar locations. It is worth mentioning that propanal and 1-propanol have been synthesized in experiments with ice analogues (Qasim et al. 2019) using atom addition reactions, and in the case of propanol, via  $\text{CH}_3\text{OH}$  ice UV irradiation (Tenelanda-Osorio et al. 2022). Both propanal (starless core TMC-1; Agúndez et al. 2023) and propanol (Galactic Centre; Belloche et al. 2022; Jiménez-Serra et al. 2022) have been securely detected in the gas phase. Figure 12 shows that these three alcohols have absorption features around 6.8, 7.2 and 7.5  $\mu\text{m}$ . However, the relative intensities among these bands for these three molecules are different. For example, ethanol has similar intensities at these three bands, whereas 1-propanol and propanal have different intensities by factors of 3–4. In the case of 1-propanol, the fit of the 7.2  $\mu\text{m}$  band would require twice more absorption at 6.8  $\mu\text{m}$  than observed in IRAS 2A. On the other hand, propanal could contribute to the blue wing of the 7.2  $\mu\text{m}$  band. We highlight, however, that in addition to  $\text{HCOO}^-$ ,  $\text{NH}_2\text{CHO}$  can also contribute

<sup>4</sup> <http://www1.univap.br/gaa/nkabs-database/S3.txt>



**Fig. 12.** Experimental IR spectra of ethanol, propanal and propanol compared to IRAS 2A spectrum in the range between 6.8–8.6  $\mu\text{m}$ . The grey area is not considered in the fits, but it is shown here to highlight the C–H stretching mode of these molecules. For better readability of this figure, the gas-phase emission lines between 6.8–7.2  $\mu\text{m}$  are masked.

to the same absorption feature (see Section 4.4 and Figure 10). Another caveat is that both 1-propanol and propanal IR spectra correspond to pure molecules, and therefore spectral differences because of the chemical environment are not perceived in this analysis.

Other than alcohols, hydrocarbons may also contribute to the 7.2 and 7.4  $\mu\text{m}$  bands. In Appendix L, we show a comparison of IRAS 2A spectrum with pure  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  around the 7  $\mu\text{m}$  bands and beyond 11  $\mu\text{m}$ . As a result, it can be seen that  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_6$  could contribute to the red wing of the 7.2  $\mu\text{m}$  band. However, their absorption bands longwards of 11  $\mu\text{m}$  exceed the absorption profile in IRAS 2A. Based on these comparisons, the statistical analysis, and different choices for the silicate (Figure B.1) and local continuum (Figure J.1) we can conclude that  $\text{CH}_3\text{CH}_2\text{OH}$  is the alcohol that contributes most to the 7.2  $\mu\text{m}$  band in addition to  $\text{HCOO}^-$ . The systematic analysis of additional high S/N MIRI data is necessary to obtain robust constraints of larger COMs.

## 5. Discussion

In this section, we discuss the implications of our results from the analysis of the 6.8–8.6  $\mu\text{m}$  region in a low- and high-mass source. This discussion is focused on the presence of simple and neutral species ( $\text{CH}_4$ ,  $\text{SO}_2$ ,  $\text{HCOOH}$ ,  $\text{H}_2\text{CO}$ ), simple and ionic species ( $\text{OCN}^-$ ,  $\text{HCOO}^-$ ), and complex organic molecules ( $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{OCHO}$ ,  $\text{CH}_3\text{COOH}$ ). This section ends with a direct comparison between the ice abundances in the low-mass protostar, IRAS 2A, and the ice bulk abundances in comet 67P/G-C. The goal of this comparison is to evaluate the COM inheritance scenario in solar-type protostellar environments. Because of this, we do not perform the same comparison with IRAS 23385.

### 5.1. Chemical complexity of protostellar ices

In this work, we expand the COMs ice inventory by reporting the detection of at least two vibrational modes of COMs frozen in protostellar ices. We consider secure detections in the cases of

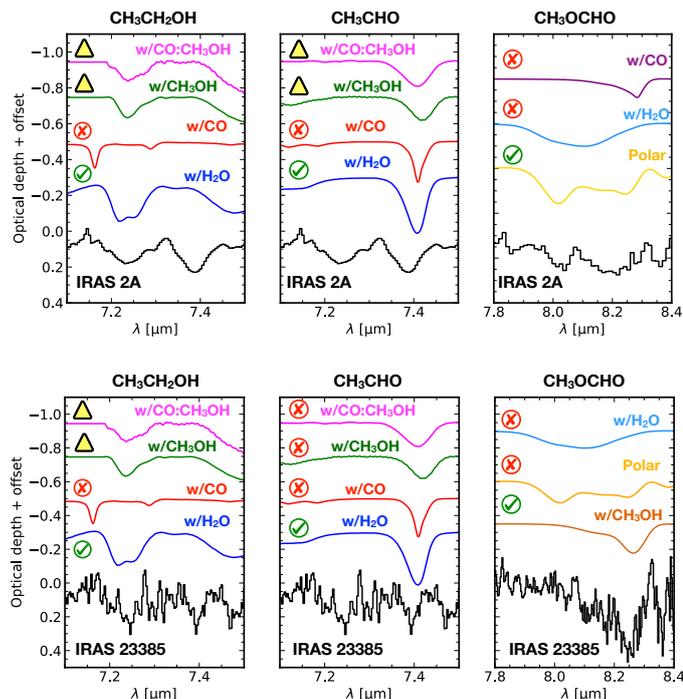
$\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , and  $\text{CH}_3\text{OCHO}$ .  $\text{CH}_3\text{COOH}$  also has two vibrational modes and a high recurrence in the degeneracy analysis of IRAS 2A. However, its presence depends on silicate subtraction and local continuum determination and therefore it is considered a tentative detection. This series of molecules are chemically related and strongly supports laboratory experiments and computational simulations that suggest COMs formation in the solid phase. We also note that all these COMs are commonly detected in the gas phase in hot core sources and are among the most abundant ones (e.g., Chen et al. 2023). A detailed comparison between gas and ice abundances is left to a future paper (Chen et al. in prep.). Below we discuss particular aspects of the COMs solid phase detections reported in this work.

#### 5.1.1. A polar ice environment

In both protostars, the  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , and  $\text{CH}_3\text{COOH}$  (continuum-dependent) molecules are diluted in a polar environment (i.e., molecules with high dipole moment), in particular, dominated by  $\text{H}_2\text{O}$  ice. In the general case where  $\text{H}_2\text{O}$  is the major ice component, this means that COM features are under the strong influence of the water ice polarity. In Figure 13, we compare the MIRI observations with the band shape of three COMs in the best fit, the same COMs in an apolar ice matrix, for instance, mixed with CO ice, and finally, in a  $\text{CH}_3\text{OH}$ -rich environment.  $\text{CH}_3\text{CH}_2\text{OH}$  mixed with  $\text{H}_2\text{O}$  band shape at 7.25  $\mu\text{m}$  agrees better with the data than the mixture with CO that has narrow and separate bands compared with the observations of IRAS 2A and IRAS 23385. In the case of the IRAS 2A observations, which has a higher signal-to-noise ratio,  $\text{CH}_3\text{CH}_2\text{OH}:\text{CO}$  could, potentially, contribute to faint features at 7.16 and 7.29  $\mu\text{m}$ . However, this particular ice mixture is not part of the possible solutions selected by the ENIGMA code. If present, it would have an ice column density one order of magnitude lower than ethanol mixed with water ice. The other mixtures with  $\text{CH}_3\text{OH}$  are less recurrent because of the narrow 7.2  $\mu\text{m}$  and the stronger 7.5  $\mu\text{m}$  that in the global fit makes the 7.2  $\mu\text{m}$  less prominent. In the case of  $\text{CH}_3\text{CHO}$ , the apolar mixture ( $\text{CH}_3\text{CHO}:\text{CO}$ ) makes the  $\text{CH}_3$  deformation mode narrow by a factor of 2 and red-shifted by 0.02  $\mu\text{m}$ . In the case of  $\text{CH}_3\text{OH}$ -rich mixtures, the peak is red-shifted by 0.03  $\mu\text{m}$  and the feature is broader.

This result does not necessarily contradict laboratory experiments that show that COMs are formed via hydrogenation of CO molecules (e.g., Fuchs et al. 2009) and C atoms (Fedoseev et al. 2022), as well as that a fraction of  $\text{CH}_3\text{OH}$  ice is mixed with CO (Cuppen et al. 2011). Instead, it points towards a strong effect of  $\text{H}_2\text{O}$  ice on the spectral IR bands of COMs. Moreover, results from the JWST-Ice Age program (McClure et al. 2023), suggest that a fraction of  $\text{CH}_3\text{OH}$ , the most abundant COM, coexists with  $\text{H}_2\text{O}$  in the same ice matrix in cold prestellar clouds. This can be linked to another formation scheme,  $\text{CH}_4 + \text{OH}$ , as studied by Qasim et al. (2020). Regardless of whether  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{CH}_2\text{OH}$  reside in a  $\text{H}_2\text{O}$ - or  $\text{CH}_3\text{OH}$ -rich ice, the important message is that the IR band shapes that resemble better the observations are induced by a polar environment.

Finally,  $\text{CH}_3\text{OCHO}$  seems to be primarily mixed with another polar environment that includes  $\text{CH}_3\text{OH}$  instead of  $\text{H}_2\text{O}$ . The spectral shape of  $\text{CH}_3\text{OCHO}$  mixed with  $\text{H}_2\text{O}$  has a broader profile centred at 8.1  $\mu\text{m}$  which does not match well the observations. From the degeneracy analysis of IRAS 23385, it is not completely excluded as a solution, but in the global fits, the presence of  $\text{HCOOH}$  discards this component as part of the fit. The mixture with CO creates a sharp peak at 8.25  $\mu\text{m}$  that devi-

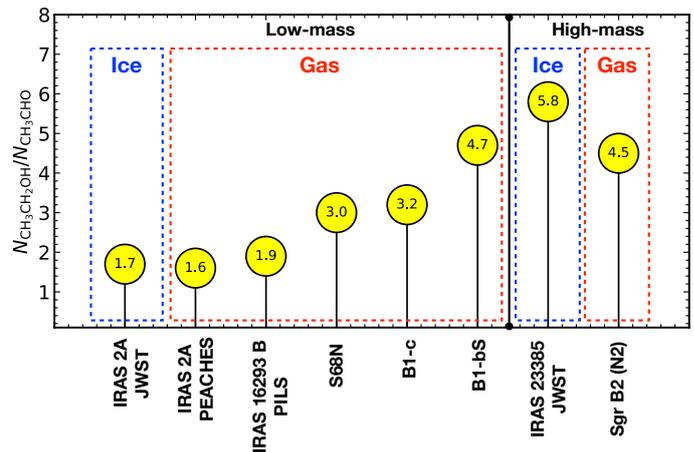


**Fig. 13.** Comparisons between the IR spectra of COMs in different ice matrices with the observed bands of IRAS 2A (top) and IRAS 23385 (bottom). The green checkmarks indicate the data providing the best fit. Excluded data are given by the red cross. Data not part of the best fit and with lower recurrence are indicated by the yellow triangle. The term “polar” in the right panels refers to CO:H<sub>2</sub>CO:CH<sub>3</sub>OH and it is the original label published in [Terwisscha van Scheltinga et al. \(2021\)](#).

ates from the observations. The differences between the chemical environment of CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CHO compared to CH<sub>3</sub>OCHO could indicate that methyl formate in IRAS 23385 may have experienced a physical process different from those in IRAS 2A. We discuss this possibility below in Section 5.1.2.

### 5.1.2. Evidence of ice thermal processing?

Among the ice features identified in this work, CH<sub>3</sub>OCHO has different spectral shapes in IRAS 2A and IRAS 23385, regardless of the local continuum choice. While the fit of the IRAS 2A spectrum contains CH<sub>3</sub>OCHO mixed with CO:H<sub>2</sub>CO:CH<sub>3</sub>OH, in IRAS 23385, the CH<sub>3</sub>OCHO mixed with CH<sub>3</sub>OH provides the best fit, and excludes other solutions (see right panels in Figure 13). A possible cause for this difference can be due to thermal processing, in particular ice distillation. In this process, the most volatile species desorbs from the ice while other species with higher sublimation temperatures remain. For example, during the CH<sub>3</sub>OH formation via CO hydrogenation (e.g., [Watanabe & Kouchi 2002](#); [Fuchs et al. 2009](#)) both CH<sub>3</sub>O and HCO are formed (e.g., [Chuang et al. 2016](#); [Garrod et al. 2022](#); [Chen et al. 2023](#)), leading to CH<sub>3</sub>OCHO. H<sub>2</sub>CO is also an intermediate step towards the CH<sub>3</sub>OH formation. In a trivial situation, it is expected that at low temperature (< 30 K) CH<sub>3</sub>OCHO should be mixed with CO, H<sub>2</sub>CO and CH<sub>3</sub>OH, the exact components of the ice mixture used to fit the IRAS 2A spectrum. When this ice is warmed up to 50-100 K, CO ice is fully desorbed and H<sub>2</sub>CO is partially desorbed, and the ice would be composed mostly of CH<sub>3</sub>OCHO and CH<sub>3</sub>OH. Because of the low S/N spectrum of IRAS 23385 we cannot definitely conclude if H<sub>2</sub>CO is present in the ices toward this source.



**Fig. 14.** Ethanol/acetaldehyde ratio in the gas and solid phases towards different sources.

### 5.1.3. Gas vs. ice: CH<sub>3</sub>CH<sub>2</sub>OH/CH<sub>3</sub>CHO ratio

CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CHO are chemically linked since the double hydrogenation of acetaldehyde in the solid state leads to ethanol ([Fedoseev et al. 2022](#)). In this regard, the ratio of these two molecules provides a way to understand the hydrogenation efficiency of solid-phase molecules to form larger species in protostars.

Figure 14 compares the inferred CH<sub>3</sub>CH<sub>2</sub>OH/CH<sub>3</sub>CHO ratios in the solid phase with those found in the gas phase of many protostars. A persistent ratio of CH<sub>3</sub>CH<sub>2</sub>OH and CH<sub>3</sub>CHO above the unity has been observed in the gas phase with sensitive observations towards protostars in both low- and high-mass star-forming regions (e.g., [Yang et al. 2021](#); [Jørgensen et al. 2020](#); [van Gelder et al. 2020](#); [Chen et al. 2023](#)). For example, the ratios summarized by [Jørgensen et al. \(2020\)](#) for IRAS 16293B and Sgr(B2) N2 are 1.9 and 4.5, respectively. For low-mass protostars, the CH<sub>3</sub>CH<sub>2</sub>OH/CH<sub>3</sub>CHO ratio taken from [van Gelder et al. \(2020\)](#) are 3.2 (B1-c), 3.0 (S68N), and <4.7 (B1-bS). For the first time, a comprehensive analysis of the 6.8-8.6 μm JWST data allows us to observe the same trend in the solid phase. The CH<sub>3</sub>CH<sub>2</sub>OH/CH<sub>3</sub>CHO ratios derived in this work are 1.7 and 5.8 for IRAS 2A and IRAS 23385, respectively.

This overall trend in protostars suggests that the ethanol/acetaldehyde ratio in the gas phase reflects those in the solid phase. This is a strong hint that ices are the birthplace of COMs detected in the gas phase. Additionally, these COMs are inherited from molecular cloud stages where the ice hydrogenation is efficient to form saturated molecules (e.g., [Fedoseev et al. 2022](#)). We also mention that a full three-phase chemical modelling of these sources, assuming reactions within the bulk of the ice, on the ice surface, and in the gas phase can help us constrain the ice chemistry from the observed ice column densities, and provide a more complete explanation for the ethanol/acetaldehyde ratio in both gas and solid-phase. In fact, recent three-phase chemical modelling work by [Garrod et al. \(2022\)](#) assuming general physical conditions of molecular clouds during collapse and warm-up as well as with non-diffusive ice chemistry confirms that the solid-and gas-phase ratios of ethanol/acetaldehyde are consistent with the results presented in this paper.

## 5.2. Ions in icy grain mantles

The presence of ions in interstellar ices has long been proposed in the literature as a result of the energetic processing of ice mantles (e.g., Grim & Greenberg 1987; Strazzulla & Palumbo 1998; Allamandola et al. 1988; Martinez et al. 2014; Pilling et al. 2010) and acid-base reactions (e.g., Novozamsky et al. 2001). Among these ions,  $\text{OCN}^-$  has been detected in several protostellar envelopes (e.g., van Broekhuizen et al. 2005), and recently with JWST in the Chameleon I molecular cloud towards background stars (McClure et al. 2023). Other ions, such as  $\text{HCOO}^-$ , were proposed as one of the carriers of the 7.2 and 7.4  $\mu\text{m}$  by Schutte et al. (1999) based on the IR peak position.

In the analysis presented in this work, we find that both  $\text{HCOO}^-$  and  $\text{OCN}^-$  are important contributors to signals in the range between 6.8–8.6  $\mu\text{m}$ . In particular, an important aspect to highlight regarding  $\text{HCOO}^-$  is the same relative intensities of the 7.2 and 7.4  $\mu\text{m}$  bands at low temperature (see Appendix H), which is considered the main carrier of the absorption profiles in the two protostars presented in this work. The fact that higher temperature  $\text{HCOO}^-$  profiles do not match well the observations indicates that the acid-base reaction occurs in cold regions of the protostellar envelope without further thermal processing. One could argue that the  $\text{HCOO}^-$  profile at 14 K is degenerate with the data at 150 K as seen in Appendix H. However, the full IR spectrum of  $\text{HCOO}^-$  has an intense peak at 6.3  $\mu\text{m}$  that is around 8 times stronger than the 7.2 and 7.4  $\mu\text{m}$  bands, and therefore can not be the main carrier of those bands. This strongly suggests that acid-base reactions occur in IRAS 2A and IRAS 23385 and that ions cannot be neglected when interpreting the IR observations.

The formation of  $\text{HCOO}^-$  can occur via the acid-base reaction involving  $\text{H}_2\text{O}:\text{HCOOH}:\text{NH}_3$ . This is explained by theoretical calculations of  $\text{HCOOH}(\cdot\text{H}_2\text{O})_n$  clusters (Park & Woon 2006). In particular, formic acid partially ionizes when mixed with  $\text{H}_2\text{O}$ , forming  $\text{HCOO}^-$  and  $\text{H}_3\text{O}^+$  via proton exchange (Theule et al. 2011). Another reaction to form  $\text{HCOO}^-$  was studied by Bergner et al. (2016), in which only  $\text{HCOOH}$  and  $\text{NH}_3$  are present in the ice, without any  $\text{H}_2\text{O}$ .

Similar to  $\text{HCOO}^-$ ,  $\text{OCN}^-$  is efficiently formed via acid-base reaction, which has been studied in laboratory experiments starting with  $\text{HNCO}$  and  $\text{NH}_3$  (Schutte & Khanna 2003; Raunier et al. 2003; van Broekhuizen et al. 2004). A large fraction of  $\text{OCN}^-$  is produced in these experiments, as well as the counter ion,  $\text{NH}_4^+$  to maintain the electric neutrality. A possible difficulty in this approach is the high abundance of  $\text{HNCO}$  in the ice needed to synthesize  $\text{OCN}^-$ , associated with the non-detection of this molecule in ices yet. However, gas-phase observations (e.g., Hernández-Gómez et al. 2019) show high abundances of  $\text{HNCO}$  and laboratory experiments in the ice by Fedoseev et al. (2015) and Noble et al. (2015) show that  $\text{HNCO}$  can be rapidly formed via an exothermic solid-phase reaction between  $\text{NH}$  and  $\text{CO}$ . Additionally, the non-detection of  $\text{HNCO}$  in ices (e.g., McClure et al. 2023) could be related to the low abundance after being converted into  $\text{OCN}^-$ . The presence of  $\text{OCN}^-$  and  $\text{HNCO}$  in ices has a strong astrobiological appeal.  $\text{HNCO}$  participates as a peptide bond between two single amino acids as shown by Fedoseev et al. (2015). Moreover, irradiation experiments of ice samples containing  $\text{OCN}^-/\text{HNCO}$  would lead to the formation of amino acids and their anions, as well. Finally, we highlight that although  $\text{NH}_4^+$  is one of the byproducts of this acid-base reaction, it does not contribute to the absorption bands covered in this work, and therefore, it is not discussed here.

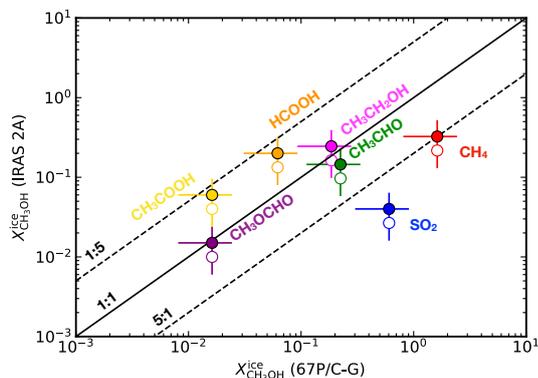
Another mechanism for the  $\text{OCN}^-$  formation is via UV irradiation (van Broekhuizen et al. 2005), which is discussed as being less dominant in low-mass protostars. This route requires high UV fluxes and an abundance of around 30% of  $\text{NH}_3$  in the ice. The former condition is satisfied for high-mass protostars, but not otherwise. In fact, a recent paper by Onaka et al. (2022) shows a clear correlation in the high-mass-source AFGL 2006 between the  $\text{OCN}^-$  ice column density with the flux intensity of the  $\text{HI Br}\alpha$  line. This hydrogen recombination line is a tracer of strong UV radiation and supports an  $\text{OCN}^-$  formation induced by UV photons. Other mechanisms, such as UV-induced flux by cosmic rays are not enough to produce significant amounts of  $\text{OCN}^-$ , and low-mass stellar UV would not reach the regions where ice is located. The latter condition exceeds the abundances estimated in the literature for both low- and high-mass protostars, which is between 2% and 15% (Bottinelli et al. 2010).

## 5.3. Similarities and differences between IRAS 2A, IRAS 23385 and the Comet 67P/G-C

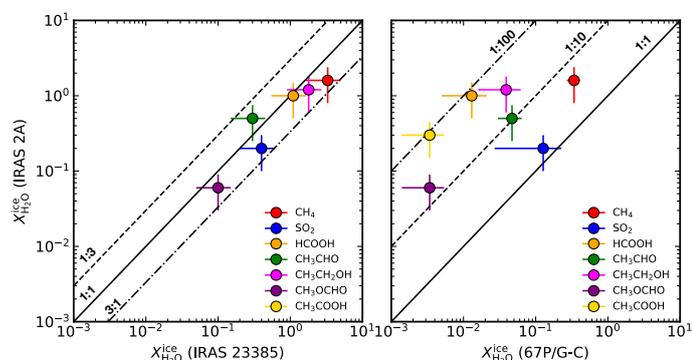
Gas-phase comparisons between the abundances of CHO-bearing COMs with respect to  $\text{CH}_3\text{OH}$  in low- and high-mass protostars, and with the bulk composition of the comet 67P/G-C were made by Drozdovskaya et al. (2019) and Jørgensen et al. (2020). The main conclusion is that there is a good correlation between the abundances of gas-phase COMs in high- and low-mass star-forming regions. On the other hand, there are also differences between the low-mass protostar (IRAS 16293B) and the comet 67P/G-C. In particular, the COMs abundances onto the comet 67P/G-C are enhanced by a factor of up to 10. This difference is interpreted as ice inheritance followed by chemical alteration towards later protostellar phases.

In Figure 15, we show a comparison between the ice CHO-bearing COMs abundances in IRAS 2A and in the comet 67P/G-C, both with respect to methanol ice. We stress that the peak of the methanol band in IRAS 2A is saturated, and the comparisons are made by assuming that the real methanol ice column density is higher by a factor of 2–3 based on the wings of the C–O band at 9.74  $\mu\text{m}$  (see Appendix K). Under this assumption, we see that COMs and the volatile  $\text{CH}_4$  correlate well with the cometary abundances within a factor of 5. This agrees with previous conclusions that these COMs are inherited by comets from early protostellar stages. The scatter, however, can be attributed to further chemical alteration at later stages, or slightly different initial composition in the parental molecular cloud. It is also interesting that the volatiles,  $\text{CH}_4$  and  $\text{SO}_2$  are enriched in the comet 67P/G-C. This could indicate that these molecules are also formed in the gas phase and condensed at later stages in the comet. However, more analysis of other JWST observations is needed to draw strong conclusions from this correlation.

In Figure 16, we show a comparison between the COMs abundances with respect to  $\text{H}_2\text{O}$  ice in IRAS 2A, IRAS 23385 and the comet 67P/G-C. The abundances in the low- and high-mass protostar are very close to a linear correlation, which agrees with the results from Jørgensen et al. (2020) between IRAS 16293B and Sgr B2(N2). On the other hand, the COMs abundances compared to  $\text{H}_2\text{O}$  ice are lower in the comet 67P/G-C than in IRAS 2A. Such a high abundance of molecules in low-mass protostars with respect to  $\text{H}_2\text{O}$  ice was noticed before for other molecules, such as  $\text{NH}_3$  (Kawakita & Mumma 2011), and  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$  (Öberg et al. 2011). The reason is unclear, but it can indicate selective ice destruction of these species compared to  $\text{H}_2\text{O}$  ice in the protosolar nebula or that those COMs



**Fig. 15.** Comparison between ice abundances with respect to  $\text{CH}_3\text{OH}$  ice in IRAS 2A and the comet 67P/G-C (Rubin et al. 2019). Full and hollow circles show the abundances considering  $N_{\text{CH}_3\text{OH}}^{\text{ice}} = 1.5 \times 10^{18} \text{ cm}^{-2}$  and  $1.3 \times 10^{18} \text{ cm}^{-2}$ , respectively. The solid line indicates the 1:1 abundance relation, and the dashed lines indicate a cometary abundance lower and higher by a factor of 5.



**Fig. 16.** Comparison between ice abundances with respect to  $\text{H}_2\text{O}$  ice. The left panel shows the ice abundances in IRAS 2A and IRAS 23385. The solid line indicates the 1:1 abundance relation, whereas the dashed and dot-dashed lines indicate the enhancement and diminution of IRAS 23385 abundance by a factor of 3. The right panel compares the ice abundances between IRAS 2A and the comet 67P/G-C from Rubin et al. (2019). The solid line indicates the same as in the left panel. The dot-dashed and dashed lines indicate a cometary abundance lower by a factor of 10 and 100, respectively.

1412 were formed in a carbon-poor protostellar envelope (Öberg et al.  
1413 2011).

## 1414 6. Conclusions

1415 This paper presents a comprehensive analysis in the range  
1416 between 6.8–8.6  $\mu\text{m}$  of JWST spectra observed towards the  
1417 IRAS 2A and IRAS 23385 protostars. We perform spectral fits  
1418 exploring a vast number of IR laboratory spectra that cover, simple  
1419 molecules, ions and COMs. The main conclusions are summarised  
1420 below:

- 1421 – The 7.7  $\mu\text{m}$  band is fully resolved in the MIRI spectrum  
1422 of IRAS 2A and IRAS 23385. As found in previous studies,  
1423  $\text{CH}_4$  ice is the main carrier of this band. In addition to  
1424  $\text{CH}_4$ , our analysis shows that  $\text{OCN}^-$  and  $\text{SO}_2$  contribute  
1425 to the blue wing of the 7.7  $\mu\text{m}$  band.  $\text{SO}_2$  was tentatively  
1426 detected based on *ISO* and *Spitzer* observations, and based on a  
1427 statistical analysis we confirm that  $\text{SO}_2$  is present in ices  
1428 towards IRAS 2A. For IRAS 23385,  $\text{SO}_2$  is classified as likely  
1429 detection because of a lower S/N and statistical arguments.

In the case of  $\text{OCN}^-$ , this is the first time that this ion is  
1430 attributed to the 7.7  $\mu\text{m}$  band. Besides the statistical analy-  
1431 sis confirming this detection,  $\text{OCN}^-$  is also seen at 4.59  $\mu\text{m}$   
1432 in IRAS 2A with NIRSpect observation, thus confirming the  
1433 feature at 7.7  $\mu\text{m}$ .  
1434

- The 7.2 and 7.4  $\mu\text{m}$  bands observed in IRAS 2A and  
1435 IRAS 23385 are mainly due to the formate ion ( $\text{HCOO}^-$ ).  
1436 Since this ion is efficiently formed via acid-base reactions,  
1437 and given the detection of  $\text{OCN}^-$  at 7.65  $\mu\text{m}$ , these results  
1438 demonstrate that this type of chemical reaction may be rather  
1439 common in interstellar ices.  
1440
- The earlier suggestions that  $\text{CH}_3\text{CH}_2\text{OH}$  (ethanol) and  
1441  $\text{CH}_3\text{CHO}$  (acetaldehyde) contribute to the absorption pro-  
1442 files at 7.2 and 7.4  $\mu\text{m}$ , respectively, are confirmed in this  
1443 work. In addition, we find that  $\text{CH}_3\text{CH}_2\text{OH}$  contributes to  
1444 other bands in the range considered in this work, most no-  
1445 tably, at 6.8–7.05  $\mu\text{m}$  and 7.4–7.6  $\mu\text{m}$ . Other possibilities,  
1446 such as hydrocarbons ( $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ) and more com-  
1447 plex alcohols (1-propanol, propanal) are less likely based on  
1448 their absorption profiles. In the case of  $\text{CH}_3\text{CHO}$ , it also con-  
1449 tributes to the range between 6.9–7.2  $\mu\text{m}$ .  
1450
- We find robust evidence that  $\text{CH}_3\text{OCHO}$  is present in the  
1451 ices towards IRAS 2A and IRAS 23385. At least two strong  
1452 bands of this molecule are found between 8.1–8.35  $\mu\text{m}$  and  
1453 8.45–8.6  $\mu\text{m}$ . The statistical analysis shows that this spectral  
1454 component cannot be excluded as a solution for the fit. Based  
1455 on the criteria for a firm identification,  $\text{CH}_3\text{OCHO}$  is classi-  
1456 fied as a secure detection. We also find that another COM,  
1457  $\text{CH}_3\text{COOH}$  (acetic acid), is present in the fits of IRAS 2A  
1458 and cannot be excluded based on the confidence interval  
1459 analysis for two out of three choices of continuum. However,  
1460 since it is not found in IRAS 23385, and the local continuum  
1461 strongly affects the shape of the bands around 7.8  $\mu\text{m}$ , we  
1462 classify acetic acid only as a likely detection. More compar-  
1463 isons with other JWST data will elucidate at which level if  
1464 acetic acid is present in interstellar ices.  
1465
- The COMs found in this work are likely mixed in a polar en-  
1466 vironment. For example,  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CHO}$  fit bet-  
1467 ter the observations when mixed with  $\text{H}_2\text{O}$ . These molecules  
1468 mixed with CO have spectral profiles that deviate from the  
1469 observed protostellar. In the case of  $\text{CH}_3\text{COOH}$ , the mixture  
1470 with  $\text{H}_2\text{O}$  ice also provides a good fit to the IRAS 2A spec-  
1471 trum. In the case of  $\text{CH}_3\text{OCHO}$ , the two protostars show dif-  
1472 ferent spectral shapes. This differentiation could be related  
1473 to ice distillation in IRAS 23385, the high-mass protostar.  
1474
- Ice-gas ratios between  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CHO}$  show val-  
1475 ues above unity in both gas and ice phases. This suggests  
1476 solid-phase reactions for the formation of these molecules.  
1477 In addition, the high abundance of  $\text{CH}_3\text{CH}_2\text{OH}$  shows that  
1478 saturated molecules efficiently form in ices because of the  
1479 high amount of hydrogen available.  
1480
- For the first time, we compare ice COMs abundances relative  
1481 to  $\text{CH}_3\text{OH}$  ice in a protostar and the comet 67P/G-C. Our  
1482 results indicate that the COMs ice abundances in the comet  
1483 67P/G-C correlate well with those in the protostar within a  
1484 factor of 5, which strongly suggests that COMs in comets are  
1485 significantly inherited from earlier protostellar phases. In the  
1486 case of  $\text{CH}_4$  and  $\text{SO}_2$  with respect to  $\text{CH}_3\text{OH}$  ice, we find an  
1487 enhancement in the comet 67P/G-C. On the other hand, the  
1488 abundance comparison with respect to  $\text{H}_2\text{O}$  ice shows that  
1489 the COMs,  $\text{SO}_2$  and  $\text{CH}_4$  are depleted in the comet.  
1490

The results presented in this paper illustrate how JWST,  
1491 aided by laboratory experiments, is fully capable of probing the  
1492

- chemical complexity in interstellar ices. Future work using more JWST data with high S/N (e.g., IRAS 15398; Yang et al. 2022) will enable us to verify the recurrence of the COMs found in this paper in other sources, and consequently, assess the robustness of these detections. Another outlook would be the determination of ice-gas ratios of COMs more complex than CH<sub>3</sub>OH. Ultimately, an analysis based on a large sample will help us to further answer the question: to what extent chemical complexity can be reached in interstellar ices?
- Acknowledgements.** The following National and International Funding Agencies funded and supported the MIRI development: NASA; ESA; Belgian Science Policy Office (BELSPO); Centre Nationale d'Études Spatiales (CNES); Danish National Space Centre; Deutsches Zentrum für Luft- und Raumfahrt (DLR); Enterprise Ireland; Ministerio De Economía y Competitividad; The Netherlands Research School for Astronomy (NOVA); The Netherlands Organisation for Scientific Research (NWO); Science and Technology Facilities Council; Swiss Space Office; Swedish National Space Agency; and UK Space Agency. We thank the anonymous reviewer for the careful reading of our manuscript and the comments and suggestions that improved the clarity of this work. WRMR, EvD, K.S, N.B, McG, L.F and HL acknowledge the funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 291141 MOLDISK). WRMR thanks Niels Ligterink and Maria Drozdovskaya for useful discussions about the 67P/G-C comet abundances. We are grateful for continuing support through NOVA, the Netherlands Research School for Astronomy, the NWO through its Dutch Astrochemistry Program (DANII). The present work is closely connected to ongoing research within INTERCAT, the Center for Interstellar Catalysis located in Aarhus, Denmark. L.M. acknowledges the financial support of DAE and DST-SERB research grants (SRG/2021/002116 and MTR/2021/000864) from the Government of India. T.R. acknowledges support from ERC grant no. 743029 EASY. T.H. acknowledges support from the ERC Advanced grant no. Origins 83 24 28. H.B. acknowledges support from the Deutsche Forschungsgemeinschaft in the Collaborative Research Center (SFB 881) "The Milky Way System" (sub-project B1). P.J.K. acknowledges financial support from the Science Foundation Ireland/Irish Research Council Pathway programme under Grant Number 21/PATH-S/9360. A.C.G. has been supported by PRIN-INAF MAIN-STREAM 2017 "Protoplanetary disks seen through the eyes of new generation instruments" and from PRIN-INAF 2019 "Spectroscopically tracing the disk dispersal evolution (STRADE)". K.J. acknowledges the support from the Swedish National Space Agency (SNSA).
- ## References
- Adams, F. C., Lada, C. J., & Shu, F. H. 1987, *ApJ*, 312, 788  
 Agúndez, M., Loison, J. C., Hickson, K. M., et al. 2023, *A&A*, 673, A34  
 Allamandola, L. J., Sandford, S. A., & Valero, G. J. 1988, *Icarus*, 76, 225  
 Argyriou, I., Glasse, A., Law, D. R., et al. 2023, *A&A*, 675, A111  
 Avni, Y. & Bahcall, J. N. 1980, *ApJ*, 235, 694  
 Baeck, T., Fogel, D., & Michalewicz, Z. 2000, *Evolutionary Computation 2: Advanced Algorithms and Operators*, Evolutionary computation (Taylor & Francis)  
 Balucani, N., Ceccarelli, C., & Taquet, V. 2015, *MNRAS*, 449, L16  
 Belloche, A., Garrod, R. T., Zingsheim, O., Müller, H. S. P., & Menten, K. M. 2022, *A&A*, 662, A110  
 Belloche, A., Maury, A. J., Maret, S., et al. 2020, *A&A*, 635, A198  
 Bergner, J. B., Öberg, K. I., Garrod, R. T., & Graninger, D. M. 2017, *ApJ*, 841, 120  
 Bergner, J. B., Öberg, K. I., Rajappan, M., & Fayolle, E. C. 2016, *ApJ*, 829, 85  
 Berné, O., Martin-Drumel, M.-A., Schroetter, I., et al. 2023, *Nature*, 621, 56  
 Beuther, H., van Dishoeck, E. F., Tychoniec, L., et al. 2023, *A&A*, 673, A121  
 Bisschop, S. E., Fuchs, G. W., Boogert, A. C. A., van Dishoeck, E. F., & Linnartz, H. 2007, *A&A*, 470, 749  
 Blake, G. A., Sutton, E. C., Masson, C. R., & Phillips, T. G. 1987, *ApJ*, 315, 621  
 Boogert, A. C. A., Brewer, K., Brittain, A., & Emerson, K. S. 2022, *ApJ*, 941, 32  
 Boogert, A. C. A., Gerakines, P. A., & Whittet, D. C. B. 2015, *ARA&A*, 53, 541  
 Boogert, A. C. A., Huard, T. L., Cook, A. M., et al. 2011, *ApJ*, 729, 92  
 Boogert, A. C. A., Pontoppidan, K. M., Knez, C., et al. 2008, *ApJ*, 678, 985  
 Boogert, A. C. A., Schutte, W. A., Helmich, F. P., Tielens, A. G. G. M., & Wooden, D. H. 1997, *A&A*, 317, 929  
 Bottinelli, S., Boogert, A. C. A., Bouwman, J., et al. 2010, *ApJ*, 718, 1100  
 Bottinelli, S., Ceccarelli, C., Williams, J. P., & Lefloch, B. 2007, *A&A*, 463, 601  
 Boudin, N., Schutte, W. A., & Greenberg, J. M. 1998, *A&A*, 331, 749  
 Bouilloud, M., Fray, N., Bénilan, Y., et al. 2015, *MNRAS*, 451, 2145  
 Bouwman, J., Ludwig, W., Awad, Z., et al. 2007, *A&A*, 476, 995  
 Brinch, C., Jørgensen, J. K., & Hogerheijde, M. R. 2009, *A&A*, 502, 199  
 Brönsted, J. N. 1923, *Recueil des Travaux Chimiques des Pays-Bas*, 42, 718  
 Bushouse, H., Eisenhamer, J., Dencheva, N., et al. 2022, *spacetelescope/jwst: JWST 1.6.2*, Zenodo  
 Casoli, F., Dupraz, C., Gerin, M., Combes, F., & Boulanger, F. 1986, *A&A*, 169, 281  
 Cazaux, S., Tielens, A. G. G. M., Ceccarelli, C., et al. 2003, *ApJ*, 593, L51  
 Cesaroni, R., Beuther, H., Ahmadi, A., et al. 2019, *A&A*, 627, A68  
 Chen, Y., van Gelder, M. L., Nazari, P., et al. 2023, *A&A*, 678, A137  
 Chiar, J. E. & Tielens, A. G. G. M. 2006, *ApJ*, 637, 774  
 Chu, L. E. U., Hodapp, K., & Boogert, A. 2020, *ApJ*, 904, 86  
 Chuang, K. J., Fedoseev, G., Ioppolo, S., van Dishoeck, E. F., & Linnartz, H. 2016, *MNRAS*, 455, 1702  
 Chuang, K. J., Fedoseev, G., Qasim, D., et al. 2020, *A&A*, 635, A199  
 Colzi, L., Rivilla, V. M., Beltrán, M. T., et al. 2021, *A&A*, 653, A129  
 Coutens, A., Persson, M. V., Jørgensen, J. K., Wampfler, S. F., & Lykke, J. M. 2015, *A&A*, 576, A5  
 Cuppen, H. M., Penteado, E. M., Isokoski, K., van der Marel, N., & Linnartz, H. 2011, *MNRAS*, 417, 2809  
 Dartois, E., Schutte, W., Geballe, T. R., et al. 1999, *A&A*, 342, L32  
 Dartois, E., Thi, W. F., Geballe, T. R., et al. 2003, *A&A*, 399, 1009  
 De Simone, M., Codella, C., Testi, L., et al. 2017, *A&A*, 599, A121  
 Do-Duy, T., Wright, C. M., Fujiyoshi, T., et al. 2020, *MNRAS*, 493, 4463  
 Dominik, C., Min, M., & Tazaki, R. 2021, *OpTool: Command-line driven tool for creating complex dust opacities*  
 Dorschner, J., Begemann, B., Henning, T., Jaeger, C., & Mutschke, H. 1995, *A&A*, 300, 503  
 Drozdovskaya, M. N., van Dishoeck, E. F., Rubin, M., Jørgensen, J. K., & Alltwegg, K. 2019, *MNRAS*, 490, 50  
 Ehrenfreund, P., Bernstein, M. P., Dworkin, J. P., Sandford, S. A., & Allamandola, L. J. 2001, *ApJ*, 550, L95  
 Fedoseev, G., Ioppolo, S., Zhao, D., Lamberts, T., & Linnartz, H. 2015, *MNRAS*, 446, 439  
 Fedoseev, G., Qasim, D., Chuang, K.-J., et al. 2022, *ApJ*, 924, 110  
 Fuchs, G. W., Cuppen, H. M., Ioppolo, S., et al. 2009, *A&A*, 505, 629  
 Gálvez, O., Maté, B., Herrero, V. J., & Escribano, R. 2010, *ApJ*, 724, 539  
 Garrod, R. T., Jin, M., Matis, K. A., et al. 2022, *ApJS*, 259, 1  
 Geballe, T. R. 1984, *Occasional Reports of the Royal Observatory Edinburgh*, 12, 56  
 Gerakines, P. A., Schutte, W. A., & Ehrenfreund, P. 1996, *A&A*, 312, 289  
 Gibb, E. L., Whittet, D. C. B., Boogert, A. C. A., & Tielens, A. G. G. M. 2004, *ApJS*, 151, 35  
 Gieser, C., Beuther, H., Semenov, D., et al. 2021, *A&A*, 648, A66  
 Gieser, C., Beuther, H., van Dishoeck, E. F., et al. 2023, *arXiv e-prints*, arXiv:2309.10410  
 Greenfield, P. & Miller, T. 2016, *Astronomy and Computing*, 16, 41  
 Grim, R. J. A., Baas, F., Geballe, T. R., Greenberg, J. M., & Schutte, W. A. 1991, *A&A*, 243, 473  
 Grim, R. J. A. & Greenberg, J. M. 1987, *ApJ*, 321, L91  
 Harris, C. R., Millman, K. J., van der Walt, S. J., et al. 2020, *Nature*, 585, 357  
 Herbst, E. & van Dishoeck, E. F. 2009, *ARA&A*, 47, 427  
 Hernández-Gómez, A., Sahnoun, E., Caux, E., et al. 2019, *MNRAS*, 483, 2014  
 Holland, J. H. 1975, *Adaptation in natural and artificial systems: an introductory analysis with applications to biology, control, and artificial intelligence* (Ann Arbor: University of Michigan Press)  
 Holtom, P. D., Bennett, C. J., Osamura, Y., Mason, N. J., & Kaiser, R. I. 2005, *ApJ*, 626, 940  
 Hudgins, D. M., Sandford, S. A., Allamandola, L. J., & Tielens, A. G. G. M. 1993, *ApJS*, 86, 713  
 Hudson, R. L. & Ferrante, R. F. 2020, *MNRAS*, 492, 283  
 Hudson, R. L., Ferrante, R. F., & Moore, M. H. 2014a, *Icarus*, 228, 276  
 Hudson, R. L. & Gerakines, P. A. 2019, *MNRAS*, 485, 861  
 Hudson, R. L., Gerakines, P. A., & Moore, M. H. 2014b, *Icarus*, 243, 148  
 Hudson, R. L., Loeffler, M. J., Ferrante, R. F., Gerakines, P. A., & Coleman, F. M. 2020, *ApJ*, 891, 22  
 Hudson, R. L., Moore, M. H., & Cook, A. M. 2005, *Advances in Space Research*, 36, 184  
 Ioppolo, S., Fedoseev, G., Chuang, K. J., et al. 2021, *Nature Astronomy*, 5, 197  
 Jiménez-Serra, I., Rodríguez-Almeida, L. F., Martín-Pintado, J., et al. 2022, *A&A*, 663, A181  
 Jørgensen, J. K., Belloche, A., & Garrod, R. T. 2020, *ARA&A*, 58, 727  
 Jørgensen, J. K., Bourke, T. L., Myers, P. C., et al. 2005, *ApJ*, 632, 973  
 Kawakita, H. & Mumma, M. J. 2011, *ApJ*, 727, 91  
 Koza, J. R. 1992, *Genetic programming: on the programming of computers by means of natural selection*, Complex adaptive systems. 09800994X (Cambridge, MA [etc.]: The MIT Press)  
 Kruczkiewicz, F., Vitorino, J., Congiu, E., Theulé, P., & Dulieu, F. 2021, *A&A*, 652, A29  
 Kurtz, S., Hofner, P., & Álvarez, C. V. 2004, *ApJS*, 155, 149

- 1645 Labiano, A., Argyriou, I., Álvarez-Márquez, J., et al. 2021, *A&A*, 656, A57
- 1646 Lacy, J. H., Carr, J. S., Evans, Neal J., I., et al. 1991, *ApJ*, 376, 556
- 1647 Ligterink, N. F. W., Ahmadi, A., Luitel, B., et al. 2022, *ACS Earth and Space Chemistry*, 6, 455
- 1648 Looney, L. W., Mundy, L. G., & Welch, W. J. 2000, *ApJ*, 529, 477
- 1649 Lowry, T. M. 1923, *Journal of the Society of Chemical Industry*, 42, 43
- 1650 Manigand, S., Jørgensen, J. K., Calcutt, H., et al. 2020, *A&A*, 635, A48
- 1651 Marechal, Y. 1987, *J. Chem. Phys.*, 87, 6344
- 1652 Martínez, R., Bordalo, V., da Silveira, E. F., & Boechat-Roberty, H. M. 2014, *MNRAS*, 444, 3317
- 1653 Maté, B., Herrero, V. J., Rodríguez-Lazcano, Y., et al. 2012, *ApJ*, 759, 90
- 1654 McClure, M. K., Rocha, W. R. M., Pontoppidan, K. M., et al. 2023, *Nature Astronomy*, 7, 431
- 1655 Min, M., Hovenier, J. W., & de Koter, A. 2005, *A&A*, 432, 909
- 1656 Molinari, S., Faustini, F., Testi, L., et al. 2008, *A&A*, 487, 1119
- 1657 Molinari, S., Testi, L., Brand, J., Cesaroni, R., & Palla, F. 1998, *ApJ*, 505, L39
- 1658 Morbidelli, A., Karato, S.-I., Ikoma, M., et al. 2018, *Space Sci. Rev.*, 214, 110
- 1659 Morbidelli, A., Lunine, J. I., O'Brien, D. P., Raymond, S. N., & Walsh, K. J. 2012, *Annual Review of Earth and Planetary Sciences*, 40, 251
- 1660 Moreno, M. A., Maté, B., Rodríguez-Lazcano, Y., et al. 2013, *Journal of Physical Chemistry A*, 117, 9564
- 1661 Nazari, P., van Gelder, M. L., van Dishoeck, E. F., et al. 2021, *A&A*, 650, A150
- 1662 Noble, J. A., Theule, P., Congiu, E., et al. 2015, *A&A*, 576, A91
- 1663 Novozamsky, J. H., Schutte, W. A., & Keane, J. V. 2001, *A&A*, 379, 588
- 1664 Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2008, *ApJ*, 678, 1032
- 1665 Öberg, K. I., Boogert, A. C. A., Pontoppidan, K. M., et al. 2011, *ApJ*, 740, 109
- 1666 Öberg, K. I., Bottinelli, S., & van Dishoeck, E. F. 2009a, *A&A*, 494, L13
- 1667 Öberg, K. I., Fraser, H. J., Boogert, A. C. A., et al. 2007, *A&A*, 462, 1187
- 1668 Öberg, K. I., Garrod, R. T., van Dishoeck, E. F., & Linnartz, H. 2009b, *A&A*, 504, 891
- 1669 O'Brien, D. P., Izidoro, A., Jacobson, S. A., Raymond, S. N., & Rubie, D. C. 2018, *Space Sci. Rev.*, 214, 47
- 1670 Onaka, T., Sakon, I., & Shimonishi, T. 2022, *ApJ*, 941, 190
- 1671 Ortiz-León, G. N., Loinard, L., Dzib, S. A., et al. 2018, *ApJ*, 865, 73
- 1672 Ossenkopf, V. & Henning, T. 1994, *A&A*, 291, 943
- 1673 Park, J.-Y. & Woon, D. E. 2006, *ApJ*, 648, 1285
- 1674 Perotti, G., Jørgensen, J. K., Fraser, H. J., et al. 2021, *A&A*, 650, A168
- 1675 Pilling, S., Andrade, D. P. P., Do Nascimento, E. M., et al. 2011, *MNRAS*, 411, 2214
- 1676 Pilling, S., Seperuelo Duarte, E., Domaracka, A., et al. 2010, *A&A*, 523, A77
- 1677 Poch, O., Istiqomah, I., Quirico, E., et al. 2020, *Science*, 367, aaw7462
- 1678 Pontoppidan, K. M., Dullemond, C. P., van Dishoeck, E. F., et al. 2005, *ApJ*, 622, 463
- 1679 Pontoppidan, K. M., van Dishoeck, E. F., & Dartois, E. 2004, *A&A*, 426, 925
- 1680 Potapov, A., Fulvio, D., Krasnokutski, S., Jäger, C., & Henning, T. 2022, *Journal of Physical Chemistry A*, 126, 1627
- 1681 Poteet, C. A., Whittet, D. C. B., & Draine, B. T. 2015, *ApJ*, 801, 110
- 1682 Qasim, D., Fedoseev, G., Chuang, K. J., et al. 2020, *Nature Astronomy*, 4, 781
- 1683 Qasim, D., Fedoseev, G., Chuang, K. J., et al. 2019, *A&A*, 627, A1
- 1684 Quénard, D., Jiménez-Serra, I., Viti, S., Holdship, J., & Coutens, A. 2018, *MNRAS*, 474, 2796
- 1685 Rachid, M. G., Brunken, N., de Boe, D., et al. 2021, *A&A*, 653, A116
- 1686 Rachid, M. G., Rocha, W. R. M., & Linnartz, H. 2022, *A&A*, 665, A89
- 1687 Rachid, M. G., Terwisscha van Scheltinga, J., Koletzki, D., & Linnartz, H. 2020, *A&A*, 639, A4
- 1688 Raunier, S., Chiavassa, T., Marinelli, F., Allouche, A., & Aycard, J. P. 2003, *Chemical Physics Letters*, 368, 594
- 1689 Reipurth, B., Rodríguez, L. F., Anglada, G., & Bally, J. 2002, *AJ*, 124, 1045
- 1690 Rieke, G. H., Wright, G. S., Böker, T., et al. 2015, *PASP*, 127, 584
- 1691 Rocha, W. & Pilling, S. 2014, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 123, 436
- 1692 Rocha, W. R. M., Perotti, G., Kristensen, L. E., & Jørgensen, J. K. 2021, *A&A*, 654, A158
- 1693 Rocha, W. R. M., Pilling, S., de Barros, A. L. F., et al. 2017, *MNRAS*, 464, 754
- 1694 Rocha, W. R. M., Rachid, M. G., Olsthoorn, B., et al. 2022, *A&A*, 668, A63
- 1695 Rubin, M., Altwegg, K., Balsiger, H., et al. 2019, *MNRAS*, 489, 594
- 1696 Sandell, G., Knee, L. B. G., Aspin, C., Robson, I. E., & Russell, A. P. G. 1994, *A&A*, 285, L1
- 1697 Schutte, W. A., Boogert, A. C. A., Tielens, A. G. G. M., et al. 1999, *A&A*, 343, 966
- 1698 Schutte, W. A. & Khanna, R. K. 2003, *A&A*, 398, 1049
- 1699 Shimonishi, T., Onaka, T., Kato, D., et al. 2010, *A&A*, 514, A12
- 1700 Skinner, C. J., Tielens, A. G. G. M., Barlow, M. J., & Justtanont, K. 1992, *ApJ*, 399, L79
- 1701 Skouteris, D., Balucani, N., Ceccarelli, C., et al. 2018, *ApJ*, 854, 135
- 1702 Slavicinska, K., Rachid, M. G., Rocha, W. R. M., et al. 2023, *A&A*, 677, A13
- 1703 Strazzulla, G. & Palumbo, M. E. 1998, *Planet. Space Sci.*, 46, 1339
- 1704 Taquet, V., López-Sepulcre, A., Ceccarelli, C., et al. 2015, *ApJ*, 804, 81
- 1705 Tenelanda-Osorio, L. I., Bouquet, A., Javelle, T., et al. 2022, *MNRAS*, 515, 5009
- 1706 Terwisscha van Scheltinga, J., Ligterink, N. F. W., Boogert, A. C. A., van Dishoeck, E. F., & Linnartz, H. 2018, *A&A*, 611, A35
- 1707 Terwisscha van Scheltinga, J., Marcandalli, G., McClure, M. K., Hogerheijde, M. R., & Linnartz, H. 2021, *arXiv e-prints*, arXiv:2105.02226
- 1708 Theule, P., Duvernay, F., Ilmane, A., et al. 2011, *A&A*, 530, A96
- 1709 Thi, W. F., van Dishoeck, E. F., Dartois, E., et al. 2006, *A&A*, 449, 251
- 1710 Tobin, J. J., Dunham, M. M., Looney, L. W., et al. 2015, *ApJ*, 798, 61
- 1711 van Broekhuizen, F. A., Keane, J. V., & Schutte, W. A. 2004, *A&A*, 415, 425
- 1712 van Broekhuizen, F. A., Pontoppidan, K. M., Fraser, H. J., & van Dishoeck, E. F. 2005, *A&A*, 441, 249
- 1713 van Dishoeck, E. F., Bergin, E. A., Lis, D. C., & Lunine, J. I. 2014, in *Protostars and Planets VI*, ed. H. Beuther, R. S. Klessen, C. P. Dullemond, & T. Henning, 835–858
- 1714 van Dishoeck, E. F., Grant, S., Tabone, B., et al. 2023, *Faraday Discussions*, 245, 52
- 1715 van Dishoeck, E. F., Kristensen, L. E., Mottram, J. C., et al. 2021, *A&A*, 648, A24
- 1716 van Gelder, M. L., Ressler, M. E., van Dishoeck, E. F., et al. 2023, *arXiv e-prints*, in press, arXiv:2311.17161
- 1717 van Gelder, M. L., Tabone, B., Tychoniec, L., et al. 2020, *A&A*, 639, A87
- 1718 Vazart, F., Ceccarelli, C., Balucani, N., & Skouteris, D. 2022, *ApJ*, 941, 196
- 1719 Watanabe, N. & Kouchi, A. 2002, *ApJ*, 571, L173
- 1720 Weingartner, J. C. & Draine, B. T. 2001, *ApJ*, 548, 296
- 1721 Wells, M., Pel, J. W., Glasse, A., et al. 2015, *PASP*, 127, 646
- 1722 Witke, P., Min, M., Pinte, C., et al. 2016, *A&A*, 586, A103
- 1723 Wright, G. S., Rieke, G. H., Glasse, A., et al. 2023, *PASP*, 135, 048003
- 1724 Wright, G. S., Wright, D., Goodson, G. B., et al. 2015, *PASP*, 127, 595
- 1725 Yang, Y.-L., Green, J. D., Pontoppidan, K. M., et al. 2022, *ApJ*, 941, L13
- 1726 Yang, Y.-L., Sakai, N., Zhang, Y., et al. 2021, *ApJ*, 910, 20
- 1727 Yarnall, Y. Y., Gerakines, P. A., & Hudson, R. L. 2020, *MNRAS*, 494, 4606
- 1728 Zasowski, G., Kemper, F., Watson, D. M., et al. 2009, *ApJ*, 694, 459
- 1729 Zucker, C., Schlafly, E. F., Speagle, J. S., et al. 2018, *ApJ*, 869, 83
- 1730 Öberg, K. I. 2016, *Chemical Reviews*, 116, 9631, pMID: 27099922

- 
- <sup>1</sup> Laboratory for Astrophysics, Leiden Observatory, Leiden University, P.O. Box 9513, NL 2300 RA Leiden, The Netherlands. e-mail: rocha@strw.leidenuniv.nl
- <sup>2</sup> Leiden Observatory, Leiden University, PO Box 9513, NL 2300 RA Leiden, The Netherlands
- <sup>3</sup> Max Planck Institut für Extraterrestrische Physik (MPE), Giessenbachstrasse 1, 85748 Garching, Germany
- <sup>4</sup> Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA
- <sup>5</sup> Dublin Institute for Advanced Studies, Dublin, Ireland
- <sup>6</sup> Max Planck Institute for Astronomy, Königstuhl 17, 69117 Heidelberg, Germany
- <sup>7</sup> INAF-Osservatorio Astronomico di Capodimonte, Salita Moiarriello 16, 80131 Napoli, Italy
- <sup>8</sup> UK Astronomy Technology Centre, Royal Observatory Edinburgh, Blackford Hill, Edinburgh EH9 3HJ, UK
- <sup>9</sup> Department of Experimental Physics, Maynooth University, Maynooth, Co Kildare, Ireland
- <sup>10</sup> Department of Space, Earth and Environment, Chalmers University of Technology, Onsala Space Observatory, 439 92 Onsala, Sweden
- <sup>11</sup> European Southern Observatory, Karl-Schwarzschild-Strasse 2, 85748 Garching bei München, Germany
- <sup>12</sup> SETI Institute 189 Bernardo Avenue, 2nd Floor, Mountain View, CA 94043, USA
- <sup>13</sup> School of Earth and Planetary Sciences, National Institute of Science Education and Research, Jatni 752050, Odisha, India
- <sup>14</sup> Homi Bhabha National Institute, Training School Complex, Anushaktinagar, Mumbai 400094, India
- <sup>15</sup> NASA Postdoctoral Program Fellow, NASA Ames Research Center, Moffett Field, CA, USA
- <sup>16</sup> Bay Area Environmental Research Institute and NASA Ames Research Center, Moffett Field, CA 94035, USA

## Appendix A: 9.8 $\mu\text{m}$ band compared to ISO and Spitzer sources

Figures A.1 and A.2 show comparisons with the silicate feature towards GCS 3 and with other low- and high-mass protostars observed with *Spitzer* and *ISO*. The first note is that both IRAS 2A and IRAS 23385 have a broader 9.8  $\mu\text{m}$  silicate profile compared to GCS 3. This highlights the need of considering different grain compositions when subtracting the silicate absorption band. Secondly, IRAS 2A and IRAS 23385 show a similar blue side of the spectrum with other sources. On the other hand, the red profile has more differences, which are related to the amount of  $\text{H}_2\text{O}$  ice towards the source. In fact, icy-grain models by Ossenkopf & Henning (1994) show that coagulated icy grains have a prominent spectral bump around 12  $\mu\text{m}$  because of the  $\text{H}_2\text{O}$  ice libration band.

## Appendix B: Effect of using different silicates for subtraction in IRAS 2A

In Section 3.1, we describe how the silicate feature is removed from IRAS 23385 and IRAS 2A MIRI-MRS spectra using a synthetic silicate profile combining olivine and pyroxene. In this section, we compare subtractions using different profiles to check how this step affects the shape of the 6.8–8.6  $\mu\text{m}$  region. Figure B.1 (top) shows three silicate profiles, scaled to IRAS 2A spectrum, i) the synthetic silicate used in Section 3.1, ii) the silicate profile of GCS 3, and iii) the  $\text{MgSiO}_3$  profile taken from Poteet et al. (2015). The peak optical depths are set to match the synthetic silicate profile. We point out that this comparison is focused on the 6.8–8.6  $\mu\text{m}$  region, and therefore mismatches of these silicate spectra at longer wavelengths are not relevant for this specific analysis. We briefly mention SiO (silica), as another possible candidate for the blue wing of the 9.8  $\mu\text{m}$  band. However, silica has not been found in absorption in protostars so far and its relatively narrow profile at 18  $\mu\text{m}$  is not seen in both sources investigated in this paper. Nevertheless, if present, SiO would not affect the COMs bands investigated in this paper because of its broadband at around 8.3  $\mu\text{m}$ . At most, it could slightly reduce the  $\text{HCOOH}$  ice column density.

Figure B.1 (bottom) shows the silicate subtracted optical depth spectrum of IRAS 2A. Both synthetic and enstatite silicates result in similar spectral profiles between 6.8–8.6  $\mu\text{m}$ . On the other hand, the silicate subtraction using GCS 3 creates an unrealistic absorption excess (also observed in Boogert et al. (2008)) that deviates from the other two profiles.

## Appendix C: List of laboratory data

A comprehensive list of molecules was used in this paper to search for the best fit of the region between 6.8 and 8.6  $\mu\text{m}$ . This list includes COMs in different mixtures as well as simple molecules. The full list is shown in Table C.1.

## Appendix D: Acetic acid and $\text{OCN}^-$ band strengths

Most of the band strengths for the molecules detected in the range addressed in this paper are available in the literature. However, to the best of our knowledge, the band strengths of acetic acid and  $\text{OCN}^-$  between 6.8 and 8.6  $\mu\text{m}$  were not calculated before. In particular, the band strength of acetic acid at 5.8  $\mu\text{m}$  is often assumed to be the same as, or corrected from, the gas-phase acetic acid (e.g., Öberg et al. 2009b; Chuang et al. 2020) based on Marechal (1987).

We derive the absolute ( $A$ ) and apparent ( $A'$ ) band strengths of acetic acid. The absolute band strengths are derived from the imaginary refractive index, by the following equation:

$$A = \frac{m}{\rho N_A} \int_{\nu_1}^{\nu_2} 4\pi\nu k(\nu) d\nu \quad (\text{D.1})$$

where  $m$  is the molar mass of acetic acid in  $\text{g mol}^{-1}$  (60.052),  $\rho$  is the density of acetic acid ( $0.892 \text{ g cm}^{-3}$ ; Hudson et al. 2020),  $N_A$  is the Avogadro's number,  $\nu$  is the wavenumber and  $k$  is the imaginary refractive index. We derive  $k$  using the recent version of the NKABS code (Rocha & Pilling 2014). This code calculates the real ( $n$ ) and imaginary ( $k$ ) refractive index from the absorbance spectrum ( $Ab_{s,\nu}$ ). The input spectrum is taken from Hudson & Gerakines (2019), who also estimated the thickness of the ice ( $d = 2.1 \mu\text{m}$ ) and the refractive index around 700 nm ( $n_0 = 1.29$ ). The  $n$  and  $k$  values are shown in Figure D.1. Finally, the band strengths derived for two acetic acid bands are listed in Table D.1.

The apparent band strength is calculated by:

$$A' = 2.303 \frac{m}{\rho N_A d} \int Ab_{s,\nu} d\nu \quad (\text{D.2})$$

As one can see, both  $A$  and  $A'$  values for acetic acid are similar.

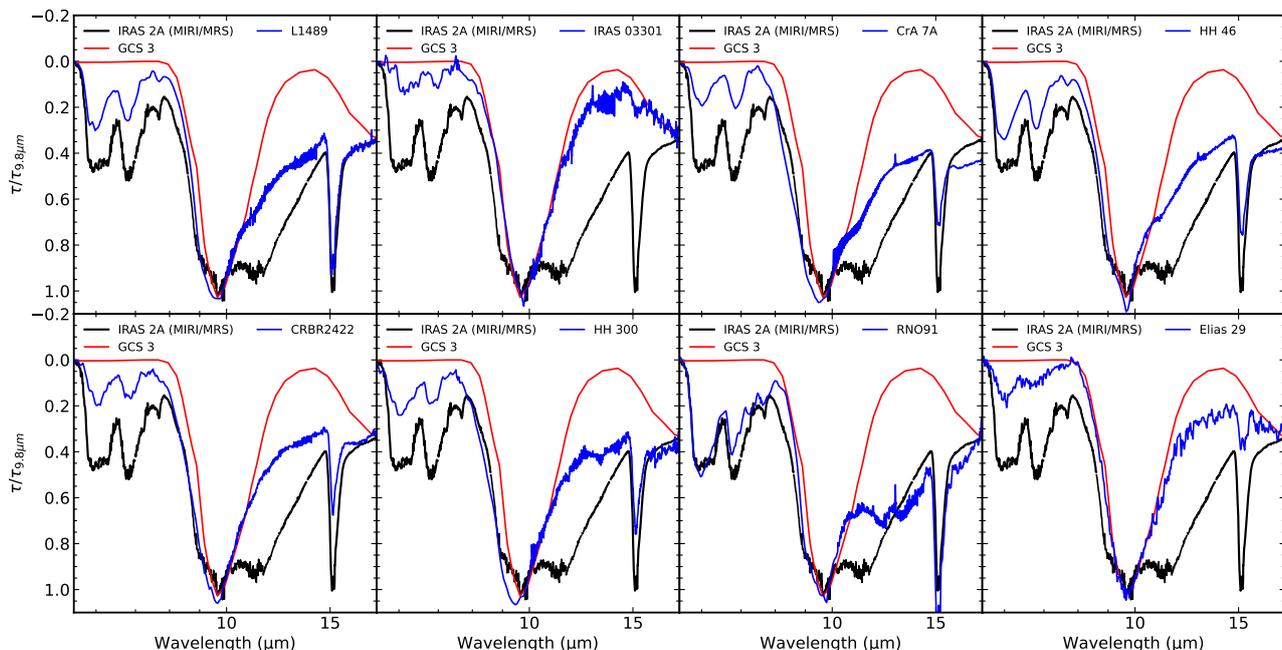
In the case of  $\text{OCN}^-$ , we derive the apparent band strength at 7.62  $\mu\text{m}$  ( $1312 \text{ cm}^{-1}$ ). The  $\text{OCN}^-$  band at 4.59  $\mu\text{m}$  ( $2175 \text{ cm}^{-1}$ ) is used as a reference since the band strength is known ( $1.3 \times 10^{-16} \text{ cm molecule}^{-1}$ ; van Broekhuizen et al. 2005). We use the following equation to derive the  $\text{OCN}^-$  apparent band strength at 7.62  $\mu\text{m}$ :

$$A'_{7.62\mu\text{m}} = 1.3 \times 10^{-16} \frac{\int Ab_{s,1312\text{cm}^{-1}} d\nu}{\int Ab_{s,2175\text{cm}^{-1}} d\nu}, \quad (\text{D.3})$$

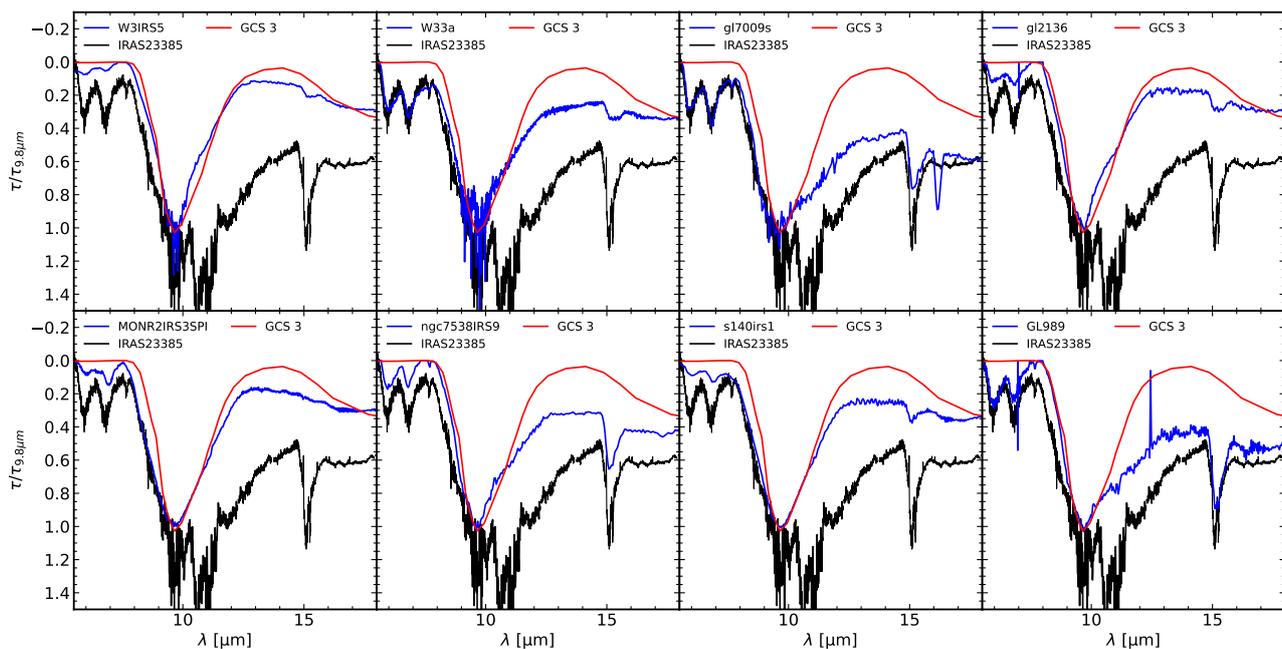
where  $Ab_{s,2175\text{cm}^{-1}}$  and  $Ab_{s,1312\text{cm}^{-1}}$  are the  $\text{OCN}^-$  bands at the given wavelengths.

## Appendix E: Laboratory spectra: removing $\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}$ ice features

In this section, we demonstrate how to remove the  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  features of COMs spectra containing these two molecules in the range between 6.5 and 9.0  $\mu\text{m}$ . This process is necessary when analysing the observational spectrum between 6.8 and 8.6  $\mu\text{m}$  using local continuum subtraction. Figure E.1 (top) shows the  $\text{H}_2\text{O}:\text{CH}_3\text{CH}_2\text{OH}$  ice spectrum (Terwisscha van Scheltinga et al. 2018) and the polynomial (4th-order) function used to trace a baseline under the  $\text{CH}_3\text{CH}_2\text{OH}$  bands. In this spectrum, the ethanol features overlap with the broad shoulder of the  $\text{H}_2\text{O}$  ice bending mode, which is represented by the polynomial fit. In Figure E.1 (bottom), we show the  $\text{CH}_3\text{OH}:\text{CH}_3\text{CH}_2\text{OH}$  IR spectrum (Terwisscha van Scheltinga et al. 2018). Since both molecules are alcohols they share functional groups, which makes it harder to isolate the ethanol features of methanol. Because of the high dilution factor (20:1), it is not feasible to disentangle the features of the two molecules below 6.8  $\mu\text{m}$ , and therefore, we separate the  $\text{CH}_3\text{CH}_2\text{OH}$  bands between 6.9 and 8.6  $\mu\text{m}$ . The step is performed in three stages: (i) high-order polynomial (7th) between 6.9–7.15  $\mu\text{m}$  to remove the  $\text{CH}_3\text{OH}$  shoulder, (ii) 3rd-order polynomial between 7.15–7.45  $\mu\text{m}$  to isolate the ethanol band at 7.2  $\mu\text{m}$  and account for the strong curvature in the data, and (iii) 5th-order polynomial between 7.45–8.7  $\mu\text{m}$  to extract the other ethanol bands.



**Fig. A.1.** Comparison among MIRI/JWST spectrum of IRAS 2A, the silicate profile of GCS 3 and *Spitzer*/IRS spectrum of different low-mass protostars. These spectra are normalized by the optical depth at 9.8  $\mu\text{m}$ .

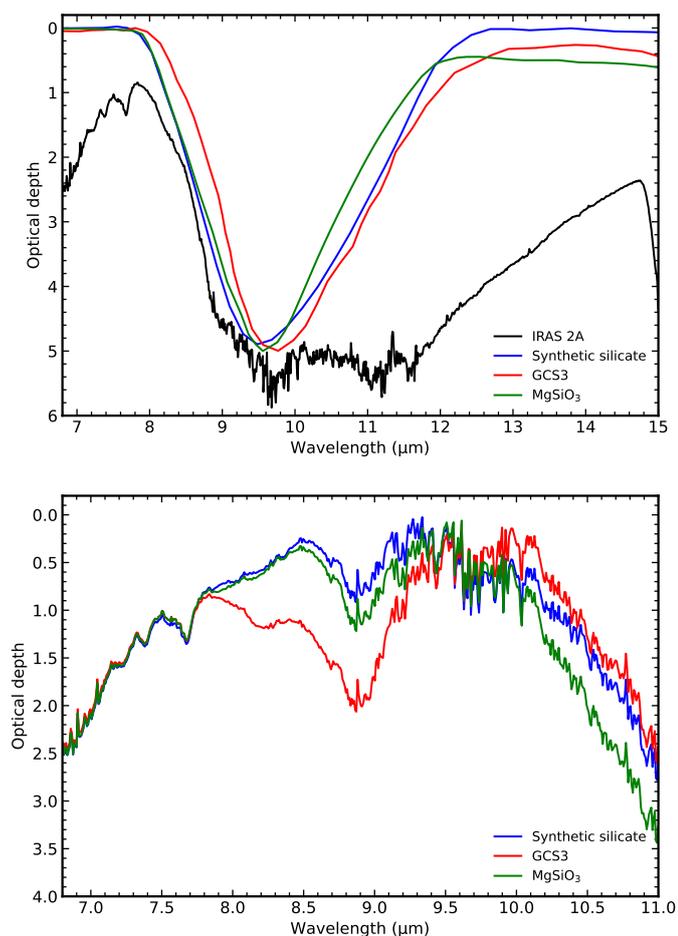


**Fig. A.2.** Comparison among MIRI/JWST spectrum of IRAS 23385, the silicate profile of GCS 3 and *Spitzer*/IRS spectrum of different low-mass protostars. These spectra are normalized by the optical depth at 9.8  $\mu\text{m}$ .

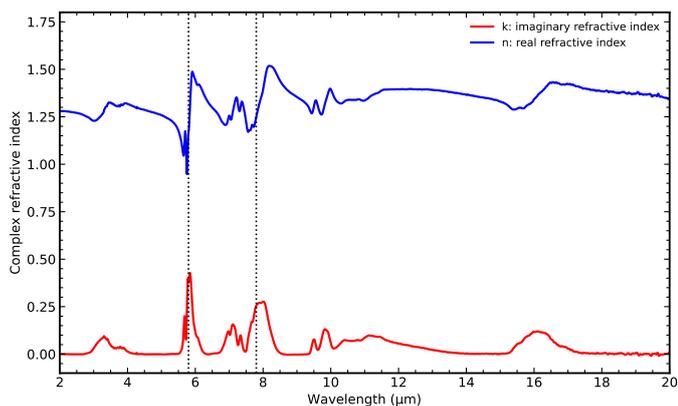
## Appendix F: Laboratory baseline correction: avoiding spurious features

IR spectra of ices are recorded in the laboratory using Fourier Transform Infrared Spectroscopy (FTIR) and interference effects are corrected using a spline or polynomial function, the so-called baseline correction. In Figure F.1 we show the baseline correction of the  $\text{H}_2\text{O}:\text{CH}_3\text{CH}_2\text{OH}$  IR spectrum at 15 K. Panels a and b show the laboratory spectrum and a 7th-order polynomial used to correct the interference effect. The difference between these two panels is that in panel a, we use as many points as possi-

ble to trace the baseline, whereas in panel b, we use only half of the points available in the range of 7.8–8.5  $\mu\text{m}$ . This creates a small fluctuation in the polynomial function. Zoom-ins of both cases are shown in panels c and d, respectively. In panel e, we show the baseline data. The spectrum with no polynomial inflexion contains the real  $\text{CH}_3\text{CH}_2\text{OH}$  IR features, whereas the other data has spurious features at 8.0 and 8.3  $\mu\text{m}$ . This demonstrates that care must be taken when correcting IR spectrum baselines to avoid creating spurious features.



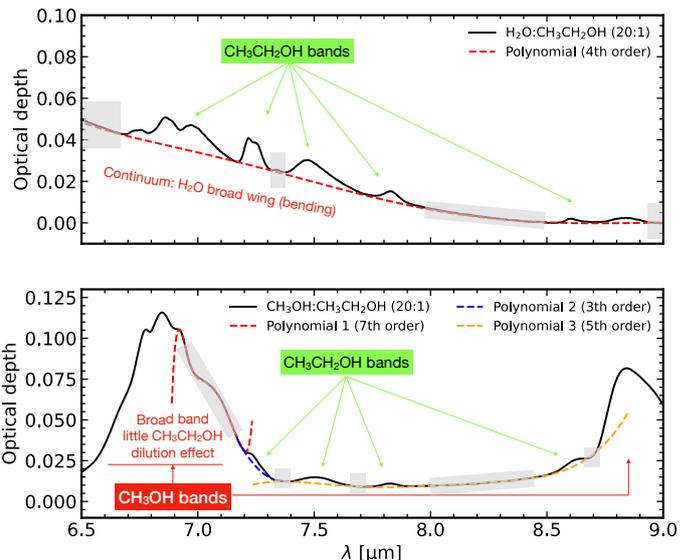
**Fig. B.1.** Comparing silicate profiles in IRAS 2A. The top panel shows the synthetic silicate providing the best fit in IRAS 2A (blue) compared to GCS 3 (red) and enstatite (green) silicate model from [Poteet et al. \(2015\)](#). The bottom panel shows the IRAS 2A spectrum after removing the three silicate models.



**Fig. D.1.** Optical contacts of acetic acid. Vertical dotted lines indicate the features with band strength calculated in this paper.

## Appendix G: Incremental version of the fits for IRAS 2A and IRAS 23385

Figure [G.1](#) displays the best fits for IRAS 2A (left) and IRAS 23385 (right) by adding one component at a time in each panel. This allows understanding better how each component contributes to the fit.



**Fig. E.1.** Isolating the  $\text{CH}_3\text{CH}_2\text{OH}$  ice bands from  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  ices. Polynomial functions anchored at the points indicated by the grey areas are used. The top panel shows the ethanol mixed with  $\text{H}_2\text{O}$  ice, and the bottom panel displays the mixture with  $\text{CH}_3\text{OH}$ .

## Appendix H: $\text{HCOO}^-$ at 14, 150 and 210 K

We compare the absorption profiles of  $\text{HCOO}^-$  at three temperatures (14 K, 150 K, 210 K) with the 7.2 and 7.4  $\mu\text{m}$  bands in IRAS 2A and IRAS 23385 (Figure [H.1](#)). Our analysis shows that the spectrum at 14 K provides the best fit. The spectrum at 150 K is excluded because the second peak ( $\sim 7.4 \mu\text{m}$ ) is broader and shifted compared to the observations. Likewise, the band shape of the highest temperature data (150 K) does not match with both protostars.

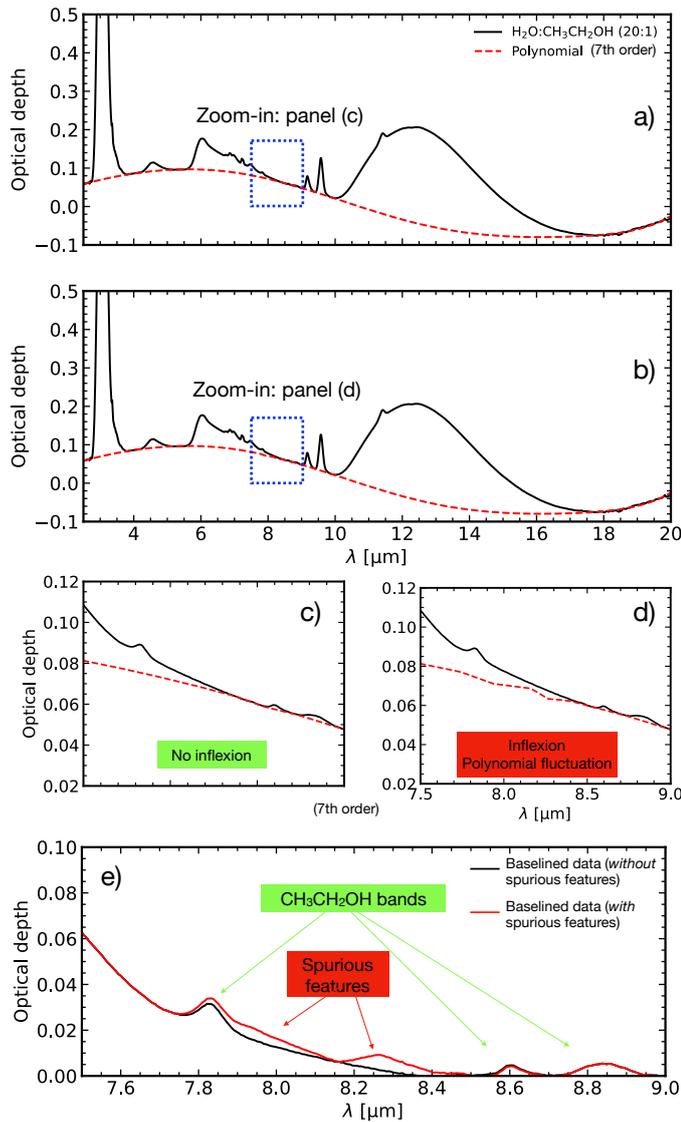
## Appendix I: Confidence intervals

The top and bottom panels in Figure [I.1](#) show the confidence intervals for IRAS 2A in the ranges of 6.8–7.5 and 7.8–8.6, respectively. The confidence intervals for IRAS 23385 are shown in Figures [I.2](#) and [I.3](#). For IRAS 2A, it can be noted that all components are essential to the fit, and cannot be excluded. On the other hand, for IRAS 23385, the  $\text{SO}_2$  band can be excluded as a solution if the  $\text{OCN}^-$  band is slightly intense.

## Appendix J: Different local continuum profiles between 6.8 and 8.6 $\mu\text{m}$ - IRAS 2A

The first three panels of Figure [J.1](#) show different continuum profiles between 6.8–8.6  $\mu\text{m}$  in the IRAS 2A spectrum. The top panel is the version adopted for the analysis in this paper that traced a third-order polynomial to the guiding points. The second panel displays the fourth-order polynomial where the red dot is added to the guiding points. In this case, the continuum is slightly elevated at shorter wavelengths to accommodate the fit to the extra point at 8.5  $\mu\text{m}$ . The third panel presents the continuum when two extra points are added ( $\lambda = 7.8 \mu\text{m}$  and 8.5  $\mu\text{m}$ ), and a sixth-order polynomial is used. All subtracted spectra using these three approaches are shown in the bottom panel of Figure [J.1](#).

New fits for IRAS 2A are performed on the other two optical depth spectra obtained from different local continuum choices, which are shown in Figure [J.2](#). The panel at the top shows that all



**Fig. F.1.** Baseline correction of the IR ice spectrum of  $\text{H}_2\text{O}:\text{CH}_3\text{CH}_2\text{OH}$  data. Panels a and b show the IR ice spectra and the baselines. The blue dotted squares highlight the zoom-ins shown in panels c and d displaying polynomial baselines without and with little inflexion, respectively. Panel e demonstrates the effect of non-accurate baseline subtraction in the ice spectrum.

## Appendix K: Water and methanol ice column densities

1968

1969

The water ice column densities in both protostars are calculated from the libration mode around  $12.5 \mu\text{m}$ . To determine the profile of the band, we combine water ice spectra at different temperatures (Figure K.1). As pointed out by Boogert et al. (2008), this band is sensitive to the grain geometry. For this reason, we assume small spherical water ice grains which is consistent with Boogert et al. (2008) to fit the libration mode best. The optical constants for ices at 15, 75, and 160 K are taken from Rocha et al. (2022). The water libration band is fitted with two components representing different temperatures. It is likely that the libration band is sensitive to a range of temperatures between 15 and 160 K, but addressing this is beyond the scope of this work. Despite this simplification, one can note that only cold water ice is not enough to fit the libration band of IRAS 23385 and IRAS 2A. In particular, IRAS 2A has a strong blue wing excess that requires  $\text{H}_2\text{O}$  ice at 160 K. The water ice column density is shown in Table 2.

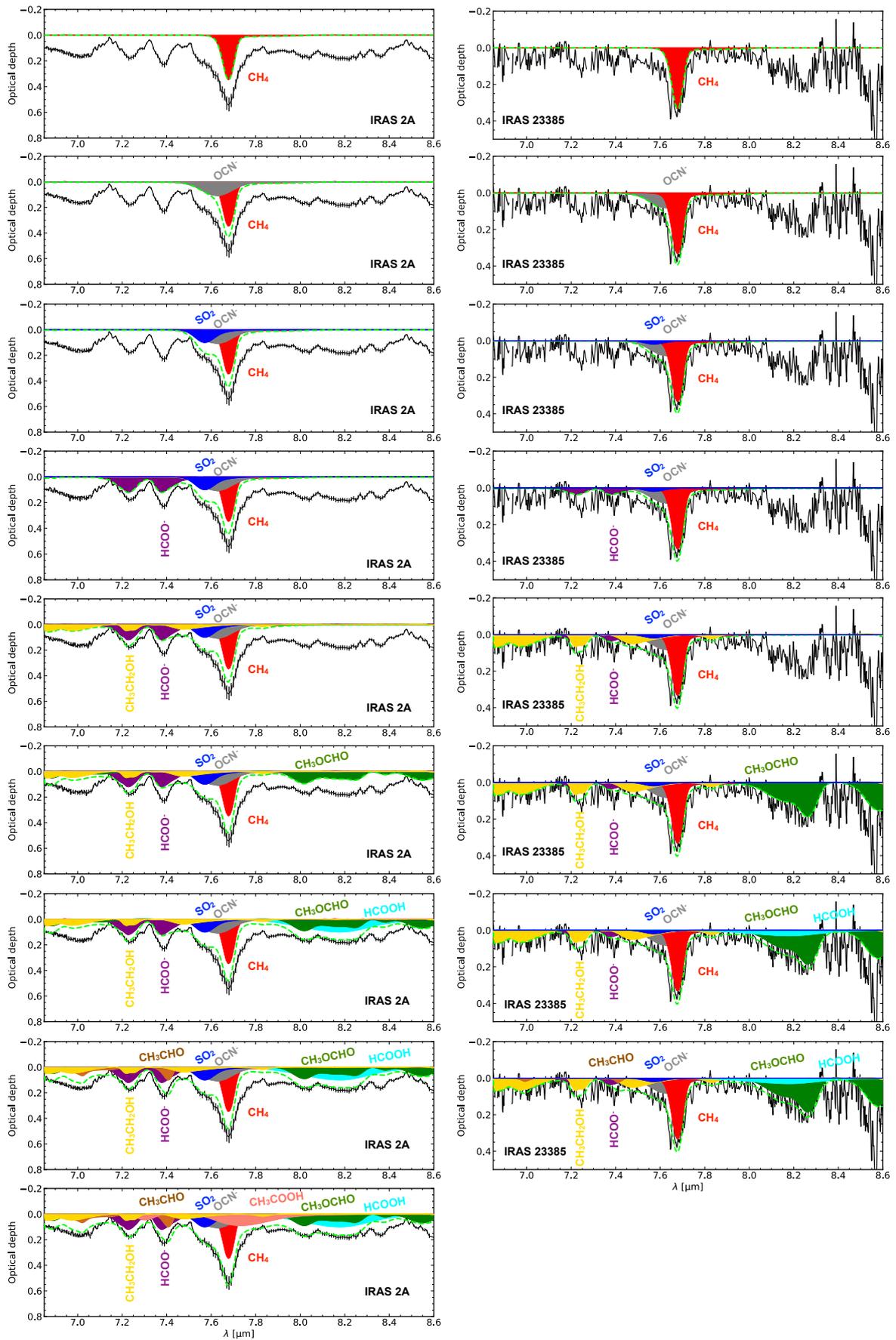
In the case of  $\text{CH}_3\text{OH}$  ice, we use the band at  $9.8 \mu\text{m}$  to derive a column density. We fit a Gaussian profile to the feature at  $9.8 \mu\text{m}$  (solid curve in Figure K.2) and multiply it by a factor of 2 (dashed curve) and 3 (dotted curve). It is unlikely that the solid curve accounts for all  $\text{CH}_3\text{OH}$  absorption, and therefore the  $\text{CH}_3\text{OH}$  ice column densities used in this paper correspond to the other two Gaussian profiles.

## Appendix L: Comparison with hydrocarbons

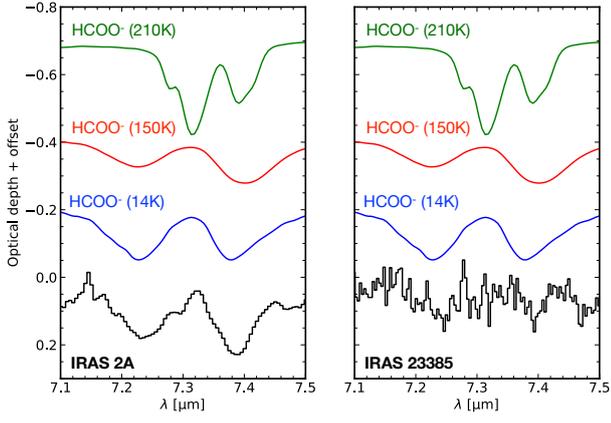
1994

Because of the degeneracy intrinsic to the ice fittings, particularly regarding COMs that share the same functional groups, we show in this section a comparison of hydrocarbons ( $\text{C}_x\text{H}_y$ ) with the IRAS 2A spectrum. These molecules participated in the global fits between  $6.8$  and  $8.6 \mu\text{m}$ , but are discarded as solutions. Therefore, these comparisons serve as an additional check that these components are not part of the global minimum solution. Figure L.1 shows scaled IR spectra of pure  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  compared to IRAS 2A. The scaling factors are arbitrarily chosen to match the IRAS 2A absorption profile at  $7.3 \mu\text{m}$ . It can be seen that  $\text{C}_2\text{H}_4$  does not have any contribution to the  $7.2$  and  $7.4 \mu\text{m}$ . On the other hand, the absorption bands of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_6$  that could be hidden at  $7.3 \mu\text{m}$ , exceed the IRAS 2A absorption profiles around  $12$  and  $13.5 \mu\text{m}$ .

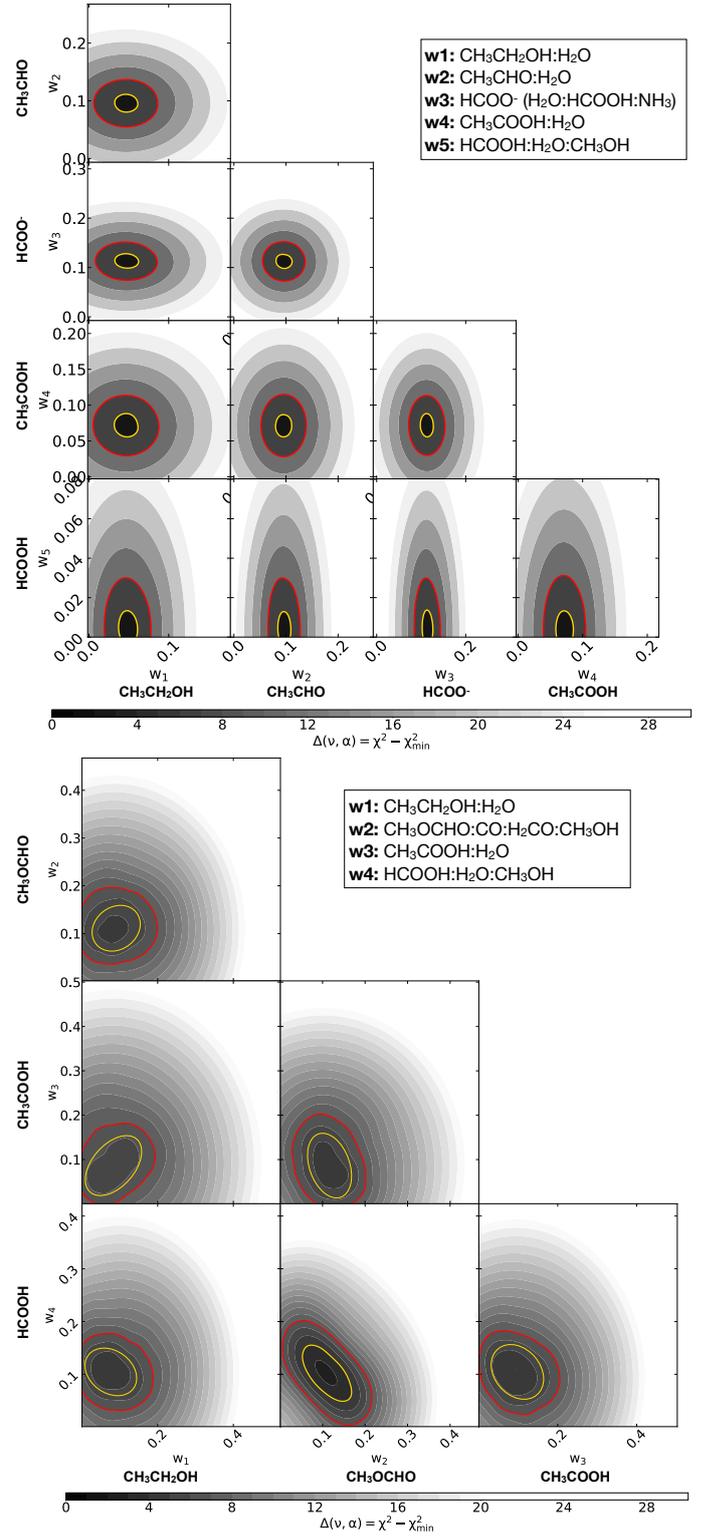
1956 components remain needed to reach the best fit. Only the  $8.5 \mu\text{m}$   
 1957 band of  $\text{CH}_3\text{OCHO}$  exceeds the observations, and this is caused  
 1958 by the guiding point added at  $8.5 \mu\text{m}$ . The bottom panel of Fig-  
 1959 ure J.2 shows another fit, where two extra points are added at  
 1960  $7.8$  and  $8.5 \mu\text{m}$ . This version of the fit keeps all components, ex-  
 1961 cept  $\text{CH}_3\text{COOH}$ , which is excluded because of the anchor point  
 1962 added at  $7.8 \mu\text{m}$ , where  $\text{CH}_3\text{COOH}$  has a strong feature. Other  
 1963 issues are seen in this fit, for example, around  $7 \mu\text{m}$ ,  $7.3 \mu\text{m}$ , and  
 1964 a poor fit between  $7.8$  and  $8.6 \mu\text{m}$ . Despite all these differences,  
 1965 this analysis shows that  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{OCHO}$   
 1966 are still robust detections, and cannot be excluded from the fits  
 1967 of the IRAS 2A spectrum.



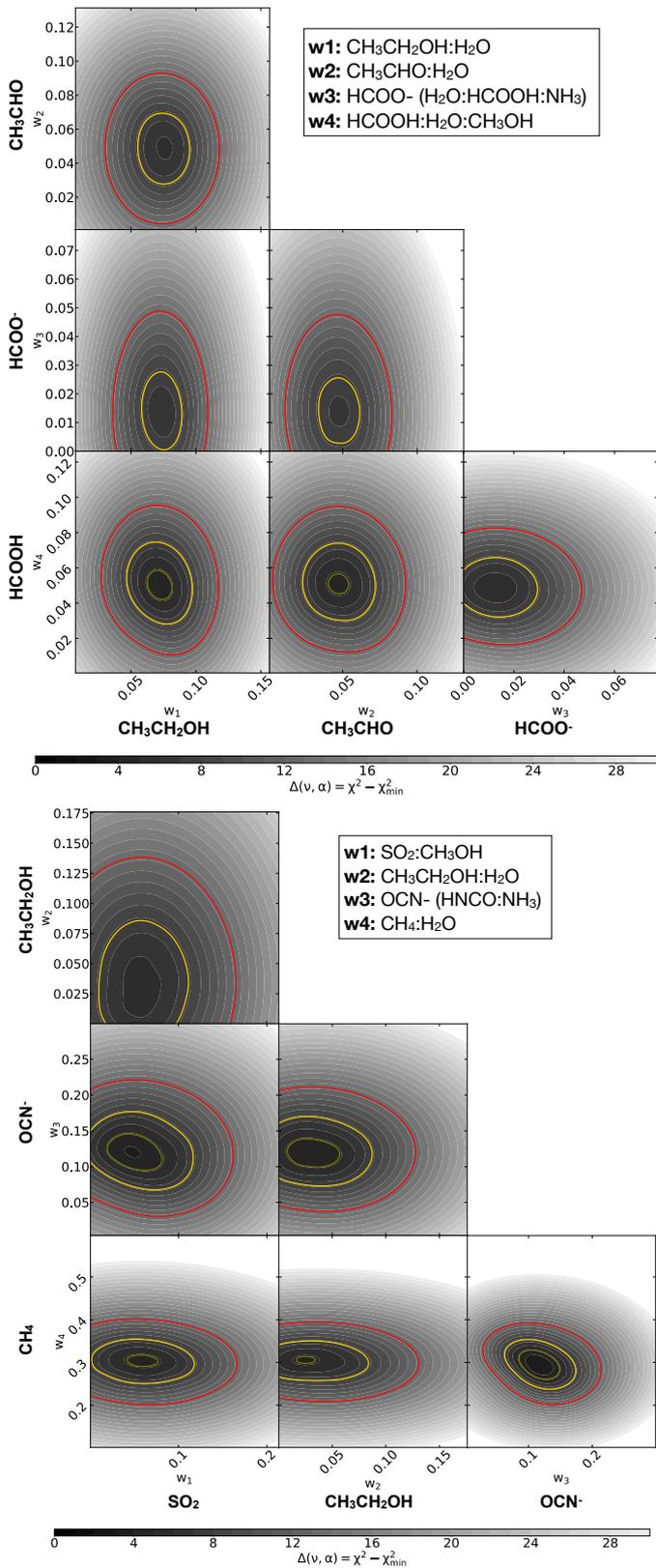
**Fig. G.1.** Incremental version from top to bottom of the best fits with the ENIGMA fitting tool for IRAS 2A (left) and IRAS 23385 (right). The molecule label follows the colour code of the laboratory components in the fit.



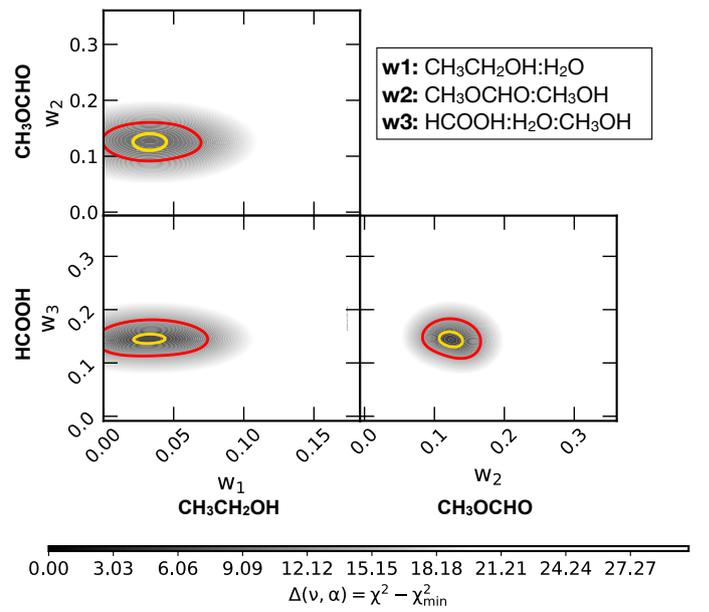
**Fig. H.1.** Comparison between the 7.2 and 7.4  $\mu\text{m}$  band of IRAS 2A (left) and IRAS 23385 (right) with the  $\text{HCOO}^-$  absorption profiles at 14, 150 and 210 K. These IR ice spectra are taken from [Gálvez et al. \(2010\)](#).



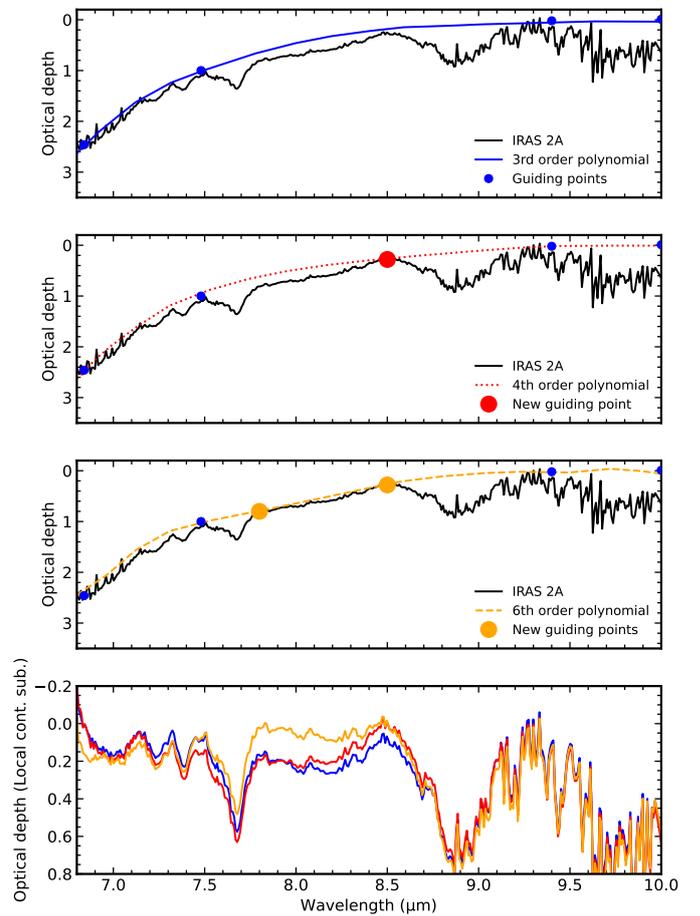
**Fig. I.1.** The top and bottom corner plots show the IRAS 2A coefficient confidence intervals for the range between 6.86–7.5 (top) and 7.8–8.6  $\mu\text{m}$  (bottom), respectively.



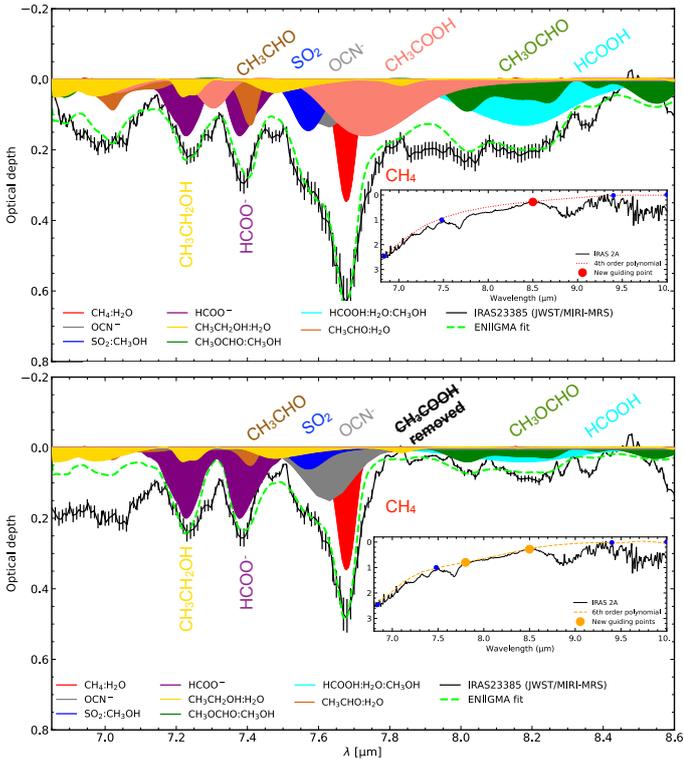
**Fig. I.2.** The top and bottom corner plots show the IRAS 23385 coefficient confidence intervals for the range between 6.86–7.5 (top) and 7.5–7.8 μm (bottom), respectively.



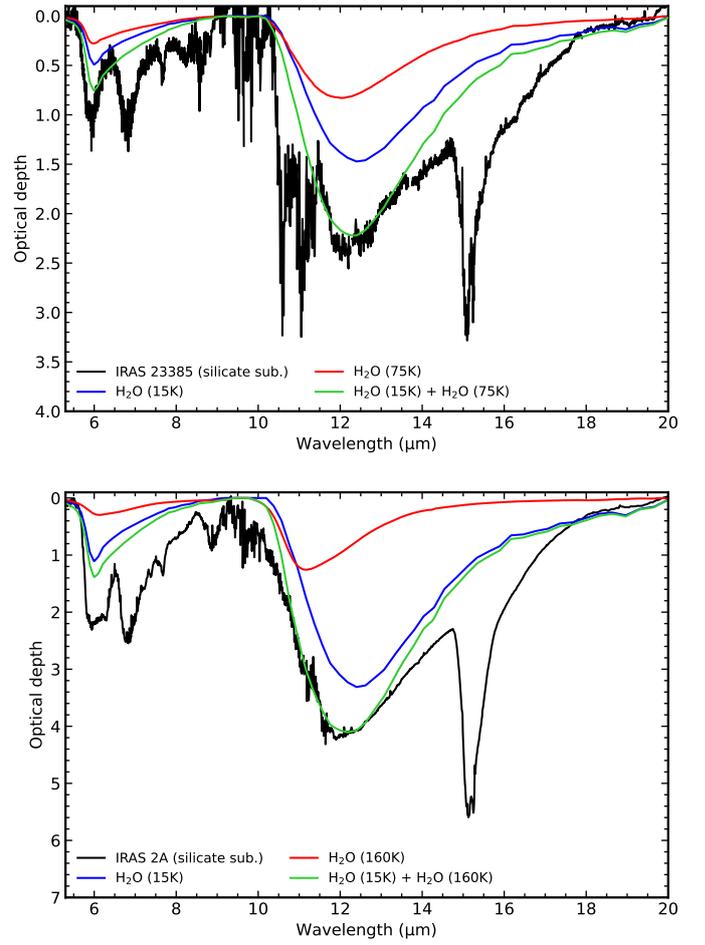
**Fig. I.3.** Same as in Figure I.2, but for the range 7.8–8.6 μm.



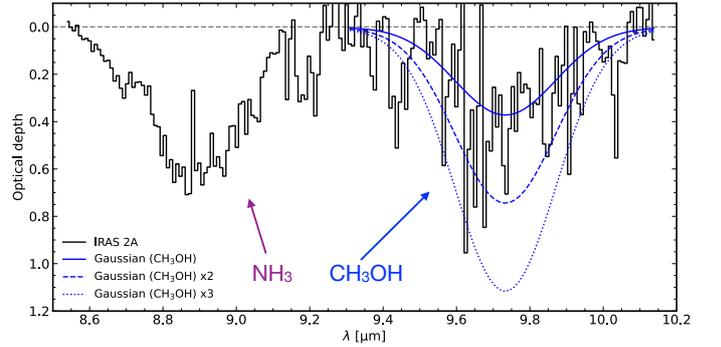
**Fig. J.1.** Effect of the continuum choice on the local continuum subtracted spectrum of IRAS 2A. The first panel shows the continuum adopted as the best model in this paper. The second and third panels show two other continuum options by adding the red and orange points, respectively. The optical depth subtracted spectra are shown in the fourth panel.



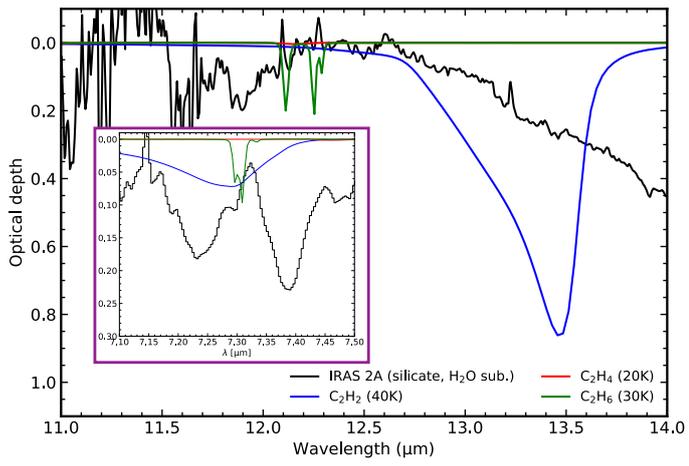
**Fig. J.2.** Alternative fits of IRAS 2A optical depth spectrum with different local continuum choices (see Figure J.1). The top panel shows the fits with all the components after subtracting the red local continuum with an extra point at  $8.5 \mu\text{m}$ . The bottom panel shows the same as in the top panel, but considering two extra points for the local continuum ( $7.8$  and  $8.5 \mu\text{m}$ ). Only  $\text{CH}_3\text{COOH}$  is excluded in this fit.



**Fig. K.1.** Fits for the  $\text{H}_2\text{O}$  ice libration band for IRAS 23385 (top) and IRAS 2A (bottom). The best fit is found by combining two  $\text{H}_2\text{O}$  ice grain-shaped corrected spectra: 15K and 75 K for IRAS 23385 and 15 K and 160 K for IRAS 2A.



**Fig. K.2.**  $\text{NH}_3$  and  $\text{CH}_3\text{OH}$  features in the bottom of the silicate band and  $\text{H}_2\text{O}$  ice subtracted spectra of IRAS 2A. Three Gaussian profiles are scaled to the  $\text{CH}_3\text{OH}$  band to indicate different ice column densities.



**Fig. L.1.** Comparison between the 7.2 and 7.4  $\mu\text{m}$  band of IRAS 2A (silicate and H<sub>2</sub>O ice subtracted) and hydrocarbons (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>).

**Table C.1.** Laboratory data tested in the global fit performed with ENIIGMA.

Label	Temperature (K)	Resolution (cm <sup>-1</sup> )	Database <sup>a</sup>	Reference
<b>Simple molecules (less than 6 atoms) and hydrocarbons</b>				
H <sub>2</sub> O	15–160	2.0	LIDA	[1]
CH <sub>4</sub>	10–30	1.0	OCdb	[2]
HCOOH	15–165	1.0	LIDA	[3]
SO <sub>2</sub> :CH <sub>3</sub> OH (1:1)	15	1.0	LIDA	[4]
H <sub>2</sub> O:CH <sub>4</sub> (10:1)	15	1.0	UNIVAP	[5]
C <sub>2</sub> H <sub>2</sub>	15	1.0	NASA	[6]
C <sub>2</sub> H <sub>4</sub>	15	1.0	NASA	[7]
C <sub>2</sub> H <sub>6</sub>	15	1.0	NASA	[7]
<b>Ions</b>				
OCN <sup>-</sup> :HNCO:NH <sub>3</sub> (1:1)	15	1.0	LIDA	[8]
HCOO <sup>-</sup> :H <sub>2</sub> O:NH <sub>3</sub> :HCOOH (100:2.6:2)	14–210	1.0	LIDA	[9]
HCOO <sup>-</sup> :NH <sub>3</sub> :HCOOH (1.3:1)	14–210	1.0	LIDA	[9]
<b>COMs (more than 6 atoms)</b>				
CH <sub>3</sub> OH	10–120	1.0	OCdb	[2]
CH <sub>3</sub> CHO	15–120	1.0	LIDA	[10]
CH <sub>3</sub> CN	15–150	1.0	LIDA	[11]
CH <sub>3</sub> OCH <sub>3</sub>	15–100	1.0	LIDA	[10]
CH <sub>3</sub> COCH <sub>3</sub>	15–100	1.0	LIDA	[11]
CH <sub>3</sub> CH <sub>2</sub> OH	15–150	1.0	LIDA	[10]
CH <sub>3</sub> OCHO	15–120	1.0	LIDA	[12]
CH <sub>3</sub> COOH	10	1.0	NASA	[13]
CH <sub>3</sub> NH <sub>2</sub>	10	1.0	LIDA	[14]
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	13	1.0	NASA	[15]
HC(O)CH <sub>2</sub> CH <sub>3</sub>	10	1.0	NASA	[16]
CH <sub>3</sub> CH <sub>2</sub> OH:H <sub>2</sub> O (1:20)	15–160	1.0	LIDA	[10]
CH <sub>3</sub> CH <sub>2</sub> OH:CO (1:20)	15, 30	1.0	LIDA	[10]
CH <sub>3</sub> CH <sub>2</sub> OH:CH <sub>3</sub> OH (1:20)	15–150	1.0	LIDA	[10]
CH <sub>3</sub> CH <sub>2</sub> OH:CO:CH <sub>3</sub> OH (1:20:20)	15–150	1.0	LIDA	[10]
CH <sub>3</sub> CHO:H <sub>2</sub> O (1:20)	15–120	1.0	LIDA	[10]
CH <sub>3</sub> CHO:CO (1:20)	15, 30	1.0	LIDA	[10]
CH <sub>3</sub> CHO:CH <sub>3</sub> OH (1:20)	15–140	1.0	LIDA	[10]
CH <sub>3</sub> CHO:CO:CH <sub>3</sub> OH (1:20:20)	15–120	1.0	LIDA	[10]
CH <sub>3</sub> OCH <sub>3</sub> :H <sub>2</sub> O (1:20)	15–160	1.0	LIDA	[10]
CH <sub>3</sub> OCH <sub>3</sub> :CO (1:20)	15, 30	1.0	LIDA	[10]
CH <sub>3</sub> OCH <sub>3</sub> :CH <sub>3</sub> OH (1:20)	15–120	1.0	LIDA	[10]
CH <sub>3</sub> OCH <sub>3</sub> :CO:CH <sub>3</sub> OH (1:20:20)	15–100	1.0	LIDA	[10]
CH <sub>3</sub> COCH <sub>3</sub> :H <sub>2</sub> O (1:20)	15–160	1.0	LIDA	[11]
CH <sub>3</sub> COCH <sub>3</sub> :CO (1:20)	15, 30	1.0	LIDA	[11]
CH <sub>3</sub> COCH <sub>3</sub> :CO <sub>2</sub> (1:20)	15–100	1.0	LIDA	[11]
CH <sub>3</sub> COCH <sub>3</sub> :CH <sub>3</sub> OH (1:20)	15–140	1.0	LIDA	[11]
CH <sub>3</sub> COCH <sub>3</sub> :H <sub>2</sub> O:CO <sub>2</sub> (1:2.5:2.5)	15–160	1.0	LIDA	[11]
CH <sub>3</sub> COCH <sub>3</sub> :CO:CH <sub>3</sub> OH (1:2.5:2.5)	15–140	1.0	LIDA	[11]
CH <sub>3</sub> OCHO:H <sub>2</sub> O (1:20)	15–120	1.0	LIDA	[12]
CH <sub>3</sub> OCHO:CO (1:20)	15–120	1.0	LIDA	[12]
CH <sub>3</sub> OCHO:H <sub>2</sub> CO (1:20)	15–120	1.0	LIDA	[12]
CH <sub>3</sub> OCHO:CO:H <sub>2</sub> CO:CH <sub>3</sub> OH (1:20:20:20)	15–120	1.0	LIDA	[12]
CH <sub>3</sub> COOH:H <sub>2</sub> O (1:20)	10	1.0	NASA	[13]
CH <sub>3</sub> NH <sub>2</sub> :H <sub>2</sub> O (1:20)	15–150	1.0	LIDA	[14]
CH <sub>3</sub> NH <sub>2</sub> :NH <sub>3</sub> (1:20)	15–150	1.0	LIDA	[14]
CH <sub>3</sub> NH <sub>2</sub> :CH <sub>4</sub> (1:20)	15–150	1.0	LIDA	[14]
CH <sub>3</sub> CN:H <sub>2</sub> O (1:20)	15–150	1.0	LIDA	[11]
CH <sub>3</sub> CN:CO (1:20)	15–100	1.0	LIDA	[11]
NH <sub>2</sub> CHO:H <sub>2</sub> O (7:100)	15–160	1.0	LIDA	[17]
NH <sub>2</sub> CHO:CO (4:100)	15–34	1.0	LIDA	[17]
HCOCH <sub>2</sub> OH:H <sub>2</sub> O (1:18)	10	1.0	NASA	[18]

**Notes.** [1] Öberg et al. (2007), Gerakines et al. (1996); [2] Hudgins et al. (1993); [3] Bisschop et al. (2007); [4] Boogert et al. (1997); [5] Rocha et al. (2017); [6] Hudson et al. (2014a); [7] Hudson et al. (2014b); [8] Novozamsky et al. (2001); [9] Gálvez et al. (2010); [10] Terwisscha van Scheltinga et al. (2018); [11] Rachid et al. (2022); [12] Terwisscha van Scheltinga et al. (2021); [13] No reference found - taken from the NASA Ice Database (Pure: <https://science.gsfc.nasa.gov/691/cosmicice/spectra/refspec/Acids/CH3COOH/ACETIC-W.txt>, Mixture: [https://science.gsfc.nasa.gov/691/cosmicice/spectra/8\\_compounds/Combined\\_spectra\\_2018-12-20.xlsx](https://science.gsfc.nasa.gov/691/cosmicice/spectra/8_compounds/Combined_spectra_2018-12-20.xlsx)); [14] Rachid et al. (2021); [15] Hudson & Gerakines (2019); [16] Yarnall et al. (2020); [17] Slavicinska et al. (2023); [18] Hudson et al. (2005). <sup>a</sup>LIDA: The Leiden Ice Database for Astrochemistry (<https://icedb.strw.leidenuniv.nl/>); OCdb: The Optical Constant Database (<https://ocdb.smce.nasa.gov/>); UNIVAP: <https://www1.univap.br/gaa/nkabs-database/data.htm>; NASA Cosmic Ice Laboratory: <https://science.gsfc.nasa.gov/691/cosmicice/spectra.html>

**Table D.1.** Absolute and apparent band strengths of acetic acid.

$\lambda_{\text{central}}$	$A_{\text{abs}}$ (cm molec <sup>-1</sup> )	$A_{\text{apr}}$ (cm molec <sup>-1</sup> )
5.8	$7.5 \times 10^{-17}$	$7.3 \times 10^{-17}$
7.82	$4.6 \times 10^{-17}$	$4.6 \times 10^{-17}$