Synthesis of the first nitrogen-heterocycles in interstellar ice analogs containing methylamine (CH$_3$NH$_2$) exposed to UV radiation: Formation of trimethylentriamine (TMT, c-(-CH$_2$-NH)$_3$) and hexamethyldetramine (HMT, (CH$_2$)$_6$N$_4$).

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ABSTRACT
Hexamethyldetramine has drawn a lot of attention due to its potential to produce prebiotic species. This work aims to gain a better understanding in the chemical processes concerning methylamine under astrophysically relevant conditions. In particular, this work deeps into the formation of N-heterocycles in interstellar ice analogs exposed to UV radiation, which may lead to the formation of prebiotic species.

Experimental simulations of interstellar ice analogs were carried out in ISAC. ISAC is an ultra-high vacuum chamber equipped with a cryostat, where gas and vapour species are frozen forming ice samples. Infrared and ultraviolet spectroscopy were used to monitor the solid phase, and quadrupole mass spectrometry served to measure the composition of the gas phase. The variety of species detected after UV irradiation of ices containing methylamine revealed the presence of 12 species which have been already detected in the ISM, being 4 of them typically classified as complex organic molecules: formamide (HCONH$_2$), methyl cyanide (CH$_3$CN), CH$_3$NH and CH$_3$CHNH. Warming up of the irradiated CH$_3$NH$_2$-bearing ice samples lead to the formation of trimethylentriamine (TMT), a N-heterocycle precursor of HMT, and the subsequent synthesis of HMT at temperatures above 230 K.

Key words: Astrochemistry – Methods: laboratory: molecular – techniques: spectroscopy – software: simulation – ultraviolet: ISM – ISM: molecules

1 INTRODUCTION
Molecules with six or more atoms including at least one C atom are known as complex organic molecules (COMs) (Herbst & van Dishoeck 2009). COMs have been detected in dense interstellar clouds and circumstellar regions. Deep inside dense clouds, the interstellar UV field cannot penetrate and dust temperature decreases to around 10 K. At these low temperatures, H$_2$O and other molecules including CO, CO$_2$, CH$_3$OH, CH$_4$, or NH$_3$ accrete onto dust grains forming ice mantles. These ice mantles are exposed to secondary-UV photons generated by the interaction between cosmic rays and hydrogen molecules, as well as direct cosmic ray impact, producing radicals and ions which can lead to the formation of new species. Some intermediate species can react at low temperature, while others remain in the ice until the temperature increases and thermal energy is enough to overcome the activation barriers to form new species. Up to now, more than 200 different molecules have been detected in the gas phase toward interstellar and circumstellar environments, including around 50 COMs. An important fraction of these species is thought to be produced in ice mantles.

Among them, methylamine (CH$_3$NH$_2$) has drawn considerable attention due to its potential to produce prebiotic species. It was first detected in Sagitarius B2 and Orion A molecular clouds with column densities ranging from 1×10$^{15}$ cm$^{-2}$ to 4×10$^{15}$ cm$^{-2}$ (Kaifu et al. 1974; Fourikis et al. 1974; Belloche et al. 2013). Goesmann et al. (2015) and Altwegg et al. (2017) reported CH$_3$NH$_2$ abundances from 0.6% to 1.2% relative to H$_2$O on comet 67P/Churyumov-Gerasimenko. Finally, CH$_3$NH$_2$ has also been detected in hot cores. Ohishi et al. (2019) reported the presence of CH$_3$NH$_2$ in G10.47+0.03 while Bøgelund et al. (2019) observed column densities between 3.0×10$^{15}$ and 2.7×10$^{17}$ in three dif-
fert hot cores from the high-mass star forming region NGC 6334I.

Different mechanisms have been proposed for methylamine formation under astrophysical conditions. In the gas phase, Herbst (1985) modelled the possible association between CH$_3^+$ ions and NH$_3$ molecules to produce CH$_3$NH$_2$, concluding that it was an efficient route to produce methylamine under interstellar conditions, despite the existence of exothermic reaction channels. Gardner & McNesby (1980) and Ogura et al. (1989) reported the formation of methylamine from photolysis of gas mixtures containing CH$_4$ and NH$_3$. In their experiments, UV-irradiation produced CH$_3^+$ and NH$_2^+$ radicals able to recombine to produce CH$_3$NH$_2$. This pathway was also explored in ice samples by Kim & Kaiser (2011) and Förstel et al. (2017), who carried out electron bombardment and photon irradiation of CH$_4$;NH$_3$ ice mixtures, respectively, reporting the formation of methylamine in both works. An alternative route is the successive hydrogenation of gas phase HCN molecules, analogous to the formation of H$_2$CO and CH$_3$OH from CO molecules, as pointed out by Dickens et al. (1997) and Theule et al. (2011).

Several experiments reveal the potential of CH$_3$NH$_2$ to form prebiotic molecules. Holton et al. (2005) prepared CH$_3$NH$_2$:CO$_2$ binary ice mixtures which resulted in glycine (NH$_2$CH$_2$COOH) formation under electron bombardment. Bossa et al. (2009a) reproduced the same ice mixture in a water dominated ice. They found evidence on the formation of methylammonium methylcarbamate, [CH$_3$NH$_2$]CH$_3$NHCOO$^-$, a glycine salt precursor in astrophysical environments dominated by thermal and UV processing. In the same year, Lee et al. (2009) reported the formation of several COMs from UV irradiation of CH$_3$NH$_2$:CO$_2$ mixtures on top of a H$_2$O ice.

The main motivation to study the UV-photoprocessing of methylamine-bearing ices in this work is to gain a better understanding on the formation of N-heterocycles in interstellar ice analogs. In particular, we targeted the synthesis of hexamethylenetetramine (HMT), a molecule commonly identified among the refractory products in ice irradiation experiments, and its precursor, trimethylentriamine (TMT).

Hexamethylenetetramine (C$_6$N$_4$H$_{12}$, HMT) is a molecule of prime interest in astrochemistry. Firstly, it is a stable molecule efficiently made by UV or ion processing of interstellar ice analogs, which remains in the generated organic residue at room temperature (Briggs et al. 1992; Cottin et al. 2001). Second, it may catalyze organic reactions leading to the formation of other COMs (Vinogradoff et al. 2012). Third, its acid hydrolysis leads to the formation of several aminoacids (Fox & Windsor 1970). HMT has been recently detected in Murchison (846±37 ppb), Murray (29±9 ppb) and Tagish Lake (671±9 ppb) carbonaceous chondrites, as well as the methyl, amino, hydroxy and hydroxymethyl derivatives of HMT (see Oba et al. 2020). The synthesis of HMT derivatives in ice irradiation experiments was previously reported (Muñoz Caro et al. 2004; Sandford et al. 2020; Materese et al. 2020; Urso et al. 2020).

HMT can be produced from condensation reaction between ammonia and formaldehyde in aqueous solution (Meissner et al. 1954, Fig. 1). This synthetic pathway has been typically applied to ice chemistry (Bernstein et al. 1995; Muñoz Caro & Schutte 2003; Vinogradoff et al. 2013, and references therein). Basically, the proposed synthetic route is as follows. CH$_3$OH is easily dehydrogenated by UV radiation to produce formaldehyde, or formaldehyde is formed, albeit less efficiently, from hydrogenation of CO in the ice (Briggs et al. 1992; Muñoz Caro & Schutte 2003; Muñoz Caro et al. 2004). The reaction between a carbonyl group and a primary amine typically leads to the formation of imine groups (R=N-R'), releasing a water molecule. Thus, from formaldehyde and ammonia, methylenimine (CH$_3$NH) is obtained. This highly reactive methylenimine polymerises, leading to a 6-member stable ring, known as trimethylentriazine (TMT). Methylene groups are electron-deficient units which incorporate hydroxymethyl radicals to form 1,3,5-trihydroxymethyltrihydmethylentriazine (TMT-tri).

The latter leads to HMT in presence of ammonia. The last step, however, only takes place at high temperatures, when ammonia is already thermally desorbed to the gas phase in the ice irradiation and warm-up experiments. Indeed, Muñoz Caro & Schutte (2003) observed the formation of HMT at room temperature monitoring the growth of its main absorption bands in the IR spectra at 1007 and 1234 cm$^{-1}$. These authors proposed the presence of carboxylate ammonium salts, which would remain in the ice at high temperature, able to provide the amino groups.

Vinogradoff et al. (2012, 2013) and references therein deepened in the formation mechanism of HMT. Those works reported measurements of complex ice mixtures, confirming that formaldehyde reacts with ammonia to produce methylenimine (CH$_3$NH). However, the stability of organic rings favours the cyclation of the 6-member species CH$_3$NH-CH$_3$NH-CH$_3$NH, leading to the production of TMT (Vinogradoff et al. 2012). TMT is then converted into HMT near room temperature.

Within this work, we explore an alternative mechanism in the production of HMT. We have focused on the primary steps and the intermediate species. We have calculated the theoretical IR spectrum of TMT since we found no spectrum for this species in the literature. The validity of this calculation was checked comparing the calculated HMT spectrum to the one measured in the laboratory. Gardner & McNesby (1982) reported the preferential formation of CH$_3$NH from UV irradiation of CH$_3$NH$_2$ molecules, supported by the efficient formation of H$_2$ molecules. By using methylamine, we have been able to study in more depth the chemical pathways of C-N bearing molecules in different environments. Noble gas matrix isolation experiments were also carried out to isolate CH$_3$NH molecules, thus allowing the study of its spectroscopic features and radical formation. This will be explained in more detail in the paragraphs below.

In addition to the primary processes leading to HMT, we also studied the formation of other photoproducts arising upon UV irradiation of methylamine. When H$_2$O is added to CH$_3$NH$_2$ in the ice, in a likely more realistic astrophysical scenario, oxygenated species are formed. Some of them, such as HCN, HNCO or HCONH$_2$ were found in comet 67P/Churyumov-Gerasimenko surface during the Rosetta mission (Goessmann et al. 2015), and confirmed by Allweg et al. (2017) using DFMS spectra from the orbiter. Finally, we produced a well-studied residue by irradiation of H$_2$:O:CH$_3$OH:NH$_3$ ice mixture for comparison with the methylenimine ice experiments (Bernstein et al. 1995; Muñoz Caro & Schutte 2003; Vinogradoff et al. 2013)

The present paper is structured as follows. Sect. 2 explains the experimental procedure used during the experimental simulations, as well as the calculated IR spectra. Sect. 3 is divided into four
subsections. Sect. 3.2 presents the different features of CH$_3$NH$_2$ in the three environments studied in this work. Sect. 3.3 explores the different rate of H$_2$ subtraction during UV irradiation of the different ice matrices. Sect. 3.4 focuses on the formation of photoproducts at 8 K in the different ice mixtures. Sect. 3.6 goes deeper into the formation of large species, such as TMT, which only takes place at higher temperatures. Finally, Sect. 4 and Sect. 5 summarizes the main results and present the astrophysical implications.

2 EXPERIMENTAL

2.1 ISAC experimental simulations

Experiments were carried out in the Interstellar Astrochemistry Chamber (ISAC), fully described in Muñoz Caro et al. (2010). ISAC is an Ultra-High Vacuum (UHV) chamber with a base pressure of 4x10$^{-11}$ mbar equipped with a closed-cycle helium cryostat able to reach temperatures of 8 K in a MgF$_2$/KBr substrate used for ice deposition.

For the experiments, highly distilled MilliQ water was obtained from a Millipore water distribution system IQ-7000. For matrix experiments, Xe was acquired from Praxair with a 99.999% purity. Methylamine was purchased from Merck group diluted for ice deposition.

Gases and vapours were introduced in the main chamber through a capillary tube of 1 mm internal diameter at normal incidence angle with respect to the MgF$_2$ substrate at pressures ranging from 2x10$^{-7}$ to 1x10$^{-6}$ for the different experiments. To ensure the purity of the ice mixtures, a quadrupole mass spectrometer (QMS, Pfeiffer Vacuum, Prisma QMS 200) was placed in the injection system, thus avoiding any contamination and providing a method to achieve the desired ratio between the components. The gas phase was monitored continuously in the main chamber using another QMS (Pfeiffer Vacuum, Prisma QMS 200) equipped with a Channeltron detector. For matrix isolation experiments, Xe pressure (monitored by $\tau_\nu = 131$) was adjusted to measure an ion current at least two orders of magnitude larger than the one measured for the most intense fragment from methylamine ($\tau_\nu = 30$). In addition, Xe has three natural isotopes with similar abundances, thus, the real ratio Xe:CH$_3$NH$_2$ turned out to be around 10.000:1, providing a good isolation of CH$_3$NH$_2$ molecules. This is supported by the dissappearance of the N-H stretching vibrations in the IR spectrum, as explained in Sect. 3.2.

Fourier-transform infrared spectroscopy (FTIR) transmittance spectra were recorded using a Bruker VERTEX 70 with a resolution of 1-2 cm$^{-1}$, equipped with a deuterated triglycine sulfate (DGTS) detector to monitor the solid phase. IR spectra of the ice samples were performed before and after deposition of the ice, after each irradiation interval, and during the warming up. From the infrared spectra, the column density was estimated following eq. 1, where $A$ is the band strength in cm$^{-1}$ molecule$^{-1}$, $\tau_\nu$ is the optical depth, and $d\nu$ is the wavenumber differential in cm$^{-1}$. For methylamine, the adopted band strength is the one reported by Holtom et al. (2005), 4.3x10$^{-18}$ cm molecule$^{-1}$ for the 1613 cm$^{-1}$ IR band. For H$_2$O, a value of 2.0x10$^{-16}$ cm molecule$^{-1}$ for its 3259 cm$^{-1}$ IR band was used (Hagen et al. 1981). For methanol, 1.8x10$^{-17}$ cm molecule$^{-1}$ for its 1025 cm$^{-1}$ IR band (D’Hendecourt et al. 1986). Finally, for NH$_3$, a value of 1.7x10$^{-17}$ cm molecule$^{-1}$ for its 1070 cm$^{-1}$ IR band was adopted (Sandford & Allamandola 1993).

$$N = \frac{1}{A} \int_{\text{band}} \tau_\nu \, d\nu.$$  (1)

For optically thick ices, the ratio between the components was estimated from the ion current measured by the QMS during the deposition of the ice samples, which showed a good agreement with the values calculated from IR spectroscopy.

Ice samples were irradiated with a F-type microwave discharged hydrogen lamp (MDHL) from Opthos instruments. The light emitted by the MDHL enters the ISAC chamber through a MgF$_2$ window, and radiation is guided to the deposition substrate through a quartz tube inside the chamber. The UV-flux was measured at the end of the quartz tube with a calibrated Ni mesh to know the flux at the sample position (see González Díaz et al. 2019). Vacuum ultraviolet spectroscopy was carried out using a McPherson 0.2 m focal length UV monochromator (model 234/302) placed in front of the MDHL. The UV-absorption cross section of the ice samples was obtained applying eq. 2, where $I_\nu(\lambda)$ is the transmitted intensity, $I_0(\lambda)$ is the incident intensity, $\sigma(\lambda)$ is the UV-absorption cross section of the ice, and $N$ is the column density derived from the IR spectra, following Cruz-Díaz et al. (2014).

$$I_\nu(\lambda) = I_0(\lambda) \times e^{-\sigma(\lambda)N}.$$  (2)
After ice irradiation, temperature programmed desorption (TPD) experiments were performed. A LakeShore 331 temperature controller connected to a silicon diode sensor with a sensibility better than 0.1 K was used to warm up the ice samples at 0.3 K/min up to 300 K. QMS data were recorded continuously and FTIR spectra were measured every 5 K during warm-up.

For $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3$ experiments, $\text{H}_2\text{O}$ and $\text{CH}_3\text{OH}$ were introduced through the main gas line in ISAC, while $\text{NH}_3$ was introduced through a second capillary tube, using a secondary gas line specifically designed for corrosive species.

2.2 IR spectra simulations

The calculation of the vibrational spectra for all the species collected in Fig. 2 has been done at the harmonic level using the well-tested Density Functional Theory hybrid method B3LYP. Different basis sets were used in exploratory calculations and finally the quadruple-z quality correlation consistent aug-cc-pVQZ, which includes both polarization and diffuse functions, was used for production purposes. Frequencies presented are not scaled and intensities are referred to the highest feature in each spectrum. All the calculations were carried out by means of Gaussian16 package (Frisch et al. 2016).

3 RESULTS AND DISCUSSION

3.1 Theoretical IR spectra

Fig. 2 shows the calculated IR spectra of three species related to HMT synthesis: TMT, TMT-(CH$_2$OH)$_3$ and HMT. The infrared spectra of TMT and TMT-(CH$_2$OH)$_3$ have, to our knowledge, not been reported before. The well known IR spectrum of HMT was also calculated to illustrate the reliability of the synthetic spectra. There is a good agreement between our measured IR spectrum of HMT derivatives (Bera et al. 2019), is worth noting.

3.2 Effect of the ice environment over CH$_3$NH$_2$ ice.

Table 1 collects the different ice sample compositions, ice column density, and irradiation dose of the experiments presented in this work. Fig. 3 shows the methylamine IR features observed after deposition of CH$_3$NH$_2$ molecules in different environments (Exp. 1, 5 and 6). Pure methylamine ice exhibits features (shown in Table 2) which are in good agreement with previous works (Durig et al. 1968; Zhu et al. 2019, and references therein). When CH$_3$NH$_2$ is diluted in an inert matrix, Xe atoms in this work, intermolecular forces are reduced, and bands become narrower. N-H stretching vibrations (3500-3100 cm$^{-1}$) seem to disappear in the Xe matrix, indicative of a large decrease of its IR band strength when molecules are isolated and H bonds are inhibited (Durig & Zheng 2001). CH$_3$NH$_2$ in a CH$_3$NH$_2$:H$_2$O (1:1) ice mixture (Exp. 6) shows the same IR features observed for pure CH$_3$NH$_2$ ice, slightly red-shifted by the different intermolecular forces present in this ice, and widened, as a consequence of the interaction of CH$_3$NH$_2$ with H$_2$O neighbouring molecules. N-H stretching bands, however, are not weakened in a H$_2$O dominated ice. O-H groups in water ice can interact strongly with N-H groups, as both N and O atoms are able to establish hydrogen bonds.

TPD experiments over a non-irradiated CH$_3$NH$_2$ ice revealed no major changes in the IR spectra up to 100 K. The onset of CH$_3$NH$_2$ crystallization occurs near 100 K, CH$_3$NH$_2$ acquires a crystalline structure (Fig. 3), ejecting molecules with a low-binding energy during this process. Fig. 4 shows the thermal desorption of CH$_3$NH$_2$ in the different environments studied in this work. Pure methylamine ice sublimates from 100 K, having its maximum desorption at 142 K. The desorbed molecules are responsible for the QMS peak starting at 90 K with a maximum at 106 K in the X$_e$ ice. Thermal desorption at 142 K. The desorbed molecules are responsible for the QMS peak starting at 90 K with a maximum at 106 K in the X$_e$ ice. Pure methylamine ice sublimates from 100 K, having its maximum desorption at 142 K. The desorbed molecules are responsible for the QMS peak starting at 90 K with a maximum at 106 K in the X$_e$ ice. Pure methylamine ice sublimates from 100 K, having its maximum desorption at 142 K. The desorbed molecules are responsible for the QMS peak starting at 90 K with a maximum at 106 K in the X$_e$ ice.

Figure 2. Calculated IR spectra of three species related to HMT synthesis: TMT, TMT-(CH$_2$OH)$_3$ and HMT itself. Dash black line shows the experimental IR spectra of HMT for comparison. Absorbance was normalized to 1 in all cases.

Figure 3. IR spectra recorded after deposition of different ice samples. CH$_3$NH$_2$:Xe (pink, Exp. 5), CH$_3$NH$_2$:H$_2$O (blue, Exp. 9), and pure CH$_3$NH$_2$ at 8 K (black, Exp. 1) and 110 K (red, after crystallization process in Exp. 1). Band positions agree with those reported for pure CH$_3$NH$_2$ ice (Durig et al. 1968; Zhu et al. 2019).

Figure 4. Thermal desorption of CH$_3$NH$_2$ under different environments.
shown in the top panel of Fig. 4. Co-deposition with less-volatile H$_2$O molecules delays CH$_3$NH$_2$ thermal desorption to 164 K. Indeed, some methylamine molecules remain in the solid phase at larger temperatures, desorbing during the crystallization of H$_2$O molecules, around 175 K. From Fig. 4, it can be concluded that methylamine thermal desorption is strongly dependent on its environment, as it happens with the type of substrate when dealing with monolayer-thick ices (Chaabouni et al. 2018).

### 3.3 UV irradiation of CH$_3$NH$_2$ ice samples. H$_2$ formation and diffusion. Saturation of species

As it can be seen in Table 1, the column density of CH$_3$NH$_2$ in the pure ice samples was larger by a factor of $\geq 10$ compared to CH$_3$NH$_2$:Xe ice sample (Exp. 2 and 6). From the UV absorption cross section of methylamine presented in Fig. 5, and using eq. 2, a column density of $6.9 \times 10^{17}$ cm$^{-2}$ corresponds to about 95% UV absorption for pure methylamine ice, and $4.2 \times 10^{17}$ cm$^{-2}$ for a 95% UV absorption in the CH$_3$NH$_2$:Xe ice sample. Therefore, in our experiments, most of the CH$_3$NH$_2$ molecules in the ice were exposed to UV radiation. UV-thick ices were irradiated during the deposition process, their corresponding photon dose is shown in Table 1. The large difference between CH$_3$NH$_2$ (both pure and in H$_2$O mixture) with the UV spectrum of CH$_3$NH$_2$:Xe ice mixture (see Fig. 5) is due to the UV absorption of Xe ice, in line with the

**Table 1.** Experiments performed in this work

| Exp. | Ice sample       | $N_0$ (CH$_3$NH$_2$) | Photon dose |
|------|------------------|----------------------|-------------|
|      |                  | ($\text{cm}^{-2}$)  | Absolute ($\text{cm}^{-2}$) per molecule ($\text{cm}^{-2}$) |
| 1    | CH$_3$NH$_2$     | $2.4 \times 10^{17}$| 0           | 0           |
| 2    | CH$_3$NH$_2$     | $3.2 \times 10^{17}$| $1.0 \times 10^8$ | 3.2         |
| 3    | CH$_3$NH$_2$     | $6.1 \times 10^{17}$| $1.4 \times 10^8$ | 2.5         |
| 4    | CH$_3$NH$_2$     | $1.2 \times 10^{18}$| $1.5 \times 10^8$ | 1.1         |
| 5    | CH$_3$NH$_2$:Xe** | $2.2 \times 10^{16}$| $1.0 \times 10^8$ | 1.0         |
| 6    | CH$_3$NH$_2$:H$_2$O (1:1) | $3.9 \times 10^{17}$| $9.0 \times 10^7$ | 1.2         |
| 7    | CH$_3$NH$_2$:H$_2$O* (2:1) | $6.6 \times 10^{17}$| $2.7 \times 10^7$ | 1.5         |
| 8    | CH$_3$NH$_2$     | $1.9 \times 10^{19}$| $3.6 \times 10^5$ | 1.9         |
| 9    | CH$_3$NH$_2$:H$_2$O (1:2) | $2.0 \times 10^{18}$| $1.5 \times 10^5$ | 0.25        |

$^*$ Experiment 7 was irradiated during the warm-up, between 8 K and 110 K. This irradiation represents the 40% of the total photon dose.

$^{**}$ Absorption of Xe atoms prevented us from the quantification of methylamine photon dose, see Fig. 5.

**Table 2.** IR features of CH$_3$NH$_2$ in the different ice mixtures. For pure CH$_3$NH$_2$ ice, data agree with Darig et al. (1968); Zhu et al. (2019). For CH$_3$NH$_2$:Xe and CH$_3$NH$_2$:H$_2$O, no reference was found in the literature.

| Vibration mode | CH$_3$NH$_2$:Xe | CH$_3$NH$_2$ | CH$_3$NH$_2$:H$_2$O |
|----------------|-----------------|--------------|---------------------|
| NH$_2$ antisymmetric str. | -              | 3347         | 3354                |
| NH$_2$ symmetric str. | -               | 3286         | 3286                |
| H bonding | -               | 3182         | 3186                |
| CH$_3$ degenerate str. | 2970,2942     | 2968,2944    | 2968,2945            |
| CH$_3$ degenerate str. | 2882, 2861    | 2884, 2864   | 2919, 2878            |
| CH$_3$ symmetric str. | 2805, 2766    | 2808, 2793   | 2809, 2792            |
| NH$_2$ scissoring | 1622           | 1613         | 1612                |
| CH$_3$ degenerate bend | 1472, 1455   | 1476, 1457   | 1478, 1457            |
| NH$_2$ twist | -               | 1418         | 1421                |
|                  | -               | 1337         | -                   |
| CH$_3$ rocking | -               | 1161         | 1166                |
| C-N str. | 1045             | 1041         | 1040                |
| NH$_2$ wagging | -               | 995          | -                   |

str. = stretching; bend. = bending

**Figure 5.** UV spectra of pure CH$_3$NH$_2$ (black trace), CH$_3$NH$_2$:Xe (red trace), and CH$_3$NH$_2$:H$_2$O (blue trace) ice samples. Note that Xe atoms dominate the UV absorption in the CH$_3$NH$_2$:Xe ice sample, see text.
Fast changes between the larger and the lower H₂ signal are produced when the UV lamp is turned on and off along the irradiation period. Horizontal lines are drawn to guide the eye. Note that the y-axis is in logarithmic scale.

Figure 6. H₂ signal recorded during irradiation of CH₃NH₂ pure (Exp. 2), CH₃NH₂: Xe (Exp. 5), and CH₃NH₂H₂O (Exp. 7) ice samples. H₂ signal from irradiation of CH₄ ice is shown for comparison (Carrascosa et al. 2020).

3.4 UV irradiation of CH₃NH₂: Xe ice samples and CH₃NH₂H₂O ice samples. Photoproduts formation.

IR spectra measured during the irradiation period of CH₃NH₂, CH₃NH₂: Xe and CH₃NH₂H₂O ice samples (Exps. 2, 6 and 7) are shown in Fig. 8, and Table 3 exhibits the assignment of the IR bands. Fig. 9 summarizes the different species arising from UV irradiation at 8 K. The formation of different species at low temperature is presented starting from the simplest ice sample, CH₃NH₂: Xe to the most astrophysically relevant one, CH₃NH₂H₂O. Pure CH₃NH₂ ice sample served as an intermediate step.

3.4.1 UV irradiation of CH₃NH₂: Xe ice samples

IR spectra during the irradiation of CH₃NH₂: Xe ice samples is shown in Fig. 8a. Matrix isolation of methylamine enhances the detection of radical species. NH₂ was detected by its IR feature at 1500 cm⁻¹, in line with the position of this radical formed from UV irradiation of NH₃ (Martín-Doménech et al. 2018). The large hydrogen subtraction hampers the formation of hydrogenated species. NH₃ was, in fact, not detected at 8 K, although the low N-H stretching band strength at low temperature may hinder its detection. CH₃, which can be formed by direct decomposition of methylamine molecules at wavelengths shorter than 388 nm (Gardner & Mcnesby 1982), was detected as a minor photoproducit. Furthermore, CH₂ radicals present in the CH₃NH₂: Xe ice mixture can only react with H-radicals of H₂ molecules, as they are the only species able to move fast enough at 8 K, thus enhancing CH₄ formation.

According to Bossa et al. (2012), CH₃NH⁻ and CH₂NH₂ radicals are also expected to form directly from methylamine upon UV irradiation. The former was detected by its 1025 cm⁻¹ IR feature, while the latter was not identified, probably as a consequence of its lower formation rate (Bossa et al. 2012). Additionally, even if CH₂NH₂ is formed, it tends to react, either with CH₃ radicals to form ethylamine, CH₃CH₂NH₂, or loosing a hydrogen atom to form CH₂NH. Nitrogen atoms, however, can stabilize the electron, thus reducing the reactivity of R-NH₃ radicals.

UV irradiation of matrix isolated methylamine led, preferentially, to the formation of CH₃NH molecules by hydrogen subtraction from methylamine. As reported by Gardner & Mcnesby (1982), the dissociation of CH₃NH₂ molecules producing CH₃NH and H₂ is the most energetically favoured process concerning UV irradiation of methylamine in the gas phase. Alternatively, CH₃NH can be obtained from hydrogen elimination from CH₃NH- and -CH₂NH radicals. Methylenimine was detected through its IR features at 3193, 3160, 2219, 1651, 1113, and 1059 cm⁻¹. CH₂NH molecules can also undergo hydrogen subtraction. Thus, HCN...
HNC molecules, which are far less stable than its HCN isomer, were also detected by its IR feature at 3576 cm\(^{-1}\) (Fig. 8a). As reported by Milligan & Jacox (1967), HNC formation is enhanced in a matrix environment. The absorption at 2084 cm\(^{-1}\) is indicative of the presence of cyanide, CN\(^{-}\), species, although it could not be attributed to any specific salt.

As depicted in Table 3, UV irradiation of CH\(_3\)NH\(_2\) ice samples promotes the formation of small species, which can be produced from just one parent CH\(_3\)NH\(_2\) molecule. CH\(_3\)CN, tentatively detected in isolated methylamine UV irradiation, was the only species that involves reaction of two CH\(_3\)NH\(_2\) molecules. Indeed, CH\(_3\)CN was only detected in an advanced stage of the irradiation period, suggesting the reduced mobility of radicals at 8 K.

### 3.4.2 UV irradiation of pure CH\(_3\)NH\(_2\) ice samples

IR spectra of a pure CH\(_3\)NH\(_2\) ice sample is represented in Fig. 8b. CH\(_3\)NH\(_2\), CH\(_3\)NH\(_2\), CH\(_3\) and NH\(_2\) radicals can be directly obtained from UV irradiation of methylamine (Bossa et al. 2012). In the pure CH\(_3\)NH\(_2\) ice sample, radicals bearing NH groups appear as broad bands at both sides of the N-H stretching region of the IR spectrum. In line with Martín-Doménech et al. (2018), radicals appear readily within the irradiation period, but they are readily consumed, keeping a constant formation and destruction rate for longer irradiation times.

The lower hydrogen diffusion in the pure CH\(_3\)NH\(_2\) ice, compared to matrix isolated methylamine, is expected to produce a larger fraction of hydrogenated species, such as NH\(_3\) and CH\(_4\). NH\(_3\) and CH\(_4\) were, in fact, detected in CH\(_3\)NH\(_2\) ice samples (see Table 3 and Fig. 8b). Martín-Doménech et al. (2018) demonstrated that NH\(_2\) radicals can remain in a pure NH\(_3\) ice until thermal energy enables chemical reactions. Indeed, NH\(_2\) radicals can only react with hydrogen atoms at 8 K to form NH\(_3\) molecules in methylamine ice, explaining the plateau reached in NH\(_2\) formation in Martín-Doménech et al. (2018). The low absorbance at 1303 and 3013 cm\(^{-1}\) is indicative of a minor formation rate of CH\(_4\) in pure CH\(_3\)NH\(_2\) ice samples. Irradiation of pure methane ice also produces CH\(_3\) radicals, which react very readily to form small hydrocarbons and hydrogenated amorphous carbon, even at 8 K (Carrascosa et al. 2020, and references therein). As it will be explained later on, IR spectra from pure CH\(_3\)NH\(_2\) ice displays ethylamine (CH\(_3\)CH\(_2\)NH\(_2\)), ethylenimine (CH\(_3\)CHN\(_2\)) and acetonitrile (CH\(_3\)CN) IR features. The formation of many CH\(_3\)- bearing species suggests that CH\(_3\) radicals are more prone to react with other species rather than H- radicals, as it occurs in the CH\(_4\) ice UV irradiation experiments (Carrascosa et al. 2020). Despite the fast formation of ethane and propane, these authors showed that the reaction CH\(_3\)+ H\(\rightarrow\) CH\(_4\) is not efficient, at least in the ice surface. As a consequence, the interaction of H- radicals
in CH$_4$ ice is small and H$_2$ desorption is 100 times larger in a pure CH$_4$ ice than the one found in CH$_3$NH$_2$ ice in our experiments for similar ice thicknesses (Fig. 6).

CH$_3$: and CH$_2$NH radicals will react leading to an efficient formation of ethylamine. Ethylamine IR features overlap with those of methylamine. Yet, the relative intensity between the symmetric and the antisymmetric N-H stretching modes (Hashiguchi et al. 1984; Danger et al. 2011a) allowed us to infer its presence. The difference spectra between the irradiated and the non-irradiated methylamine ice (shown in Fig. 10) confirmed the presence of ethylamine by its IR features at 3308, 3219, 3104 and 1095 cm$^{-1}$ (see Table 3).

CH$_2$NH was tentatively detected in pure CH$_3$NH$_2$ ice by its IR bands at 1119 and 1068 cm$^{-1}$. The presence of other molecules and radicals around CH$_3$NH$_2$ molecules enhance its reactivity, lowering its abundance with respect to matrix isolated methylamine. Methylamine reaction with CH$_3$: radicals produces ethylamine (CH$_3$CHNH$_2$), which was detected by its IR features at 1438 cm$^{-1}$ and 1668 cm$^{-1}$. Dehydrogenation of CH$_3$CHNH$_2$ molecules produces CH$_3$CN, responsible of the IR band at 2254 cm$^{-1}$. Dehydrogenation of CH$_3$NH$_2$ molecules produces hydrogen cyanide, HCN. HCN molecules were not detected in pure CH$_3$NH$_2$ ice samples, but CN$^-$ anions were. As reported by Bossa et al. (2012), HCN and surrounding CH$_3$NH$_2$ molecules give rise to methylammonium cyanide [CH$_3$NH$_2$CN$^-$] salt, detected in the IR spectra by the IR features at 2654 and 2553 cm$^{-1}$ from the cation and 2069 cm$^{-1}$ from the anion (see Table 3 and Fig. 8b). This reaction is favoured by the formation of CH$_3$NH$_2^+$ cation (Zhang et al. 2017), which explains the lower formation rate of CN$^-$ in the CH$_3$NH$_2$:Xe experiment. The formation of other cyanides, however, cannot be excluded, with IR bands overlapping in the 2069 cm$^{-1}$ feature.

When referring to pure methylamine ice, we assume that some H$_2$O molecules ($\approx$ 5%) are present, due to the deposition process, as explained in Sect. 2. Although CH$_3$NH$_2$ vapour pressure is higher than that of H$_2$O, it is not possible to get rid of all the H$_2$O. Therefore, some oxygenated compounds were detected from UV irradiation of CH$_3$NH$_2$ ice. Chemical reactions between CH$_3$NH and OH radicals (formed from UV irradiation of H$_2$O molecules) are shown in Fig. 11. The nucleophylic attack of an OH radical over a carbon atom in a methylamine molecule leads to the formation of aminomethanol as an intermediate. Formamide, HCONH$_2$, formation has been reported at low temperature during UV irradiation of aminomethanol ice through radical reactions (Bossard et al. 2009a). Additionally, the nucleophylic attack by the alcohol group over the aminomethanol intermediate results in formamide formation in a barrier-less reaction, as reported by Vazart et al. (2016). Martín-Doménech et al. (2020) reported the formation of formamide from radical reaction between NH$_2$ and HCO radicals, although the relatively low formation rate of these radicals in CH$_3$NH$_2$:H$_2$O ice samples suggests a negligible formation through this mechanism in our experiments. Formamide was identified by its 1386 cm$^{-1}$ and 1635 cm$^{-1}$ IR features in Fig. 8b and Table 3 (note that the 1635 cm$^{-1}$ band is observed as a contribution to the left shoulder of the prominent band around 1610 cm$^{-1}$). These features display a weak intensity but they were highly reproducible in our experiments. As shown in Fig. 11, elimination of the amino group during the second nucleophytic attack results in formaldehyde, H$_2$CO, detected in the IR spectrum.

![Figure 8](image_url) Evolution of the IR spectra during the irradiation of three different ice samples. Vertical lines indicate the most relevant changes. The vibrational and molecular assignments are provided in Table 3.

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by its C=O stretching absorption at 1718 cm$^{-1}$, and ammonia formation (Layer 1963). Furthermore, dehydration of formamide produces HNCO, which readily undergoes hydrogen subtraction in presence of CH$_3$NH$_2$ to produce OCN$^-$ anions, detected by its main IR feature at 2156 cm$^{-1}$, and CH$_3$NH$_3^+$ cations. The relatively large band strengths of oxygenated compounds facilitate their detection, even when H$_2$O is a minor compound in the ice sample.

### 3.4.3 UV irradiation of pure CH$_3$NH$_2$:H$_2$O ice samples

The presence of methylamine was inferred in comet 67P/Churyumov-Gerasimenko and this species was detected in the gas phase toward molecular clouds and hot cores, see Sect. 1 (Goessmann et al. 2015). Pure methylamine ice, however, is not a good analog of astrophysical ices. Thus, more astrophysically realistic H$_2$O:CH$_3$NH$_2$ ice experiments were performed. The understanding of the processes in CH$_3$NH$_2$:Xe and pure CH$_3$NH$_2$ ice samples was, however, found to be crucial to understand the processes going on in this binary ice mixture.

CH$_3$NH$_2$:H$_2$O ice mixtures were prepared at different ratios between the components (see Table 1). Fig. 8c shows the evolution of the IR spectra of Exp. 6, where a column density of 3.9x10$^{17}$ cm$^{-2}$ and 3.5x10$^{17}$ cm$^{-2}$ for CH$_3$NH$_2$ and H$_2$O, respectively, was measured.

The presence of OH groups raises the reactivity of radicals within the CH$_3$NH$_2$:H$_2$O ice sample, in comparison to pure CH$_3$NH$_2$ and CH$_3$NH$_2$:Xe, preventing from the detection of radical species. The formation of ethylamine, CH$_3$CH$_2$NH$_2$ (IR bands at 3323, 3236 and 3121 cm$^{-1}$) is indicative of the presence of CH$_3$NH$_2$ and CH$_3$ radicals, as it occurs in the pure CH$_3$NH$_2$ ice sample. IR bands at 3005 and 1306 cm$^{-1}$ (CH$_4$) and 3405 and 1076 cm$^{-1}$ (NH$_3$), confirm the enhanced formation of these
species when hydrogen bonds are established.

Although the highly reactive CH$_2$NH was not identified, its presence as an intermediate species can be inferred by the presence of IR bands at 1636 and 1384 cm$^{-1}$ (related to HCN, which are enhanced when compared to pure CH$_3$N$_2$ ice samples), 1679 and 1142 cm$^{-1}$ (CH$_3$CNH), and 2830, 1729 and 1493 cm$^{-1}$ (H$_2$CO). Dehydrogenation of CH$_2$NH produces HCN. HCN was not identified in CH$_3$N$_2$-H$_2$O ice mixtures. HCN tends to react, producing CN$^-$ and OCN$^-$ species, which were identified by their absorptions at 2080 and 2162 cm$^{-1}$, respectively. CH$_3$NH$_2$ molecules can accept hydrogen atoms from HCN and HCONH$_2$ to produce the corresponding methylanmonium salts ([CH$_3$NH$_3^+$ CN$^-$] and [CH$_3$NH$_3^+$ OCN$^-$]). IR bands at 2645 and 2552 cm$^{-1}$ are indicative of the presence of CH$_3$NH$_3^+$. As it could be expected, IR spectra shown in Fig. 8b and Fig. 8c show that the presence of H$_2$O diminishes CH$_3$CN and CH$_3$CH$_2$NH$_2$ formation, while the formation of oxygenated compounds, such as OCN$^-$ and HCONH$_2$ is enhanced.

3.5 Irradiation of H$_2$O:CH$_3$OH:NH$_3$ ice analogs

We performed another experiment for comparison of the residue spectra obtained from methylamine-bearing ices with the better known residue made by irradiation and warm-up of the H$_2$O:CH$_3$OH:NH$_3$ (20:1:1) mixtures. This experiment was discussed in previous works (i.e. Bernstein et al. 1995; Muñoz Caro & Schutte 2003), and in this work, we only focus on the residue. This experiment served to check the formation of a "classical" residue under the UHV conditions of ISAC. The IR spectrum of this residue, presented in Fig. 16, is similar to the one reported in previous works.

3.6 Synthesis of large organics during warming up of UV irradiated CH$_3$N$_2$ ice samples.

The reduced mobility of most species at the low temperatures present in interstellar ice mantles (10-20 K), and reproduced in our experiments, inhibits the formation of large species prior to the warm-up phase. Furthermore, the relatively low column density values of methylamine ices from Exps. 2, 6 and 7 (see Table 1) prevented us from the detection of larger organic molecules. The irradiation of thicker methylamine ices gives us the possibility to detect larger species with our IR spectrometer. Fig. 12 shows IR spectra recorded after thermal desorption of methylamine molecules, from 180 K to 300 K. Bands located at 3345 and 3321 cm$^{-1}$ are related to the symmetric and antisymmetric modes of NH$_2$ groups, that is, primary amines, at 180 K. As the temperature increases, both vibration modes are merged, becoming indistinguishable above 240 K. The same trend is observed for CH$_3$ groups, as the band at 2948 cm$^{-1}$ dissappears at the same temperature. NH$_2$ and CH$_3$ groups can be only bonded to one group, in other words, they are located at the end of the molecules or in branched species. The absence of these groups at larger temperatures is originated by two processes: thermal desorption of species to the gas phase, and the formation of larger chains and cyclic compounds that are refractory at those temperatures. Bands located in the 1575-1625 cm$^{-1}$ range, which remain at 300 K, may be indicative of the presence of cyclic aromatic compounds.

Three different methylamine dimers can be formed from UV irradiation of methylamine, CH$_3$-NH-CH$_2$-NH$_2$ (Dimer A), CH$_3$-NH-NH-CH$_3$ (Dimer B), and NH$_2$-CH$_2$-CH$_2$-NH$_2$ (Dimer C). The three dimers have the same molecular mass, hampering its unequivocal identification. Therefore, the most likely interpretation of the results is discussed in this work, although other species may contribute to the measured ion current of each of the $m/z$ values. Fig. 13 suggests the presence of the three dimers in Exp. 8. From 125 K, the ion current measured for $m/z$ = 58 and 59 could be related to the desorption of Dimer B. The presence of methyl groups at both ends decreases the capability of the central NH groups to form hydrogen bonds due to steric interactions, thus reducing their thermal desorption temperature. In fact, although the molecular mass of Dimer B doubles that of methylamine, the absence of hydrogen bonds in Dimer B determines the co-desorption of both species. It is not surprising that hydrogen bonds highly modify the intermolecular interactions. As an example the high desorption temperature of pure NH$_3$ ice, 95 K, compared to pure CH$_4$ ice, 40 K, is due to H bonds in NH$_3$ ice (e.g. Carrascosa et al. 2020; Martín-Doménech et al. 2018). Dimer C is expected to be formed preferentially over the other dimers via reaction NH$_2$CH$_2$ + NH$_2$CH$_2$ , as methyl groups are more reactive at low temperatures than NH groups (see Sect. 3.4). The two NH$_2$ groups at both ends enhances the formation of hydrogen bonds, thus retarding thermal desorption of Dimer C to 211 K. Furthermore, the mass spectra of Dimer B and Dimer C are compared in Fig. 15 to the one measured for the 211 K peak with our QMS. Its profile highly differs from Dimer B, in particular the low intensities of $m/z$ = 45 and 60. On the contrary, the measured mass spectrum is more similar to Dimer C. It is not clear if the differences observed between the experimental data and the reported mass spectrum of Dimer C are due to variation in the fragmentation pattern due to the use of different instruments (i.e. NIST database versus our QMS), or whether there is contribution
Absorbance of a codesorbing species in our experiment, such as molecules is therefore indicative of a previous formation of reaction between three methylenimine units. Desorption of TMT was observed at 290 K (see Fig. 13). TMT is likely formed from the methyl groups. The presence/absence of water determines the preferential formation of formamide and formaldehyde, or HMT, respectively. Formamide, HCONH₂, and formaldehyde, H₂CO, can be formed at low temperature from radicalary reactions induced by UV photons (Bossa et al. 2009b).

As it will be discussed later on, thermal desorption of TMT was observed at 290 K (see Fig. 13). TMT is likely formed from the reaction between three methylenimine units. Desorption of TMT molecules is therefore indicative of a previous formation of Dimer A, and its subsequent reaction to form the more stable 6-member cyclic TMT. Reactivity of the three dimers is then explained by the preferential reactivity of CH₃ radicals when compared to NH₃ radicals. Reactivity between two CH₂ groups of NH₂CH₂ radicals produces Dimer C. However, Dimer C cannot further react, as both ends contain NH₂ groups. Dimer B formation is hampered, as it requires two NH groups to react and they react at temperatures higher than CH₃ radicals. Dimer A is thus the only dimer able to form at relatively high ratios, and to further react to produce larger species.

TPD data in Fig. 13 suggests the formation of TMT molecules and its thermal desorption at 290 K. Signals recorded for ratios larger than 87 did not show any increase at 290 K. Thus, $\frac{m}{z} = 87$, should be the molecular ion (M⁺), which coincides with the molecular mass of TMT. Despite the low ion current measured for ratios in right panel of Fig. 13, the absence of any signal at 290 K for larger $\frac{m}{z}$ ratios (e. g. $\frac{m}{z} = 129$, shown in Fig. 13), together with the blank experiment (Fig. 14), ensure the reliability of the measured ion current. The most intense fragment is obtained for $\frac{m}{z} = 86$ (M⁺-1), followed by $\frac{m}{z} = 85$ (M⁺-2). Vinogradoff et al. (2012) and references therein reported polymerization of CH₂-NH molecules to produce polymethylenimine (PMI, (-CH₂-NH₃⁻)). No IR bands related to PMI, however, were detected in our experiments. Instead, the molecular ion, $\frac{m}{z} = 87$, suggests a cyclic species formed by three CH₂-NH units. A linear molecule formed from CH₂NH polymerization will imply very reactive CH₂ and NH ends, and such molecules will further polymerize, or incorporate CH₃/NH₂ ends, thus changing the mass of the molecular ion. Finally, the presence of $\frac{m}{z} = 58$, with no contribution of $\frac{m}{z} = 59$ and 60, further suggest the presence of TMT. The loss of a -CH₂-NH⁻ fragment of TMT will give rise to $\frac{m}{z} = 58$, but no $\frac{m}{z} = 59$ or 60 fragments can be easily obtained from fragmentation of TMT molecules.

The presence of CH₂ and NH groups at room temperature and the absence of CH₃ (between 3000 - 2948 cm⁻¹) and NH₂ (only one band is observed between 3450 - 3300 cm⁻¹), while NH₂ groups would provide the symmetric and antisymmetric N-H stretching modes) absorption features at this temperature, as shown in Fig. 12, suggests that Dimer A reacts to form larger species. The addition of an aminomethyl, NH₂CH₃, group produces TMT. The latter

Figure 11. Chemical reactions of methylenimine molecules with and without surrounding OH radicals, formed from H₂O dissociation under UV photons.

Figure 12. Evolution of the IR spectrum during warming up of a pure CH₃NH₂ ice sample (Exp. 4).
Figure 13. Warming up of an irradiated CH$_3$NH$_2$ ice sample. Left: recorded QMS signal for $m/z = 58$, 59, 60, 61 and 62. These $m/z$ fragments are representative of methylamine dimers. The molecular ion of non-covalent and covalent methylamine dimers has $m/z = 62$ and 60, respectively. Right: recorded QMS signal for molecular ion of TMT ($m/z = 87$) as well as its corresponding M-1 and M-2 fragments (86 and 85, see text). No molecule is expected to desorb with a $m/z$ ratio of 129, it was used for reference.

Figure 14. Warming up of a pure CH$_3$NH$_2$ ice without any irradiation period. Left: recorded QMS signal for $m/z = 58$–62, representing $m/z$ ratios for methylamine dimers, being the non-covalent dimer ($m/z = 62$) the most abundant species. Right: recorded QMS signal for $m/z = 85$, 86, 87 in the same experiment, where no TMT formation is expected, in contrast to Fig. 13.

was observed to co-desorb with Dimer C at 212 K, but also at 290 K, by its molecular mass fragment, $m/z = 87$, 86 and 85 (see Fig. 13).

To further confirm the formation of the dimers and larger species upon UV irradiation, the warming up of a non-irradiated methylamine ice is shown in Fig. 14. The ion current measured for $m/z = 58$–62 is different to the one recorded for irradiated methylamine. Covalent dimers have a $m/z = 60$, therefore, their fragmentation give rise to $m/z$ ratios below or equal to 60. From Fig. 14, it can be concluded that $m/z = 61$ and 62 were present during the desorption with negligible contribution from $m/z = 58$, 59, and 60. The most likely explanation is that the absence of radical species prevents the formation of covalent dimers, but hydrogen bond interaction will hold pairs of molecules together, forming non-covalent (CH$_3$NH$_2$)$_2$ dimers.

Possible formation of HMT in CH$_3$NH$_2$ ice samples was also explored. Fig. 16 shows the IR spectrum of a CH$_3$NH$_2$ ice sample at 300 K. Comparison with the experimental HMT spectrum suggests that HMT is formed in low H$_2$O containing CH$_3$NH$_2$ ice samples. The organic residue remaining from the H$_2$O:CH$_3$OH:NH$_3$ ice sample, shown in Fig. 16, displays more intense bands which can be related to HMT (816, 1005, 1234, 1458, and 2868 cm$^{-1}$), reinforcing the formation of HMT through the mechanism show in Fig. 1. As shown in Fig. 17, 1004 and 1234 cm$^{-1}$ IR features can be detected from 230 K, confirming that TMT can react to
form HMT at this relatively low temperature, what may explain the absence of IR bands related to TMT, as compared to the theoretical spectrum in Fig. 2. Increasing temperatures, as explained above, cause the thermal desorption of remaining TMT molecules, while HMT remains in the refractory residue.

No HMT formation was observed in CH$_3$NH$_2$:H$_2$O ice samples. The presence of H$_2$O molecules drives the chemistry of methylamine towards the formation of oxygenated compounds. Water molecules inhibit polymerization of methylenimine, CH$_2$NH, see Fig. 11. Instead, CH$_3$NH is hydrolyzed to form formamide and formaldehyde. CH$_3$OH:H$_2$O:NH$_3$ ice samples, however, showed an increased HMT formation upon addition of water. H$_2$CO is very efficiently formed from CH$_3$OH molecules, and H$_2$O is required to avoid formaldehyde polymerization. Thus, the presence of H$_2$O favours, in this case, condensation reaction between H$_2$CO and NH$_3$ to produce CH$_2$NH, which cannot be obtained by other routes.

4 CONCLUSIONS

The reactivity of CH$_3$NH$_2$ ice under interstellar conditions was studied in the pure form, in an inert matrix (Xe), and mixed with H$_2$O in the ice, to mimic a more realistic astrophysical scenario. Methylamine-bearing ices were grown at low temperature (8 K) under UHV, and submitted to UV irradiation. From this work, several conclusions can be extracted:

- Methylamine thermal desorption is strongly dependent on its environment in the ice. The intermolecular forces established between methylamine and other species may cause thermal desorption to shift from 106 K to more than 150 K.

- The higher destruction rate of methylamine in an inert matrix suggests that a larger fraction of radicals can recombine in pure CH$_3$NH$_2$ ice to reform the parent methylamine molecule. Xe isolated CH$_3$NH$_2$, however, does not trap hydrogen atoms, preventing reformation of CH$_3$NH$_2$ molecules.

- H$_2$ molecules were not found to desorb when hydrogen bonds are established. Therefore, CH$_3$NH$_2$ and CH$_3$NH$_2$:H$_2$O ice samples showed lower H$_2$ subtraction compared to isolated CH$_3$NH$_2$ molecules in the CH$_3$NH$_2$:Xe ice mixture. Irradiation of
pure CH$_4$ ice samples, which cannot form hydrogen bonds, showed an ion current for H$_2$ molecules 100 times higher than the one measured in irradiated CH$_3$NH$_2$ pure ice.

- The retention of hydrogen within the ice samples leads to the formation of hydrogenated compounds in CH$_3$NH$_2$ and CH$_3$NH$_2$-H$_2$O ice samples over matrix isolated CH$_3$NH$_2$-Xe ice sample.

- As suggested by, e.g., Martín-Doménech et al. (2018) and Carrascosa et al. (2020), CH$_2$ radicals are more reactive at low temperatures than NH$_2$ radicals. As a result, CH$_2$-bearing compounds are abundant in the irradiated ice samples. CH$_3$CHNH$_2$, CH$_3$CN, CH$_3$CH$_2$NH$_2$ were detected in irradiated CH$_3$NH$_2$ ice samples.

- Oxygenated compounds usually exhibit larger IR band strengths, facilitating their detection. OCN$^-$, H$_2$CO and HCONH$_2$ were also detected in the IR spectra of the CH$_3$NH$_2$-H$_2$O ice mixture.

- At increasingly higher temperatures, the higher mobility of radicals enhances the formation of larger species. The formation of the three possible methylamine dimers (CH$_3$NHNHCH$_3$, NH$_2$CH$_2$CH$_2$NH$_2$ and CH$_3$NHCH$_2$NH$_2$) was discussed. NH$_2$CH$_2$CH$_2$NH$_2$ was found to be the most favoured one, followed by CH$_3$NHCH$_2$NH$_2$. TPD experiments showed the formation of the three dimers, desorbing around 140 K, 210 K and 244 K.

- Furthermore, comparing irradiated and non-irradiated methylamine ices, it was found that covalent dimers are obtained from UV-irradiation, and non-covalent (CH$_3$NH)$_2$ dimers are present even without any irradiation period.

- TMT was detected by thermal codesorption with NH$_2$CH$_2$CH$_2$NH$_2$ and pure thermal desorption at 290 K. The presence of TMT and the relatively low abundance of CH$_3$NHCH$_2$NH$_2$ suggests that TMT may be formed from the reaction between this dimer and an aminomethyl (CH$_2$NH$_2$) species.

- The absence of IR features that could be related to TMT suggest the rapid reaction of TMT molecules. Indeed, the formation of HMT was detected in UV irradiated CH$_3$NH$_2$-bearing ices at 230 K, long before HMT formation in the 'classical' H$_2$O:CH$_3$OH:NH$_3$ ice mixture, where HMT synthesis takes place near room temperature (Muñoz Caro & Schutte 2003; Vinogradoff et al. 2012).

- The addition of H$_2$O molecules to CH$_3$NH$_2$ inhibits HMT formation. Water molecules react with methylenimine, driving the chemistry towards oxygenated compounds, such as formamide and formaldehyde. On the contrary, CH$_3$OH:CH$_3$OH:CH$_3$NH$_2$ ice mixtures require the presence of water molecules to prevent formaldehyde polymerization, enhancing the formation of HMT. Therefore, depending on the ice composition, water molecules play a different role regarding HMT formation.

5 ASTROPHYSICAL IMPLICATIONS

The UV absorption cross section of CH$_3$NH$_2$ ice within the 120-180 nm range was reported in this work (see Fig. 5), measuring a value of 5.6±0.8×10$^{-18}$ molecule cm$^{-2}$ for pure CH$_3$NH$_2$ ice. The UV absorption spectrum makes it possible to calculate the photon energy absorbed by methylamine ice which can be incorporated into computational models to improve the accuracy of the simulations.

CH$_3$NH$_2$ is of particular interest in astrochemistry, as it contains a C-N bond, which is present in most biological molecules such as amino acids, DNA, or heterocyclic compounds. The first detection of methylamine in the gas phase of the interstellar medium by Kaifu et al. (1974) opened the possibility to include methylamine in solid phase ice models. Experimental simulations including methylamine have shown its potential to give rise to COMs (Holm et al. 2005; Bossa et al. 2009b; Lee et al. 2009; Vinogradoff et al. 2013). Vinogradoff et al. (2012) and references therein studied the formation mechanism of HMT and complex mixtures containing methylamine. This work focuses on the reactivity of pure methylamine ice at low temperature exposed to UV irradiation, as a primary step to understand its chemistry toward the formation of N-heterocycles, in particular TMT and HMT. The addition of water molecules approaches to a more realistic astrophysical scenario of ice mantle photoprocessing followed by warm-up.

Several COMs were formed (see Table 3). Among them, formamide, HCONH$_2$, is one of the most studied ones due to its prebiotic potential to form a full variety of species which are known to be present in our metabolism (Saladino et al. 2012). The addition of H$_2$O to the ice sample enhances the formation of HCONH$_2$, which was first detected in the ISM in Sgr B2 molecular cloud (Rubin et al. 1971), and later on in 67P/Churyumov-Gerasimenko comet during the Rosetta mission (Goesmann et al. 2015; Altwegg et al. 2017). H$_2$O molecules, as it can be derived from Fig. 7, lead to a large overall dissociation of methylamine molecules, producing a more complex chemistry.

Vinogradoff et al. (2012) reported the formation mechanism of HMT starting from a ternary H$_2$CO-NH$_3$:HCOOH ice mixture. They found evidence for the formation of the protonated form of TMT (TMT$^+$) as an intermediate species during HMT synthesis. They stated that HCOOH is crucial to stabilize CH$_3$NH allowing its presence at larger temperatures, where TMT can be thermally formed. The detection of TMT in pure CH$_3$NH$_2$ experiments, and the absence of HMT formation suggest that a complex synthesis is required to form HMT, in agreement with previous works (Vinogradoff et al. 2012, and references therein). Furthermore, this study deeps in the formation of TMT, which can lead to the synthesis of other N-heterocycles under astrophysically relevant scenarios, similar to those observed from H$_2$O:CH$_3$OH:CO:NH$_3$ ice mixtures (see, for example Meierhenrich et al. 2005; Oba et al. 2019). Formaldehyde, H$_2$CO, which is negligible in our experiments, but efficiently formed from methanol, is required for the formation of more complex heterocycles (Muñoz Caro & Schutte 2003; Vinogradoff et al. 2012).

Even though methylamine is a minor component in the gas of the interstellar medium, after accretion on ice mantles or direct formation in the ice, thermal desorption of other species in hot
cores or warm protoplanetary disk regions can increase the relative abundance of methylamine in ice mantles. Indeed, prior to the thermal desorption of methylamine molecules, other species, such as CO, CH₄, NH₃, O₂, N₂ and CO₂, should have sublimated to the gas phase. Therefore, UV-irradiation and thermal processing of the ice mantles can increase the relative abundance of methylamine photoproducts, promoting chemical reactions between them which may lead to the formation of COMs following the synthetic pathways presented in this work.

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7 DATA AVAILABILITY

The data underlying this article will be shared on reasonable request to the corresponding authors.

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