A vacuum ultraviolet photoionization study on the formation of methanimine (CH$_2$NH) and ethylenediamine (NH$_2$CH$_2$CH$_2$NH$_2$) in low temperature interstellar model ices exposed to ionizing radiation†

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Methylamine (CH$_3$NH$_2$) and methanimine (CH$_2$NH) represent essential building blocks in the formation of amino acids in interstellar and cometary ices. In our study, by exploiting isomer selective detection of the reaction products via photoionization coupled with reflectron time of flight mass spectrometry (Re-TOF-MS), we elucidate the formation of methanimine and ethylenediamine (NH$_2$CH$_2$CH$_2$NH$_2$) in methylamine ices exposed to energetic electrons as a proxy for secondary electrons generated by energetic cosmic rays penetrating interstellar and cometary ices. Interestingly, the two products methanimine and ethylenediamine are isoelectronic to formaldehyde (H$_2$CO) and ethylene glycol (HOCH$_2$CH$_2$OH), respectively. Their formation has been confirmed in interstellar ice analogs consisting of methanol (CH$_3$OH) which is isoelectronic to methylamine. Both oxygen-bearing species formed in methanol have been detected in the interstellar medium (ISM), while for methanimine and ethylenediamine only methanimine has been identified so far. In comparison with the methanol ice products and our experimental findings, we predict that ethylenediamine should be detectable in these astronomical sources, where methylamine and methanimine are present.

1. Introduction

During the last few decades, the methanimine molecule (CH$_2$NH) has received considerable attention from the astrochemistry and the astronomy communities due to its role as a potential precursor in the abiotic formation of amino acids such as glycine (NH$_2$CH$_2$COOH) – the simplest amino acid$^{1,2}$ – in the interstellar medium (ISM). Although more than 80 amino acids were identified in carbonaceous chondrites like in the Murchison meteorite$^3$ and recently glycine in the comet 81P/Wild 2,$^4$ the understanding of their fundamental formation mechanisms is still in its infancy.$^5$–$^{10}$ Glycine, alanine (CH$_3$CH(NH$_2$)COOH), valine ([CH$_3$]$_2$CHCH(NH$_2$)COOH), serine (HOCH$_2$CH(NH$_2$)COOH), and aspartic acid (HOC(O)CH$_2$CH(NH$_2$)COOH) were identified via chromatography in the room temperature residues of irradiated interstellar ice analogues containing water (H$_2$O), ammonia (NH$_3$), methanol (CH$_3$OH), hydrogen cyanide (HCN), carbon monoxide (CO), and carbon dioxide (CO$_2$).$^{10,11}$ These results elucidated a radiation induced low temperature formation pathway toward glycine commencing with the decomposition of methylamine (CH$_3$NH$_2$) via production of CH$_2$NH$_2$ together with suprathermal hydrogen atoms. The latter react with CO$_2$ to form the hydroxycarbonyl radicals (HOCO), which then recombines with the aminomethyl radicals (CH$_2$NH$_2$) to form glycine. This pathway was also supported by quantum chemistry calculations.$^{14}$ Alternatively, Kaiser et al.$^{10}$ discussed a formation pathway toward glycine (NH$_2$CH$_2$COOH) via NH$_3$ and acetic acid (CH$_3$COOH) – the latter was previously detected in irradiated CO$_2$ and methane (CH$_4$) ices$^{15,16}$ – via radical – radical recombination of radiolytically generated amino (NH$_2$) and hydroxycarbonylmethyl radicals (CH$_3$COOH).

The CH$_2$NH molecule itself – also called formaldimine due to the isoelectronic structure with formaldehyde (H$_2$CO) – was first detected in the hot core Sagittarius B2 toward the galactic center through the 64 m radio telescope via the $^{1}$–$^{11}$ multiplet$^{17}$ with a column density of $3 \times 10^{14}$ cm$^{-2}$. Follow-up searches consolidate this finding$^{18-22}$ and confirmed the presence of CH$_2$NH in L183,$^{23}$ Orion-KL,$^{1,24}$ W51, Orion 3N, G34.3+0.15,$^1$
and G19.61-0.23,25 as well as in the circumstellar shell of IRC+10216.26 Methanimine was also detected in the ultraluminous infrared galaxy Arecibo ARP 220.27 In the solar system, the atmosphere of Saturn's moon Titan also reveals an abundance of CH$_2$NH as discovered by the Cassini T5 flyby.28 Furthermore, methanimine has been detected in dust samples collected by the Stardust mission4 and was recently also observed on the comet 67P/Churyumov-Gerasimenko.29 In summary, we can find CH$_2$NH in every environment in the interstellar medium which underlines its importance in the interstellar chemistry.

However, despite the potential importance of CH$_2$NH, the underlying formation pathways are still not resolved. In the gas phase, bimolecular neutral-neutral reactions of methylidyne (CH) with NH$_3$ have been proposed to synthesize CH$_2$NH along with atomic hydrogen (H).26 In laboratory experiments, Michael et al.30 detected traces of CH$_2$NH through photolysis of CH$_3$NH$_2$ by non-monochromatic ultra violet (UV) radiation around 220 nm. However, formation rates through these pathways are too low and cannot explain the observed fractional abundances of CH$_2$NH in the interstellar medium.23,31 For instance, toward the cold cloud L183, fractional abundances of CH$_2$NH were detected at a level of 8.1 × 10$^{-10}$,1,23 but astrochemical models predict fractional abundances about one to two orders of magnitude below the actual observations. Therefore, gas phase chemistry alone cannot account for the formation of interstellar CH$_2$NH, and critical production routes are still lacking.

An alternative source for CH$_2$NH can be found in formation routes in condensed matters, i.e. within interstellar ices containing NH$_3$ and CH$_4$ exposed to ionizing radiation. Here, methanimine has been detected tentatively in broad band ultraviolet (UV) irradiated interstellar model ices carrying CH$_4$ and NH$_3$.32,33 Photolysis of CH$_3$NH$_2$ ice has also been studied by Bossa et al.34 tentatively assigning CH$_2$NH via its symmetric C–H stretching vibration at 3144 cm$^{-1}$ appearing as a shoulder of the hydrogen-bonding mode of the CH$_3$NH$_2$ parent. Woon et al.14 discussed the formation of CH$_2$NH along with CH$_3$NH$_2$ via a sequential hydrogenation of HCN, which was confirmed experimentally by Theule et al.35 Kim et al.36 demonstrated that a radical-radical recombination between methyl (CH$_3$) and amide (NH$_3$) in CH$_3$–NH$_3$ bearing ices followed by radiolysis leads ultimately to HCN and CH$_3$NH$_2$ intermediates.

The aforementioned considerations revealed that an experimental elucidation of the synthetic pathways to CH$_2$NH in low temperature interstellar analog ices exposed to ionizing radiation is still in its infancy. Nevertheless, they provide a significant potential to account for the missing CH$_2$NH source in the ISM. Previously analytical techniques have been used to detect CH$_3$NH$_2$ via low temperature fourier transform infrared spectroscopy (FTIR) of the exposed ices.34 Additionally, quadrupole mass spectrometry (QMS) coupled with electron impact ionization has been used in that study to probe CH$_2$NH subliming in the post irradiation phase into the gas phase. These approaches hold significant complications. FTIR spectroscopy represents an ideal tool to investigate the processing and decay kinetics of ‘small’ molecules such as CO, H$_2$O, CH$_3$OH, CO$_2$, CH$_4$ and H$_2$CO, along with NH$_3$ – these molecules have been detected on interstellar grains. However, the ability of infrared spectroscopy to provide useful information for the detection of complex organics formed within the ices is quite limited. Infrared spectroscopy allows the identification of functional groups of organics. This information does not always identify individual molecules since the functional groups of, for instance, amines (R–NH$_3$) and imines (RHC═NH) portray similar group frequencies in the range of 1650 cm$^{-1}$ to 1500 cm$^{-1}$ and 3500 cm$^{-1}$ to 3300 cm$^{-1}$.37 Therefore, the exclusive assignment of a newly formed molecule based on infrared bands in an unknown mixture of organics is rarely scientifically sound. Using QMS coupled with electron impact ionization to ionize the subliming molecules of the irradiated ices during the temperature programmed desorption (TPD) exploits often an electron impact ionizer operating at 70 to 100 eV electron energy. This energy range does not only ionize molecules, but also results in a significant fragmentation of the parent ion. This might even result in the absence of the molecular parent ion. Furthermore, the fragment ions of structural isomers often overlap making it difficult to decipher or even to discriminate between structural isomers. The exploitation of soft ionization with low energy electrons of a few electron volt kinetic energy has a few advantages. However, a voltage drop across the filaments of typically 1.0 eV results in electrons with a relatively broad energy distribution thus making it difficult to selectively ionize structural isomers. Therefore, alternative analytical techniques are required to elucidate the formation of CH$_2$NH in low temperature interstellar ice analogues.

In this work, we use single photon ionization (PI) coupled with a reflection time-of-flight mass spectrometer (ReTOF-MS) to detect and to distinguish structural isomers of organic molecules subliming into the gas phase during temperature programmed desorption (TPD) after exposing the ices to ionizing radiation. In comparison to traditional electron impact ionization, PI-ReTOF-MS – utilizing photon energies close to the ionization threshold of the molecules – forms gas phase ions without significant internal energy and hence ideally without fragmentation.38,39 Likewise, employing distinct photon energies of 9.93 eV, 9.10 eV, and 8.17 eV as conducted in the present work, this technique can be utilized to selectively discriminate between the structural isomers of organic molecules as previously demonstrated.40 The present study demonstrates for the first time unambiguously that CH$_2$NH can be synthesized in low temperature (5 K) interstellar model ices of CH$_3$NH$_2$, when exposed to ionizing radiation such as energetic electrons. These energetic electrons simulate secondary electrons released during the passage of galactic cosmic rays through interstellar ices.41 The present laboratory simulation experiments mirror the exposure of the interstellar ices in molecular clouds to galactic cosmic rays during a life time of a molecular cloud of typically 10$^7$ years. Considering that molecular clouds constitute the nurseries of stars and planetary systems,42–44 the identification of CH$_2$NH along with ethylenediamine (NH$_2$CH$_2$CH$_2$NH$_2$) in our experiments suggests that these molecules may have been at least partially incorporated into our solar system from interstellar matter via circumstellar disks. Finally, considering the
isoelectronicity between CH$_3$NH$_2$ and CH$_3$OH, the formation pathways of the CH$_3$NH and NH$_2$CH$_2$CH$_2$NH$_2$ molecules are compared to those of the H$_2$CO and ethylene glycol (OHCH$_2$CH$_2$OH) in interstellar model ices exposed to ionizing radiation.$^{41,45-47}$

2. Experimental methods

The experiments were performed at the W. M. Keck Research Laboratory in Astrochemistry. The experimental setup consists of a contamination-free stainless steel ultra-high vacuum chamber (UHV) operating at a base pressure of a few 10$^{-11}$ Torr backed by turbo molecular pumps and dry oil-free scroll pumps. A polished polycrystalline silver mirror within the chamber is coupled to a cold finger cooled to 5.5 ± 0.1 K using a UHV compatible closed-cycle helium compressor (Sumitomo Heavy Industries, RDK-415E). The target can be moved in two degrees of freedom, translation in the vertical axis and rotation in the horizontal plane. Methylamine gas (Sigma Aldrich; 99%) was deposited onto the cooled silver wafer plane. Methylamine gas (Sigma Aldrich; 99%) was deposited during temperature programmed desorption (TPD) by heating the substrate from 5.5 K to 320 K at a rate of 0.5 K min$^{-1}$.

To detect the subliming molecules with the PI-ReTOF-MS, the neutral molecules are subliming during TPD and are ionized by pulsed vacuum ultraviolet (VUV) laser light close to 2 nm in front of the ice sample. The ions produced are mass-resolved and detected by a multichannel plate in a dual chevron configuration and then amplified by a fast preamplifier (Ortec 9305) and shaped with a 100 MHz discriminator. Finally, the spectra are recorded using a computer-controlled multichannel scaler (FAST ComTec, P7888-1E) with 4 ns bin width triggered at 30 Hz using a pulse delay generator (Quantum Composer, 9518) and 3600 sweeps per mass spectrum per 1 K increase in temperature during TPD.

VUV radiation is generated by difference-frequency mixing ($2\omega_1 - \omega_2$) in a noble gas (krypton (Kr) or xenon (Xe)) using two dye lasers (Sirah Lasertechnik, Model Cobra-Stretch, and Precision Scan) each pumped with a Nd:YAG laser (Spectra-Physics, Models PRO-270-30). The laser wavelengths were measured using a WaveMaster laser wavelength meter (COHERENT). In order to record and monitor VUV light, a detection system consisting of a Faraday cup and a diode calibrated by the national institute of standards and technology (NIST) is placed behind the detection region. This tunable VUV photon source allows soft-ionization of molecules with almost no fragmentation.$^{49}$ In this work, we used a mixture of Rhodamine 610 and Rhodamine 640 in the first dye laser, pumped with 532 nm, to generate 607 nm. For the second VUV energy of 9.93 eV (124.9 nm). For the second VUV energy of 9.10 eV, the first dye laser with Coumarin 450 as dye is pumped with 355 nm to achieve 445.132 nm which result in $\omega_1 = 222.566$ nm by frequency doubling for the photon resonance in xenon (Xe). The second dye laser with Rhodamine 610/Rhodamine 640 is pumped with 532 nm to generate 607 nm. The final photonization energy used is 8.17 eV (151.8 nm). It is generated by different frequency mixing of $\omega_1 = 249.628$ nm and $\omega_2 = 703$ nm in the xenon gas (Xe). The first dye laser is prepared with Coumarin 303 and pumped with 355 nm to achieve a wavelength of 499.265 nm before frequency doubling. The second wavelength is generated by the laser dye LDS 867 pumped with 532 nm. An overview of the photon ionization energies and their preparation can be found in Table 1. Calibration measurements for the ReTOF reveal a potential lowering of the ionization energies of the subliming molecules by up to 0.03 to 0.04 eV due to the static electric field induced Stark effect.$^{57}$ This has been confirmed by separate calibration experiments using molecules with known ionization potentials, such as methyl bromide (CH$_3$Br) (IE = 10.540 ± 0.003 eV$^{58}$), dibromochloromethane (CHBr$_2$Cl)
(IE = 10.59 ± 0.01 eV) and hexafluoropropylene (C₃F₆) (IE = 10.60 ± 0.03 eV).

3. Computational methods

The hybrid density functional B3LYP with the cc-pVTZ basis set was employed to optimize geometries and harmonic frequencies of the species and their cations. Afterwards, their coupled cluster CCSD(T)/cc-pVDZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ energies were calculated and extrapolated to complete basis set limits, CCSD(T)/CBS, with B3LYP/cc-pVTZ zero-point energy corrections. The energy difference between the ionic and neutral states with similar geometries gives the adiabatic ionization energy. The GAUSSIAN09 program was utilized in the electronic structure calculations. Table 2 presents the calculated adiabatic ionization energies for two sets of isomers CNH₃ and C₂N₂H₈ along with the relative energies of the structural isomers considered in this study and ionization energy values from the literature. A comparison between theoretical and experimental results as a benchmark calculation reveals that the calculations overestimate the ionization energies by 0.03 eV to 0.05 eV. Molecular geometries as well as vibrational modes for the CNH₃ and C₂N₂H₈ isomers are presented in the supplement material (Tables S2 and S3, ESI†).

4. Results

Fig. 1 presents the FTIR spectra of CH₃NH₂ before (black line) and after (red line) the irradiation for the high (3500–2700 cm⁻¹) and low (1700–800 cm⁻¹) energy regions. All absorptions can be attributed to CH₃NH₂ as presented by previous studies. Their assignments are compiled in Table 3. The region from 3400 to

### Table 1

<table>
<thead>
<tr>
<th>Parameter for the vacuum ultraviolet light generation used in the present experiments. The uncertainty for VUV photon energies is 0.01 eV</th>
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<tr>
<td>Photoionization energy (eV)</td>
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<tr>
<td>Flux (10¹¹ photons s⁻¹)</td>
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</tr>
<tr>
<td>ν₁</td>
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<tr>
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<td>Nonlinear medium</td>
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### Table 2

| Calculated adiabatic ionization energies (IE) and the relative energies (E_rel) of distinct CNH₃ and C₂N₂H₈ isomers. The ‘3’ superscript indicates a triplet state |
|-------------------------------|-----------------|-----------------|-----------------|
| Structure | Molecular formula | Species | IE (eV) a | E_rel (eV) b | Literature value IE, (eV) |
| CH₂NH | Methanimine | 9.94 | 0.00 | 9.88 ± 0.07 f |
| ³CH₂N | Methylimidogen | 12.00 | 2.34 |
| CHNH₂ | Aminomethylene | 8.22 | 1.54 |
| ³CHNH₂ | Aminomethylene | 10.94 | 3.01 |
| NH₂CH₂NHCH₃ | N-Methyl-methanediamine | 8.23 | 0.23 |
| NH₂CH₂CH₂NH₂ | Ethylenediamine | 8.27 | 0.00 | 8.42 ± 0.04 d |
| CH₂NHNHCH₃ | 1,2-Dimethylhydrazine | 7.18 | 1.28 | 7.8 ± 0.1 c |
| (CH₃)₂NNH₂ | 1,1-Dimethylhydrazine | 7.24 | 1.16 | 7.29 ± 0.05 f |

a Relative ionization potential by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in eV. b Relative energy by CCSD(T)/CBS with B3LYP/cc-pVTZ zero-point energy correction in eV. c Taken from Tarasenko et al., 1986. d Taken from Wei et al., 2006. e Taken from Dibeler et al., 1959. f Taken from Moet-Ner et al., 1984.
energies, features for the scissor mode (hydrogen bonding to the nitrogen electron lone pair. At lower
(ESI†), (25/C6)0.01 CH3NH2 molecules are destroyed per eV. Naturally, this value can only be considered as
the low irradiation dose of only 1.0 ± 0.2 eV molecule−1. The intensities of the CH3NH2 fundamental vibrations are reduced
compared to the unirradiated sample by 8 ± 1% (average decrease of each fundamental band area), revealing that 0.09 ± 0.01 CH3NH2
molecules eV−1 are reacting during the radiation exposure. In the region of 3000–3200 cm−1, a shoulder at 3140 cm−1 becomes visible.
This shoulder can be attributed tentatively to the antisymmetric C–H (νa) stretching mode of CH3NH2. A second shoulder can be found at 1635 cm−1 in the NH2 scissor mode (ν4). This feature might be attributed to the C–N double bond stretching of CH2NH (Table 3).
Further, new modes around 1650 cm−1, 1550 cm−1, and 1380 cm−1 (blue arrows) could be attributed to several possible functional
groups. Around 1650 cm−1, mostly C=C and C=N stretching vibrations can be found, while features around 1550 cm−1 are most
likely associated with the amine functional group νNH scissor or NH deformation. The features around 1380 cm−1 are typical for
alkane functional groups visible by CH deformation modes. The newly formed molecules consisting of C, N, and H can be attributed
to these features. However, due to the weak appearance and overlaps of functional groups for different molecules, it is
difficult to identify individual molecules. Taking into account the energy loss of the electrons while penetrating the ices (Table S1, ESI†), (25 ± 3) × 1015 CH3NH2 molecules are destroyed
during irradiation in an area of 1 cm2. If each destroyed molecule is converted to CH2NH, 0.09 ± 0.01 molecules of CH3NH are
formed per eV. Naturally, this value can only be considered as an upper limit for the CH2NH formation, since other molecules
are formed as well based on the observation of the aforementioned functional groups and the Re-TOF-MS data as discussed
below. In conclusion, the FTIR results show the preparation and processing of CH3NH2 ice. However only tentatively results
are found for the products formed.

Table 3  Infrared absorption features of CH3NH224 and CH2NH34

<table>
<thead>
<tr>
<th>Wavenumber (cm−1) from the literature</th>
<th>Wavenumber (cm−1) this study</th>
<th>Vibration mode</th>
<th>Assignment</th>
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<td>CH3NH2</td>
<td>3332</td>
<td>ν̂40</td>
<td>NH2 antisymmetric stretching</td>
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<tr>
<td></td>
<td>3360</td>
<td>ν̂5</td>
<td>NH2 symmetric stretching</td>
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<tr>
<td></td>
<td>3191</td>
<td>ν̂13</td>
<td>H bonding</td>
</tr>
<tr>
<td></td>
<td>2942</td>
<td>ν̂14</td>
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<td></td>
<td>1636</td>
<td>ν̂4</td>
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<td>1662</td>
<td>ν̂1</td>
<td>C–N stretching</td>
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</table>

This shoulder can be attributed tentatively to the antisymmetric C–H (νa) stretching mode of CH3NH2. A second shoulder can be found at 1635 cm−1 in the NH2 scissor mode (ν4).
Compared to FTIR, the PI-ReTOF-MS detection method is significantly more sensitive and can discriminate between structural isomers – information which hardly can be extracted by alternative techniques in astrophysical ice simulation experiments. The PI-ReTOF-MS data are compiled in Fig. 2 for distinct ionization energies of 9.93 eV, 9.10 eV, and 8.17 eV while the corresponding TPD graphs for selected m/z ratios critical to the present study are presented in Fig. 3. Fig. 2a and b represent the PI-ReTOF-MS data of the unirradiated (blank) and irradiated ices, respectively, recorded with the highest photon energy of 9.93 eV. The most intense signals in the control experiment and the irradiated ice sample appear at mass-to-charge ratios (m/z) of 30, 31, 32, and 33 in the temperature range from 100 K to 120 K. The most intense ion counts as presented in Fig. 3a can be attributed to the parent molecule CH3NH2 (CH3NH2; 31 amu; IE = 8.97 ± 0.02 eV).78,79 Since CH3NH2 has an ionization energy of 8.97 eV, it cannot be observed at a photon energy of 8.17 eV (Fig. 2d). For photon energies above 9 eV, the appearance of the ion at m/z = 30 could be assigned to CNH3+ (m/z = 30), which results from atomic hydrogen loss of CH3NH2 (CH3NH2; 31 amu). Furthermore, the ion counts at m/z = 32 can be explained by protonated CH2NH2 (CH2NH2+) and the naturally occurring 13C-substituted CH3NH2 (13CH3NH2); the protonated 13C-substituted CH3NH2 (13CH3NH2+) can be linked to m/z = 33. A noticeable smaller feature can be observed in the pristine and irradiated systems at m/z = 45 desorbing at the same temperature as CH3NH2. This signal can be attributed to ionized ethylamine (CH3CH2NH2) and/or dimethylamine (CH3NHCH3). These molecules have ionization energies of 8.9 eV and 8.2 eV (Table 4), respectively, and can be attributed to tracer impurities in the CH3NH2 gas (99%). Furthermore, the ion signal at m/z = 59 can be related to propylamine (CH3CH2CH2NH2), 2-propanamine ((CH3)2CHNH2), and/or n-methyl ethanamine (CH3CH2NHCH3) which have ionization energies of 8.78 eV, 8.72 eV, and 8.15 eV, respectively (Table 4).

After the irradiation, several new mass-to-charge ratios were observed, which were absent in the blank experiment. The TPD traces are presented in Fig. 3. Due to the simplicity of the ice, the resulting molecules after the irradiation can only be composed of three elements: hydrogen (H), nitrogen (N), and carbon (C). The new signal at m/z = 29 appearing between 106 K and 124 K can only be explained by four different isomers of CNH2: CH2NH, CHNH2, triplet methylimidogen (3CH3N), and triplet aminomethylene (3CHNH2) (Table 2). The latter two isomers have ionization energies well above 9.93 eV and cannot be detected in this study. Therefore, they can be ruled out as source for the trace of m/z = 29. Based on the ionization energies of 9.88 ± 0.07 eV for CH2NH and 8.22 ± 0.05 eV for CHNH2, the two isomers can be distinguished by tuning the photoionization energy between these two ionization energies. Fig. 3a presents the TPD spectrum of m/z = 29 at 9.93 eV and 9.10 eV photoionization energy. The strong clear peak at 120 K for 9.93 eV vanishes for 9.10 eV (Fig. 3a). Based on these findings, m/z = 29 can be assigned to CH2NH. Therefore, we can conclude that CH2NH is identified as the product in the radiolysis of CH3NH2. The remaining TPD traces in Fig. 3b reveal sublimation maxima at higher temperatures between 135 K and 225 K. A mass-to-charge ratio of 60 represents the heaviest ion detected.

Fig. 2 PI-ReTOF-MS spectra of the subliming molecules recorded for the irradiated CH3NH2 ices obtained at distinct ionization energies. Panel (a) shows the non-irradiated CH3NH2 ice (blank) while panel (b), (c) and (d) present the irradiated ice analyzed at 9.93 eV, 9.10 eV and 8.17 eV photoionization energy, respectively.
It can be attributed to the molecular formula $C_2N_2H_8$ that can be assigned to four possible isomers: $NH_2CH_2CH_2NH_2$, $N$-methyl-methanediamine ($NH_2CH_2NHCH_3$), 1,1-dimethylhydrazine ([CH$_3$)$_2$NNH$_2$], and 1,2-dimethylhydrazine (CH$_3$NHNHCH$_3$). They can be distinguished via their ionization energies (Table 2). Ethylenediamine has the highest ionization energy of 8.27 eV (calculated) and 8.42 eV (experimental) followed by $NH_2CH_2NHCH_3$ with 8.23 eV. Taking the energy correction of the Stark shift (0.04 eV) and the offset of the theoretical ionization energy (0.04 eV) into account, the ionization energies of $NH_2CH_2NHCH_3$ and $NH_2CH_2CH_2NH_2$ are reduced to 8.15 eV and 8.20 eV, respectively. A photon energy of 8.17 eV is employed to distinguish between both isomers. As presented in Fig. 3b, no ion counts are detected at 8.17 eV, revealing that most likely $NH_2CH_2CH_2NH_2$ is formed during irradiation, which effectively contributes to ion counts at $m/z = 60$ in the 9.93 eV experiment. However, due to the error of ±0.05 eV on the calculated ionization energies, we cannot rule out $NH_2CH_2NHCH_3$ entirely. Nevertheless, we find ion masses at $m/z = 59, 58, 44, 43,$ and 30 which simultaneously subliming with $m/z = 60$. In comparison to an ethylenediamine photoionization study by Wei et al. 80 we can relate the ion masses in this study to the photofragments of $NH_2CH_2CH_2NH_2$ (Table 4). These findings confirm the formation of $NH_2CH_2CH_2NH_2$.

In summary, the PI-ReTOF-MS study reveals two newly formed molecules in the CH$_3$NH$_2$ ices exposed to ionizing radiation: CH$_2$NH and NH$_2$CH$_2$CH$_2$NH$_2$. Integrating over the signals in the TPD traces of $m/z = 32$ with and without irradiation helps to extract the fraction of the non-radiolyzed CH$_3$NH$_2$ molecules to be $92 \pm 4\%$. This coincides nicely with the calculated loss of about $8 \pm 1\%$ from the infrared study.

The previous experiment from Bossa et al. already proposed the formation of CH$_3$NH. In their photolysis study, they found small features in their FTIR study around 1722 cm$^{-1}$ and 1683 cm$^{-1}$ which they postulated to originate from amides or aldehydes. Therefore, they related the $m/z = 59$ during sublimation using QMS to N-methyl formamide. In their experiment, they used UV flux of $10^{15}$ photons s$^{-1}$ cm$^{-2}$. This flux converts to about 14 eV molecule$^{-1}$, which is in the same region than the energy dose used in this work. Their findings, however, only suggest the existence of N-methyl formamide, based on the QMS data. An isotope study or an analysis of the isomer structure of $m/z = 59$ as we present it in this study has not been done in their study.

### 5. Discussion

Having confirmed that CH$_2$NH and NH$_2$CH$_2$CH$_2$NH$_2$ are formed in the irradiated ices, we are discussing now the possible formation pathways. Holtom et al. 13 revealed that CH$_3$NH$_2$ can undergo unimolecular decomposition initiated by energy transfer from the impinging electrons. In particular, two hydrogen loss channels can result in either methylamidogen (CH$_3$NH) (3a) or CH$_2$NH$_2$ (4a) [see also Fig. 4]; in the present experiments. Each of these radicals can emit a hydrogen atom synthesizing CH$_2$NH (3b and 4b). These routes are highly endoergic with the
energy being supplied from the ionizing radiation via inelastic energy transfer processes. Previous infrared studies after Photolysis by Bossa et al. 34 indicated that both formation routes might lead to CH2NH. These mechanisms were also documented in gas phase studies by Reed et al. 82 utilizing UV photodissociation of CH3NH2 at 215 nm in a molecular beam. This work revealed the atomic hydrogen loss pathway and formation of methylamidogen (CH3NH3) (3a), which was enhanced by a factor of three compared to CH2NH2 (4a). A summary of the reaction pathways discussed in this study are displayed in Fig. 4.

A possible formation pathway for the NH2CH2CH2NH2 molecule could follow a barrier-less radical-radical reaction via the exoergic recombination of two CH2NH2 radicals (reaction (5)). At low temperatures, these radical–radical recombination pathways are very prominent in interstellar ices, as long as the radicals are next to each other and the recombination geometry is correct. This has been successfully demonstrated for example for the formation of ethane (CH3CH3),15,83,84 hydrazine (NH2NH2),85 diphosphine (PH2PH2),48 hydrogen peroxide (HOOH)18,67, ethylene glycol (HOCH2CH2OH),41 and hydroxylamine (NH2OH),50 via recombination of methyl (CH3), amido (NH2), phosphino (PH2), hydroxyl (OH), and amido (NH2) with hydroxyl (OH).

Ogura et al. 86 suggested a pathway in analogy to reaction (5). In their gas phase study, they photolyzed gas mixtures of CH4, NH3 and H2O with broadband UV with the highest fluxes at 185 and 254 nm. They detected NH2CH2CH2NH2 among others. It should be stressed that the overall reactions to form CH2NH and NH2CH2CH2NH2 from CH3NH2 are endoergic by 536 kJ mol−1 (reaction (6)) and 463 kJ mol−1 (reaction (7)), respectively. Therefore, these reactions cannot happen thermally at 10 K or during the warm up phase, but have to involve non-equilibrium chemistry.40 Even a hypothetical molecular hydrogen elimination (reaction (8)) is still endoergic by 104 kJ mol−1. Therefore, the reaction pathways involved demand for the presence of an external energy source provided by, e.g., secondary electrons generated by GCRs in order to successfully form the product in the ISM.

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**Table 4** Species observed and discussed in this work along with their molecular formula, mass-to-charge ratio (m/z), ionization energy (IE), appearance energy (AE) of the observed fragments, and the observed peak sublimation temperature, as well as the Gibbs free energy ΔrG°.

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical formula</th>
<th>m/z</th>
<th>IE (eV)</th>
<th>Sublimation peak (K)</th>
<th>ΔrG° (kJ mol⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>2.16</td>
<td>115</td>
<td>216ˢ</td>
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<tr>
<td>Methanimine</td>
<td>CH3NH</td>
<td>29</td>
<td>9.94ᵃ</td>
<td></td>
<td>97ᵈ</td>
</tr>
<tr>
<td>Methanimine</td>
<td>CH3NH</td>
<td>33</td>
<td>12.00ᵃ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminomethylenate</td>
<td>CHNH₂</td>
<td>29</td>
<td>8.22ᵃ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aminomethylidygen</td>
<td>CH3NH3H</td>
<td>29</td>
<td>10.94ᵃ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylamidogen</td>
<td>CH3NH</td>
<td>30</td>
<td></td>
<td></td>
<td>187ᵈ</td>
</tr>
<tr>
<td>Methylamidoxye</td>
<td>CH3NH</td>
<td>30</td>
<td></td>
<td></td>
<td>160ᵈ</td>
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<tr>
<td>Methylamine</td>
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<td>8.97ᵇ</td>
<td>115</td>
<td>−7ᵈ</td>
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<tr>
<td>Ethylamine</td>
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<td>45</td>
<td>8.9⁹ᵇ</td>
<td>115/160</td>
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<tr>
<td>Dimethylamine</td>
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<tr>
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<tr>
<td>2-Propanamidine</td>
<td>(CH3)2CHNH2</td>
<td>59</td>
<td>8.72ᵇ</td>
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<tr>
<td>N-Methyl ethanamine</td>
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<td>59</td>
<td>8.15⁹</td>
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</tr>
<tr>
<td>N-Methyl-methanediamine</td>
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<td>60</td>
<td>8.23ᵃ</td>
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<tr>
<td>Ethylenediamine</td>
<td>NH2CH2CH2NH2</td>
<td>60</td>
<td>8.27ᵃ</td>
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<tr>
<td>1,1-Dimethyldiazine</td>
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<td>60</td>
<td>7.18ᵃ</td>
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<tr>
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<td>CH3NH₃⁺⁺</td>
<td>33</td>
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</tr>
</tbody>
</table>

AE = apparent energy. 🃏 Taken from Watanabe et al., 1957.⁷⁸ 🃏 Taken from Wei et al., 2006.⁶⁰ 🃏 Taken from Ruscic et al., 2016.⁹⁹ 🃏 Taken from Lossing et al., 1987.¹⁰⁰ / Taken from Aue et al., 1979.¹⁰¹

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**Fig. 4** Summary of reaction pathways toward CH2NH and NH2CH2CH2NH2. The Gibbs free energy change of each reaction is also indicated.
6. Conclusions

The present study explored the formation of CH$_3$NH$_2$ via the unimolecular decomposition of CH$_3$NH$_2$ in interstellar ices. Methylamine is present in several interstellar clouds such as Sagittarius B2 and Orion-KL and expected to be incorporated in interstellar ices as well. Even though it is expected that CH$_3$NH$_2$ is present only as a minor component in the ice, the present experiments reveal that each CH$_3$NH product can result from fragmentation of one single CH$_3$NH$_2$ molecule. These results of our mechanistical studies are transferable to interstellar ice mixtures containing CH$_3$NH$_2$, which are exposed to ionizing radiation. The irradiation dose utilized in this study is equivalent to 10$^5$ years of the life time of a cold molecular cloud. Here, CH$_3$NH$_2$ represents an important intermediate to the abiotic formation of extraterrestrial amino acids in interstellar ices, which are essential building blocks for life on Earth. The data collected by the elegant PI-ReTOF-MS approach highlight the feasibility of next generation laboratory studies to detect radiation and reaction products of non-equilibrium ice chemistry in interstellar analog ices selectively. In addition to the formation of CH$_3$NH$_2$, the experiments confirmed the formation of NH$_2$CH$_2$CH$_2$NH$_2$ in the irradiated CH$_3$NH$_2$ ice. This has not been observed in the interstellar medium up to date. A possible explanation might be found by the lower fractional abundance of the parent molecule CH$_3$NH$_2$ in the interstellar ices compared to our analog ice samples. This delimits CH$_3$NH$_2$ molecules present in direct neighborhood to each other in the ice and thus the recombination of two subsequently formed CH$_3$NH radicals via radical–radical reaction is delimited as well. As presented earlier, methylamine and CH$_3$NH$_2$ are present in several molecular clouds and star forming regions as well as the dust samples collected by the Stardust mission and the comet 67P/Churyumov-Gerasimenko. Ethylenediamine has not been observed in the interstellar medium or in the solar system yet, but our results suggest that it should be detectable in those environments where CH$_3$NH$_2$ and CH$_2$NH have been discovered. The upper limits of CH$_3$NH and of NH$_2$CH$_2$CH$_2$NH$_2$ in this study are below 0.09 ± 0.01 and 0.045 ± 0.005 molecules eV$^{-1}$, respectively, and these formation efficiency can be utilized in future astrochemical models of non-equilibrium ice chemistry to predict its interstellar abundance. It is interesting to note that CH$_3$NH$_2$ is isoelectronic to CH$_3$OH. Methanol can reach fractions of up to 27% with respect to H$_2$O in interstellar ices. Maity et al. irradiated CH$_3$OH bearing ices at 5–10 K by energetic electrons. Here, methanol, which consists of a methyl (CH$_3$) group and a hydroxyl (OH) group (Table 5), has been found to undergo similar reaction routes compared to CH$_3$NH$_2$, which in turn carries a methyl (CH$_3$) group and an amine (NH$_2$) group. In the CH$_3$OH ice, the product H$_2$CO – isoelectronic to CH$_3$NH – was formed via either a methoxy radical (CH$_3$O) or a hydroxymethyl radical intermediate (CH$_2$OH) via unimolecular decomposition pathways (reactions (9) and (10), Table 5). These reactions are in analogy to pathways (3) and (4) in the present study and are endoergic as well. Each pair of analogous reactions has similar Gibbs free energy changes, which may induce the observed same trends of column densities of N$_{CH_3NH_2}$ > N$_{CH_3NH}$ and N$_{CH_2OH}$ > N$_{CH_2CO}$ in Sagittarius B2. Likewise, ethyleneglycol (HOCH$_2$CH$_2$OH) – isoelectronic to NH$_2$CH$_2$CH$_2$NH$_2$ – has been found to be synthesized from the hydroxymethyl (CH$_2$OH) via radical–radical reaction in CH$_3$OH ices and has been detected in the interstellar medium toward Sagittarius B2(N-LMH). This radical–radical formation is similar to the formation of NH$_2$CH$_2$CH$_2$NH$_2$ via the CH$_3$NH$_2$ in CH$_3$NH$_2$ ice in this study. Therefore, ethylenediamine is expected to be present in these interstellar environments, where CH$_3$NH$_2$ and CH$_3$NH$_2$ has been observed as well such as towards Sagittarius B2.

Conflicts of interest

There are no conflicts to declare.
Acknowledgements

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