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Methylenimine and Cyanomethanimine Synthesis from Ion Irradiation N₂-CH₄ Ice: Implication on the Formation of Prebiotic Molecules in Outer Solar System Bodies

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ABSTRACT

The synthesis of Methylenimine and Cyanomethanimine from ion irradiation of N₂-CH₄ ice was studied, in an attempt to simulate the role of medium mass cosmic rays and energetic solar particles in the processing of nitrogen-rich ices on cold astrophysical environments, such as those in the outer region of the Solar System (e.g. Pluto, Charon, Triton, Makemake and Titan). The N₂-CH₄ (90:10) ice mixture was irradiated at 9 K by 38.4 MeV ⁴⁰Ca⁹⁺ (0.96 MeV/u) at the GANIL facility (Caen/France). The evolution of the samples was monitored using in-situ Fourier transform infrared spectroscopy (FTIR). The results indicate the formation of CH₂NH and CH₂NCN, which are considered species of interest in prebiotic chemistry. Other species produced by radiolysis were HCN, HNC, hydrocarbons and nitriles. Direct comparison of the laboratory spectrum from the mixture of reaction products provides an efficient way to focus on the identification of chemical synthesis routes for the production of molecules important in the development of life that are consistent with the chemical inventory and physical conditions on frozen moons and cold objects in the outer Solar System.

1. Introduction

Methylenimine (CH₂NH) and Cyanomethanimine (CH₂NCN) are species of great astrophysical interest, since they are possible precursors of amino acids, and thus may play an important role in the formation of biological building blocks in the interstellar medium. Methylenimine was detected in dark interstellar dust clouds (Godfrey et al., 1973; Oliveira et al., 2001), and was suggested as a possible precursor for glycine and its nitrile (Hoyle and Wickramasinghe, 1976; Basiuk, 2001; Suzuki et al., 2016), while cyanomethanimine, which is proposed to be an intermediary in the prebiotic synthesis of the purine nucleobase adenine, has been detected toward the massive star-forming region Sagittarius (Sgr) B2(N) (Zaleski et al., 2013; Melosso et al., 2018). Additionally, methylenimine was shown to be formed by UV irradiation of model icy interstellar grain mantles, it may be a precursor of other complex organics present in cometary ices (Bernstein et al., 1995), and was observed in laboratory experiments with N₂-containing ices (Jacox and Milligan, 1975; Balucani, 2009).

Compounds containing CN are considered species of great interest for prebiotic chemistry since the C–N bonds can lead to the formation of several amino acids and other key prebiotic molecules (Melosso et al., 2018). In the Solar System many known small bodies in the transneptunian region, such as Sedna, Eris, Pluto, Triton, and Makemake present nitrogen and/or methane ices (Cruikshank et al., 1993; Owen et al., 1993; Cruikshank et al., 2015; Grundy et al., 2016). This icy mixture (N₂ and CH₄) is also expected to be present in aerosols in the upper atmosphere of Saturn's moon Titan (Samuelson, Nath and Borysow, 1997; Niemann et al., 2005). All of these objects are constantly exposed to cosmic rays and energetic solar particles, and other radiation sources (UV, X-rays). The incoming ionizing field can initiate several chemical and physical processes, such as sputtering, radiolysis, and the formation of radicals, which can react to lead to the synthesis of many species, including species containing C–N bonds, which are the focus of this work.

This said, the study of organic compounds on astrophysical ices is crucial to understand the chemical evolution of materials from the interstellar medium to the solar system. Our own laboratory investigations

subsequently showed the formation of CH₂NH and CH₂NCN from ion irradiation of N₂-CH₄ (90:10) ice mixtures. Considering that many icy bodies in the outer Solar System (Planets, satellites, and comets) evolve in environments rich in nitrogen, with small amounts of methane mixed with other species, seems likely that CH₂NH, as well as CH₂NCN could be a product of irradiation of the N₂-containing ices present in these icy worlds. The results of this work, detecting methylenimine and cyanomethanimine, complement previous results of our group (Pilling et al. 2009; Vasconcelos et al., 2017a,b,c), who studied the interaction between energy sources (ions, UV, X-rays, and secondary electron) on N₂-rich ices, analogue to those found in many icy bodies of the outer Solar System.

Section 2 presents details of the experimental setup employed and methodology. Results and discussions are given in section 3 with focus on reaction pathways triggered by incoming ions in the N₂-CH₄ ice. The astrophysical implications are given in Section 4, including proposed mechanisms for the formation of Methylenimine (CH₂NH) and Cyanomethanimine, as well as routes to Adenine (C₅H₅N₅) from these compounds in N₂-CH₄ rich ices in outer Solar System environments. Final remarks and conclusions are listed in Section 5.

2. Experimental setup

The experiment simulating bombardment of cosmic rays in N₂:CH₄ ice mixture (abundance ratio 90:10) at 9 K was performed with the IGLIAS (French acronym for “Irradiation of astrophysical ices”) high vacuum chamber coupled to the IRRSUD (IR Radiation SUD) beamline at the Grand Accélérateur National d’Ions Lourds (GANIL) located in Caen, France. IGLIAS was designed to study the evolution of targets with astrophysical interest at low temperature under swift heavy ion irradiation (Augé et al., 2018). The base pressure in the high vacuum chamber is 2×10^{-10} mbar. Briefly, the gas mixture commercially purchased (Sigma Aldrich, purity superior to 99,9%) were deposited (~30mbar of gas deposition) onto a ZnSe substrate kept at 9 K through a facing gas inlet. During sample deposition the chamber pressure was below 6×10^{-7} mbar. The sample was irradiated by 38.4 MeV ⁴⁰Ca⁹⁺ (0.96 Mev/u) with constant flux of 3×10^8 ion cm⁻² s⁻¹ up to the fluence of 3×10^{13} ion cm⁻². The FTIR spectrometer (Bruker Vertex 70v) of the IGLIAS set-up can record spectra from 500 to 6000 cm⁻¹ (20–1.6 μm), with 1 cm⁻¹ resolution. In this work, IR is analysed in the 600–4000 cm⁻¹ (16.6–2.5 μm) range.

Three IR spectra were recorded during the experiments (one before sample deposition to identify background, after sample deposition at 9 K (virgin sample), after sample irradiation (at the fluence of 3×10^{13} ion cm⁻²) and after sample heating to room temperature. The heating ramp employed was performed in two stages to avoid microscopic chemical explosion during heating (0.2 K/min from 9 K to 30 K and 0.5 K/m from 30 K to 300K). The experiment was performed at the first week of May 2018 with a total experiment time around 25h. The residue at room temperature was carefully removed from the vacuum chamber and kept in a hermetic vessel in vacuum for further chromatographic analysis.

The penetration depth calculated with SRIM (Ziegler et al., 2008), for this sample was around 22 microns and the calculated linear energy delivered (LED) or dE/dx was around $2.70 \pm 0.40 \times 10^3$ keV/micron (electronic regime), and 5.05 ± 0.76 keV/micron (nuclear regime). The density assumed in the SRIM calculation was $\sim 9.3 \times 10^{-1}$ g cm⁻³, by considering the values 1.027 g cm⁻³ (Scott, 1976) and 0.94 g cm⁻³ (Satorre et al., 2008) for the density of N₂ ice (average $\rho(\text{N}_2) = 0.98$ g cm⁻³), and 0.403 g cm⁻³ (Brunetto et al., 2008) and 0.47 g cm⁻³ (Satorre et al., 2008) for the density of CH₄ ice (average $\rho(\text{CH}_4)=0.44$ g cm⁻³), and by considering the proportion of the N₂:CH₄ (90:10) ice mixture. The errors in the ice densities used in this methodology (due to these differences) are estimated to be up to 15%. The calculated total column densities were obtained by measuring the area of the N₂ band at 2327 cm⁻¹ (ν_1 vibration mode), and the CH₄ band at 3020 cm⁻¹ (ν_3 vibration mode), whose A-values are 4.1×10^{-22} cm molecule⁻¹ (Bernstein and Sandford, 1999), and 3.38×10^{-19} cm molecule⁻¹ (Brunetto et al., 2008), respectively. Errors are estimated around 20%, and reflect the uncertainties in the parameters used in this methodology.

From these measurements, the thickness of the ice was about 30 μm (see the equation in Pilling et al. 2011). This value takes into account the initial column density of the order of 10^{-19} cm⁻², around an order of magnitude larger when considering other works in the literature. Considering the proportion of the ice mixture, is reasonable a band strength of N₂ as used by Bernstein and Sandford (1999), which attribute a value $\sim 4.1 \times 10^{-22}$ cm molecule⁻¹ in N₂/CH₄ mixtures (20/1), it is close to the mixture of this work. For comparison,

Bohn et al. (1994) report a A -value of $(1.3 \times 10^{-22} \text{ cm molecule}^{-1})$ in pure N_2 ice. The real value may be slightly different because the chemical environment is now different from pure N_2 ice. It is known that the chemical environment affects the band strength (as discusses by Pilling et al. 2020 and reference there). Thus, the thickness value of $\sim 30 \mu\text{m}$ is a value that seems quite reasonable considering the experimental conditions of this experiment. Table 1 list some properties of the sample and the ion beam used in this study.

Table 1

Sample and ion beam properties employed in this study.

| Sample | Temperature (K) | N_{initial} (molecules cm^{-2}) | N_{final} (molecules cm^{-2}) | d_{initial} (μm) | d_{final} (μm) | Ion energy (MeV $^{40}\text{Ca}^{9+}$) | Max fluence (ions cm^{-2}) | Max dose (eV molecule $^{-1}$) | S_e (keV/micron) |
|----------------------------------|-----------------|--|--|--|--------------------------------------|---|--------------------------------------|---------------------------------|---------------------------|
| $\text{N}_2:\text{CH}_4$ (90:10) | 9 | $\sim 6 \pm 1.2 \times 10^{19}$ | $\sim 4 \pm 0.8 \times 10^{19}$ | $\sim 30 \pm 6$ | $\sim 20 \pm 4$ | 38.4 | 3×10^{13} | $2.9 \pm 0.6 \times 10^2$ | $2.7 \pm 0.4 \times 10^3$ |

3. Results and Discussion

3.1. Identification of N_2 and CH_4 IR bands

In Fig. 1 we show the spectrum of the mixture $\text{N}_2\text{-CH}_4$ (90:10) as deposited at 9 K in the spectral region of our interest ($4000\text{--}690 \text{ cm}^{-1}$). The parental specie N_2 appear as a small peak observed at 2328 cm^{-1} (Bernstein and Sandford, 1999; Moore and Hudson, 2003). This peak is small because the N_2 molecule, although quite abundant in the sample, has no permanent dipole moment and so has no stronger IR-allowed features, but the IGLIAS high vacuum chamber used in this methodology, this allows us to observe the very weak solid- N_2 infrared absorption (details in Augé et al., 2018). This peak of N_2 is shown in detail in Fig. 1(b). With respect to CH_4 parental species, we can see its main absorptions bands centred at 1300 cm^{-1} and at 3009 cm^{-1} , ν_4 and ν_3 vibrations mode, respectively. Other vibration combination bands appear at 2815 cm^{-1} ($\nu_2 + \nu_4$), and at 3845 cm^{-1} ($3\nu_4$ mode) (Kaiser and Roessler, 1998; Moore and Hudson, 2003; Bennett et al., 2006). Among these bands of parental specie CH_4 chosen for the column density calculate, the band at 3020 cm^{-1} was considered to be adequate for analysis and quantifications, since ν_3 bands at 1304 cm^{-1} of this specie appear saturated. Its initial value of column density (about $2.4 \times 10^{18} \text{ molecules cm}^{-2}$) is almost one order of magnitude smaller than the N_2 one ($5.6 \times 10^{19} \text{ molecules cm}^{-2}$).

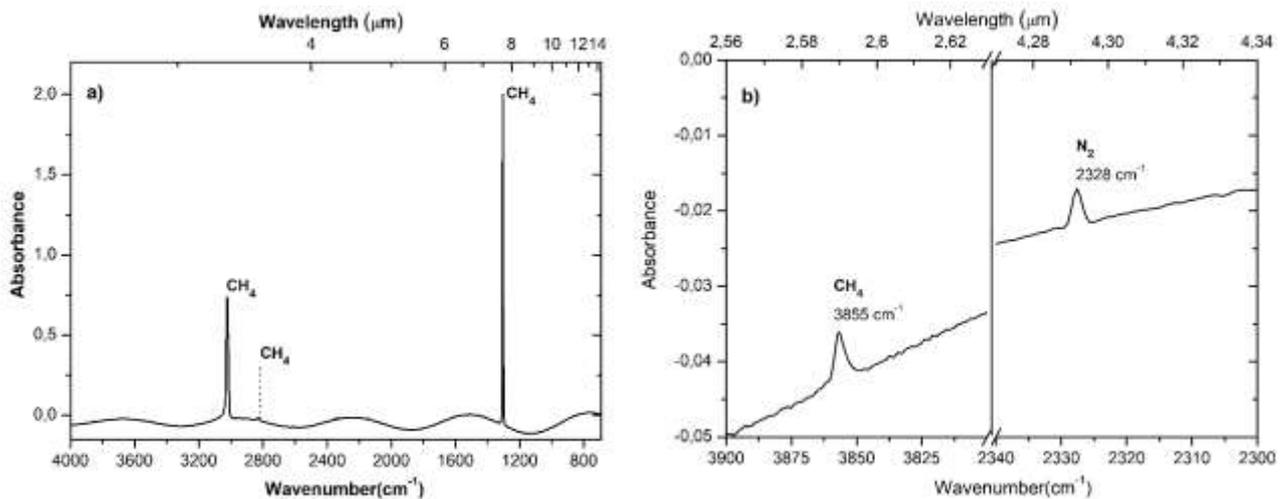


Fig. 1. Infrared spectrum of the mixture $\text{N}_2\text{-CH}_4$ (90:10) as deposited at 9 K (region $4000\text{--}690 \text{ cm}^{-1}$) before irradiation. In a) bands of all CH_4 assignments visible and b) zoom of region $3900\text{--}2300 \text{ cm}^{-1}$ (with a break between 3800 cm^{-1} to 2340 cm^{-1}) to make the bands of N_2 at 2328 cm^{-1} and CH_4 at 2328 cm^{-1} visible.

3.2. Identification of new molecules (hydrocarbons and C-N compounds)

Fig. 2 shows IR spectra for an analog astrophysical ice made with N₂-CH₄ (90:10) at 9 K. The spectrum of the unirradiated mixture is shown along with spectra after irradiation by 38.4 MeV ⁴⁰Ca⁹⁺ swift ion beams. These spectra clearly show the decrease of the CH₄ bands related to the destruction of this molecule under irradiation. Due to destruction of methane during the processing of the sample, many hydrocarbons and radicals are formed, and their absorption bands were identified. Near 821 cm⁻¹ and 2921 cm⁻¹ are features commonly attributed to ethane (C₂H₆) (Comeford and Gould, 1960; Kim et al., 2010). Ethylene (C₂H₄) can be identified from its ν₇ band at 957 cm⁻¹ (Kaiser and Roessler, 1998; Bennett et al., 2006). **Peak position of IR absorptions** for these hydrocarbons, which are an important component of hydrocarbon-rich atmospheres in the outer Solar System, such as Titan, and other KBOs, are in good agreement with our previous results in laboratory simulation of ion irradiation of pure CH₄ ice (see Vasconcelos et al., 2017c). The ethynyl radical (C₂H), one abundant polyatomic molecules yet detected in interstellar space (Tucker et al., 1974) presented features at 1726 cm⁻¹ and 1841 cm⁻¹ (Wu et al., 2013). For example, in astronomical environments, the formation of long chain polyynes (HC_{2n}H) from acetylene is believed to occur through polymerization reactions, in which ethynyl-like intermediates plays an important role, leading to the formation and destruction of polycyclic aromatic hydrocarbons (PAHs) (Doney et al., 2008; Gu et al., 2009).

Table 2

Peak positions of IR absorptions of ice mixture N₂:CH₄ (90:10) irradiated at 9 K, and at 300 K. The table also shows the spectra of the subtraction, this is, only volatiles (Organic residue at 300 K minus irradiated ice at 9K). ND is not detected.

| Wavenumber (cm ⁻¹) | Wavelength (μm) | Assignment | Species | At 9K | Organic residue at 300 K | (Organic residue at 300 K minus irradiated ice at 9K). | Ref. |
|--------------------------------|-----------------|--------------------------------------|-------------------------------------|----------|--------------------------|--|--|
| 821 | 12.18 | (ν ₁₂) | C ₂ H ₆ | detected | ND | detected | Comeford and Gould (1960), Kim et al. (2010) |
| 957 | 10.44 | (ν ₇) | C ₂ H ₄ | detected | ND | detected | Kaiser and Roessler (1998), Bennett et al. (2006) |
| 1104 | 9.05 | (ν ₂) | NH ₃ | detected | ND | detected | d'Hendecourt and Allamandola (1986) |
| 1304 | 7.66 | (ν ₄) | CH ₄ | detected | ND | detected | Kaiser and Roessler (1998), Moore and Hudson (2003), Bennett et al. (2006) |
| 1342 | 7.45 | (ν ₆) | CH ₂ NH | detected | detected | detected | Jacox and Milligan (1975), Gerakines et al (2004) |
| 1462 | 6.83 | (ν ₁₁) | N-CH ₂ NCN | detected | ND | detected | Evans et al. (1991), Gerakines et al (2004) |
| 1639 | 6.10 | (ν ₄) | CH ₂ NH | detected | detected | detected | Jacox and Milligan (1975) |
| 1726 | 5.79 | (ν ₃) | C ₂ H | detected | ND | detected | Wu et al. (2013) |
| 1841 | 5.43 | (ν ₃) | C ₂ H | detected | ND | detected | Wu et al. (2013) |
| 2037 | 4.90 | (ν ₃) | HNC | detected | detected | detected | Milligan and Jacox (1967b) |
| 2091 | 4.78 | (ν ₂), (ν ₃) | CH ₂ N ₂ /HCN | detected | ND/ detected | detected | Moore and Hudson (2003) |
| 2151 | 4.64 | (ν ₂) | NCCN | detected | detected | detected | Hudson and Moore (2004), Wu et al. (2013) |
| 2211 | 4.52 | - | N-CH ₂ NCN | detected | ND | detected | Evans et al. (1991), Gerakines et al (2004) |
| 2240 | 4.46 | - | C-HNCHCN | detected | detected | detected | Evans et al. (1991) |
| 2260 | 4.42 | (ν ₁) | CH ₃ CN | detected | ND | detected | Hudson and Moore (2004) |
| 2327 | 4.29 | (ν ₁) | N ₂ | detected | ND | detected | Bernstein and Sandford (1999), Moore and Hudson (2003) |
| 2762 | 3.62 | ? | ? | detected | ND | detected | - |
| 2825 | 3.53 | (ν ₂ + ν ₄) | CH ₄ | detected | ND | ND | Kaiser and Roessler (1998), Moore and Hudson (2003), Bennett et al. (2006) |
| 2921 | 3.42 | (ν ₈₊ , ν ₁₁) | C ₂ H ₆ | detected | ND | detected | Bennett et al. (2006) |
| 3020 | 3.31 | (ν ₃) | CH ₄ | detected | ND | detected | Kaiser and Roessler (1998), Moore and Hudson (2003), Bennett et al. (2006) |

| | | | | | | | |
|------|------|-------------|-----------------|----------|----------|----------|--|
| 3133 | 3.19 | (ν_3) | HCN | detected | ND | detected | Masterson and Khanna (1990), Moore and Hudson (2003) |
| 3312 | 2.99 | (ν_1) | HCN | detected | detected | detected | Shimanouchi (1972) |
| 3393 | 2.94 | (ν_3) | NH ₃ | detected | ND | detected | d'Hendecourt and Allamandola (1986) |
| 3855 | 2.59 | 3 ν_4 | CH ₄ | detected | ND | detected | Kaiser and Roessler (1998), Bennett et al. (2006) |

The destruction of N₂ combined with hydrogen coming from CH₄ also leads to appearance of several nitrogen containing compounds. In this way, new molecular species are formed in the ice mixture as a result of recombination or fragmentation of radicals or molecular fragments formed by radiolysis. An absorption at 2091 cm⁻¹ was assigned to the ν_2 mode of diazomethane (CH₂N₂) and agrees with the results of Moore and Hudson (2003) in experiments with N₂:CH₄ ice mixture. The broad band located at 1104 cm⁻¹ is assigned to ammonia (NH₃; ν_2 —umbrella mode) (d'Hendecourt and Allamandola, 1986). Another band of ammonia was identified at 3393 cm⁻¹ (ν_3). Near 2260 cm⁻¹ is a feature commonly attributed to acetonitrile (CH₃CN) (Hudson and Moore, 2004), whereas a characteristic found at 2151 was attributed to the Cyanogen (NCCN) (Hudson and Moore, 2004; Wu et al., 2013). Cyanogen is an important specie that has been observed in Titan's atmosphere (Hudson and Moore, 2004). Hydrogen isocyanide (HNC) is identified at about 2037 cm⁻¹ (Milligan and Jacox, 1967b; Wu et al., 2013), while hydrogen cyanide (HCN) is seen close to 3133 cm⁻¹ (Masterson and Khanna, 1990), Moore and Hudson, 2003), and 3312 cm⁻¹ (Shimanouchi, 1972). Of fundamental importance, HCN is produced both in the gaseous and solid states, and very present in icy bodies in the outer Solar System. For example, the ν_1 stretching mode band of this molecule was found in absorption in the spectrum of Pluto and Triton at 4.76- μ m (Protopapa, Boehnhardt and Herbst 2008; Burgdorf, Cruikshank and Dalle Ore, 2010). Additionally, HCN is the most abundant nitrile nitrogen in the stratosphere of Titan, and has been identified in the gas phase of the interstellar medium as well as in the comae of several comets (Yung, 1984, 1987; Magee-Sauer et al., 1999; Gerakines et al., 2004). The cited acetonitrile and cyanogen species are also species of importance in these icy environments (Hudson and Moore, 2004).

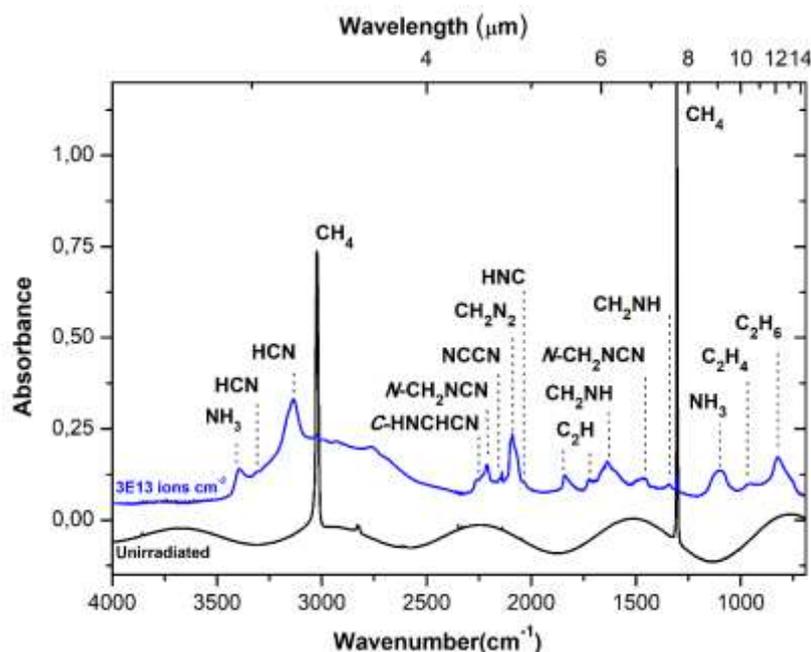


Fig. 2. Comparison between the Infrared spectra of ice mixture N₂:CH₄ (90:10) in the beginning of experiment (bottom spectrum) and after the highest radiation fluence (3×10^{13} ions cm⁻²). Molecular assignments of selected infrared bands are given. More information about detected species is presented in Table 2.

3.2.1. Methyleneimine and Cyanomethanimine synthesis

Among the complex organic molecules detected so far, special attention has been paid to the formation of two dimers of HCN, Methyleneimine (CH₂NH) and Cyanomethanimine (*N*-CH₂NCN and *C*-HNCHCN

forms). Methyleneimine was observed at 1342 cm^{-1} and 1639 cm^{-1} , corresponding to the ν_6 and ν_4 modes of this molecule, respectively. These two band positions are consistent with those found by Jacox and Milligan (1975). Gerakines, Moore and Hudson (2004) also found a characteristic of Methyleneimine near 1342 cm^{-1} in a $\text{NH}_3 + \text{HCN}$ (5:1) UV photolysis experiment. The characteristics located at 1462 cm^{-1} , 2211 cm^{-1} , and 2240 cm^{-1} are consistent with those assigned to *N*-cyanomethanimine and *C*-cyanomethanimine, respectively, by Evans et al. (1991). In section 3.2.2 we present a comparison between the location of observed peak positions to Methyleneimine and Cyanomethanimine observed in the current experiment with the values obtained in the literature. In Fig. 3 the spectral region of interest ($2300\text{--}1310\text{ cm}^{-1}$) was inserted for clarity. This spectral region shows that methyleneimine and cyanomethanimine were synthesized from the initial $\text{N}_2\text{-CH}_4$ mixture.

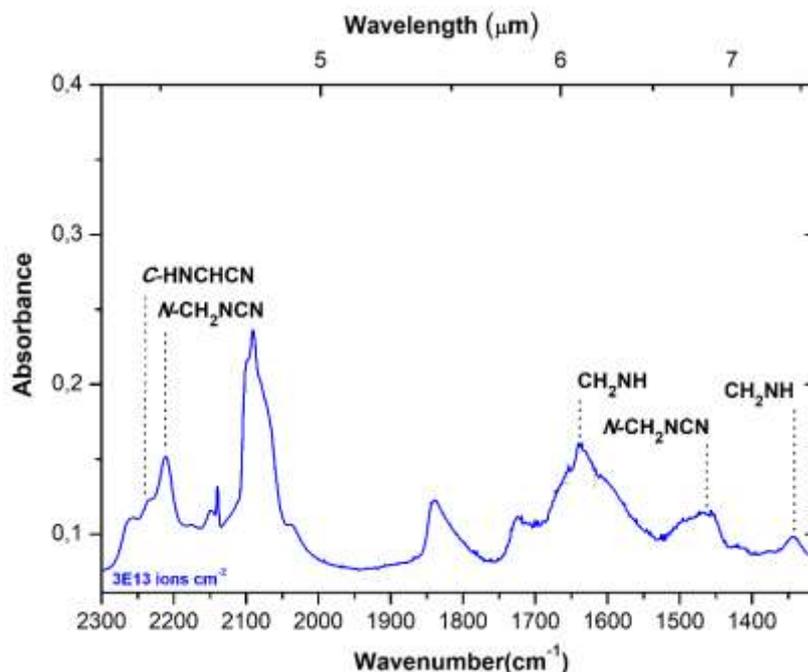


Fig. 3. Expanded view of Fig. 2 for the identification of bands of Methyleneimine (CH_2NH) and Cyanomethanimine (*N*- CH_2NCN and *C*- HNCHCN forms) produced by the bombardment of the $\text{N}_2\text{:CH}_4$ (90:10) ice at 9 K with energetic ions ($38.4\text{ MeV } ^{40}\text{Ca}^{9+}$).

3.2.2. Reaction products

Methyleneimine formation can be induced by the recombination or fragmentation of radicals or molecular fragments, such as CH , H_2 , N atoms, by radiolysis of CH_4 and N_2 molecules. This produces an appropriate intermediate species, such as HCN and HNC , which drives CH_2NH production, as follows:



which can also be photo-dissociated into $\text{HCN} + 2\text{H}$, as discussed also by Yelle et al. (2010). According to these authors, methanimine (or methyleneimine) is also produced by two reactions: recombination of N atoms (which are produced by dissociation of N_2) with CH_4 molecules, as well as recombination of NH and CH_3 radicals, both release H atoms, as follows:





For these authors, these reactions are the principal source for methanimine formation on Titan, and thus plays an essential role in the nitrogen chemistry on this largest moon of Saturn. In this way, these reactions can also play an important role on other small bodies in the outer Solar System, since cosmic rays and energetic solar particles acting on solid $\text{N}_2\text{-CH}_4$ in the atmosphere/surface of these icy bodies (e.g Pluto, Triton, Titan) produces polymeric residues. Additional polymerization of methylenimine leads to the formation of other complex organic molecules, such as hexamethylenetetramine (HMT), as previously proposed by Bernstein et al. (1995).

The production of cyanomethanimine was suggested to occur by the recombination of diazomethane CH_2N_2 and C atoms. CH_2N_2 formation by the reaction between a CH_2 radical (coming from the dissociation of CH_4) and a N_2 molecule, while C atoms can be produced, for example, by the dissociation of CH_2 radicals, according to the reactions:



These molecules will react quickly with other species, leading either to formation of hydrocarbons or to larger nitriles. Cyanomethanimine is an important species in the context of prebiotic chemistry, essentially because of its role as an intermediate in adenine formation (Oro, 1961; Evans et al., 1991). In all cases where CH_4 and N_2 (principally) molecules are relatively abundant, we can expect to observe some cyanomethanimine as well, following these reactions. Fig. 4 is a proposed diagram to show possible reaction pathways for formations of species during the experiment.

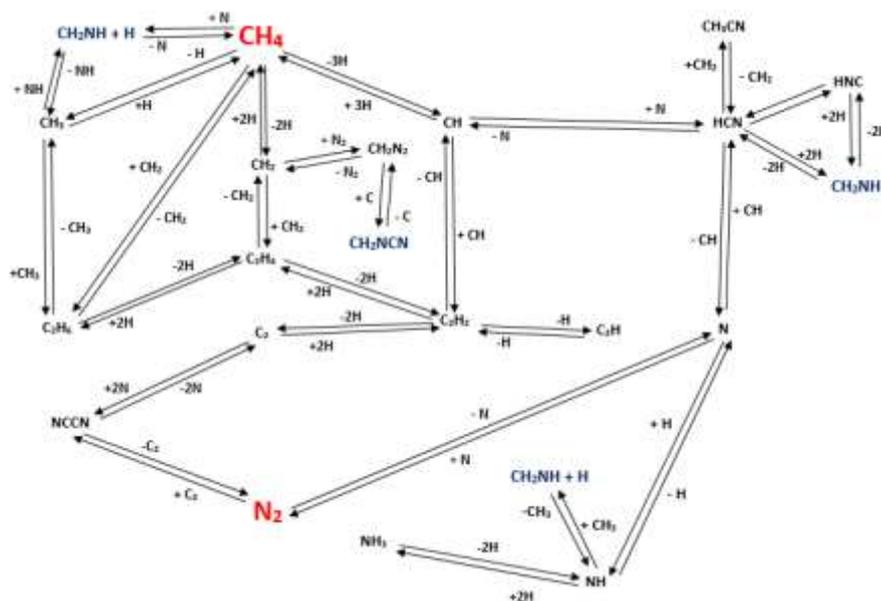


Fig. 4. Reaction pathways for formation of hydrocarbons and C-N compounds, including methylenimine and cyanomethanimine.

The band positions of products identified in this section agree with many laboratory experiments conducted by our groups, and others researches simulating the interaction of ionizing radiation with a N_2/CH_4 ice mixture on planetary atmospheres. For example, Pilling et al. (2009) identified several organic molecules, including nitriles and aromatic CN compounds with soft X-rays (and electrons beams) on Titan aerosol analogs. Vasconcelos et al. (2017b) from the energetic processing of $\text{N}_2:\text{CH}_4$ ices at 12 K and 19 K with X-rays and swift ions also found HCN, HNC, CH_2N_2 , C_2H_2 , and others. Among the main results of Bohn et al. (1994) and Moore and Hudson (2003) conducting infrared study of ion-irradiated N_2 -dominated ices at 12 K relevant to

Triton and Pluto, they showed that HCN, HNC, NH₃, diazomethane (CH₂N₂), and other molecules are products of irradiated N₂ + CH₄. Many nitriles, hydrocarbons, and nitrogen-containing compounds were also confirmed in radiation experiments (photolysis and energetic electrons) of the CH₄/N₂ ices by Wu et al. (2013), and the peaks presented in the infrared spectra in such experiments are in agreement with our experiments. No Methylenimine and/or Cyanomethanimine were observed in these experiments found in the literature. On the other hand, we have presented in this work that these species are product observed during irradiation of CH₄/N₂ ices, with consistent values with those reported by Lorencak et al. (1986) and Evans et al. (1991). The various products from chemical reactions initiated allow us discuss the possible chemical processes for the formation of the major products, including the methylenimine and Cyanomethanimine formation. The Table 3 shows a comparison of the band position for the main CN species detected in this work with those reported in the literature.

Table 3

Comparison between the locations of observed peak positions (in cm⁻¹) of some CN-bonded observed in the current experiment with the values obtained in the literature.

| Range (cm ⁻¹) | Molecule | This work | ^a Wu et al. (2013) | ^b Moore and Hudson (2003) | ^c Jacox and Milligan (1975) | ^d Evans et al. (1991). |
|---------------------------|--|-----------|-------------------------------|--------------------------------------|--|-----------------------------------|
| 1335-1350 | CH ₂ NH | 1342 | - | - | 1348 | - |
| 1450-1465 | <i>N</i> -CH ₂ NCN | 1462 | - | - | - | 1456 |
| 1635-1650 | CH ₂ NH | 1639 | - | - | 1641 | - |
| 2030-2045 | HNC | 2037 | 2034 | - | - | - |
| 2085-2100 | CH ₂ N ₂ /HCN | 2091 | - | 2096 | - | - |
| 2145-2160 | NCCN | 2151 | 2151 | - | - | - |
| 2205-2215 | <i>N</i> -CH ₂ NCN | 2211 | - | - | - | 2208 |
| 2235-2250 | <i>C</i> -HNCHCN | 2240 | - | - | - | 2240 |
| 2255-2270 | CH ₃ CN | 2260 | - | - | - | - |
| 3125-3140 | HCN | 3133 | - | - | - | - |
| 3300-3315 | HCN | 3312 | - | - | - | - |

^a N₂/CH₄ (100:1) irradiated with energetic electrons at 10 K.

^b N₂/CH₄ (100:1) irradiated with 0.8-MeV protons at 12 K.

^c UV-induced decomposition of methyl azide in argon, nitrogen, and carbon dioxide matrices at 14 K.

^d IR spectra de *N*-cyanomethanimine precursors in Ar matrix isolation at 12 K.

We observed that in the range of 1335–1350 cm⁻¹, and 1635–1650 cm⁻¹ (range where we registered methylenimine), Wu et al. (2013), and Moore & Hudson (2003) in experiments with N₂/CH₄ mixtures irradiated with electrons and protons, respectively, do not register CN-bonded species. Similarly, the authors also do not register such species in the intervals of 1450–1465 cm⁻¹, 2205–2215 cm⁻¹, and 2235–2250 cm⁻¹, in which we register signatures for Cyanomethylenimine. On the other hand, the signatures in these regions are consistent with those recorded at 1348 cm⁻¹ and 1641 cm⁻¹ para CH₂NH from Jacox and Milligan (1975), and at 1456 cm⁻¹ and 2208 cm⁻¹ for *N*-CH₂NCN from Evans et al. (1991). Additionally, in another work by Milligan (1961) from photolysis of methyl azide in argon and carbon dioxide matrices at ~ 4 K results in the appearance of CH₂NH in these regions registered in this work. Lorencak et al. (1986) in Photolysis of azidoacetonitrile in an Ar matrix at 11 K also gives *C*-HNCHCN in region about 2240 cm⁻¹. Still in relation to 1650 to 1660 cm⁻¹ range, in experiments with N₂-rich ices the N₃ specie it is a species commonly found. Moore et al. (2003) found

this specie in experiments $N_2:CH_4$ and pure N_2 at 1657 cm^{-1} , while Wu et al. (2013) provide N_3 at 1658 cm^{-1} . The closest feature in this region we found around 1639 cm^{-1} in this work and, as already mentioned, is attributed to CH_2NH at 1641 cm^{-1} by Jacox and Milligan (1975). It reveals that the set of reactions initiated by the breakdown of molecules, formation of atoms, radicals and species enabled the formation of CN species in these regions of IR spectra, in contrast with to the results seen in the works of Wu et al. (2013), and Moore & Hudson (2003).

In the case of HCN bands in the region around 2099 it is commonly attributed to both HCN (ν_3) and CH_2N_2 (ν_2), as discusses by Moore & Hudson (2003). As a reference, this region of the spectrum, in experiments $N_2 + CH_4$ by Wu et al. (2013) the authors did not find HCN in this range. Similarly, both references also do not register HCN in the 3300-3320 range. On the other hand, Hudson et al. (2014) in experiments with C_2H_2 ices at 12 K records a band at 3318 cm^{-1} for C_2H_2 , but we did a check and confirmed that a peak around 3311 is consistent with HCN, CH stretch mode (Shimanouchi 1972). Its strongest band was at 3130 cm^{-1} (ν_3) (Masterson and Khanna, 1990). Some differences in the peak positions are probably due to an enlargement and displacement of some spectral bands because the chemical environment is very peculiar with the energy deposited by the incident ions. As discussed in a recent study (Pilling et al. 2020), we found that the chemical environment affects, in addition to the band strength, also the central position and, in some cases, the profile of the bands in the IR spectra.

3.3. Sample heating

After irradiation phase, a slow heating phase was applied to the sample to allow the detection of reasonable amount of organics (tholin) at room temperature with the purpose to be further analyzed by ex-situ techniques such as gas-chromatography GC-MS and RMN (Pilling et al., 2009). The heating ramp was performed in two stages to avoid microscopic chemical explosion during heating (0.2 K/min from 9K to 30K and 0.5 K/m from 30 K to 300K). After sample heating to 300 K, a new spectra as taken and compared with the irradiated sample at 9K. Figure 5 presents a comparison between these spectra at 9 K and 300 K (organic residue), as well as the IR features of the eventual volatiles species that might be produced in the experiments at cold temperature (spectra obtained by direct subtraction between the cold and irradiated sample at 9K and solid residue at 300 K). Details of all the species detected at low temperatures, and during the sample heating, can also be seen in Table 2.

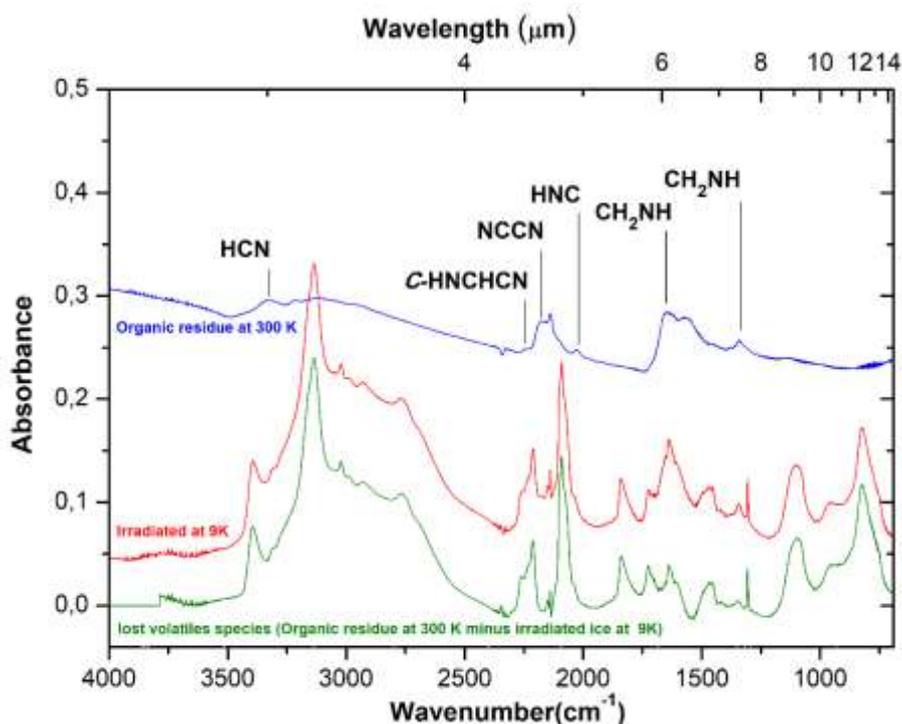


Fig. 5. Infrared spectra of the irradiated samples during the slow heating up to room temperature. For comparison purposes, the solid residue at 300 K, the spectrum of the irradiated sample at low temperatures (9 K), and the difference spectrum (subtraction between the cold and irradiated sample at 9K and solid residue at 300 K) are shown.

In the IR spectra of organic residue at 300K, we observe non-volatile species with peaks in the infrared spectrum at 1342 cm^{-1} and 1639 cm^{-1} , which correspond to the CH_2NH molecule. This spectrum also presents that HCN, NCCN and HNC are still present when the sample is heated to this temperature. Some these volatile species should be gases at this temperature. We do not know the CH_2NH desorption temperature, while know that HNC, HCN and NCCN should sublime readily well before 300 K. We believe that this may be occurring because they must be trapped (or in gas pockets) within the polymeric matrix of the organic residue produced. A discussion about trapping of volatiles species in ices can also be seen in Öberg (2009).

A weak band from C-HNCHCN appears at 2240 cm^{-1} after the heating at 300 K, whereas the bands at 1462 and 2211 cm^{-1} are not visible in the heating spectra. This suggest that methylenimine, hydrogen isocyanide, and cyanomethanimine may survive at higher temperatures in the outer Solar System environments. Additionally, the IR (estimated) spectra of volatiles species produced during irradiation might help to understand the role of these species in the surface chemistry when these ices are exposed to external or internal heating process, such as cometary and meteoritic impacts, lightning or corona discharges, tidal forces into icy objects of outer Solar System. The use of techniques of discharge or radiation source to mimic one or several of the energy sources capable of generating radicals and other activated species are of great interest, as those used in methods of tholin production, discussed by Cable et al. (2012) in order to gain a better understanding of the chemistry of Titan, for example, could provide crucial information for understanding the astrobiology in outer Solar System bodies.

4. Astrophysical Implications

Hydrocarbons and nitriles, such as C_2H_4 , C_2H_6 , HCN, HNC, CH_2N_2 , and other compounds containing C-N bonds have been observed on the surfaces of planets and their moons in the outer Solar System. In Saturn's largest moon Titan, the Cassini-Huygens mission discovered an environment composition rich in these species produced by magnetospheric particles and/or solar radiation (Waite et al., 2004, 2007; Vuitton, Yelle and McEwan 2007). Many of these species can also be present on Trans Neptunian Objects, as Triton and Pluto. NASA's New Horizons spacecraft mapped the surface of Pluto and showed that N_2 and CH_4 ices dominate its surface composition, along with other species (Grundy et al., 2016). Triton, Neptune's satellite, contains N_2 at the surface with small amounts of CH_4 mixed with other species (Cruikshank et al., 1993; Owen et al., 1993). The surface composition of Kuiper Belt objects (KBOs), such as Eris and Makemake, also present nitrogen and/or methane ices (Cruikshank et al., 2015). Cassini's instruments (e.g. INMS (Ion and Neutral Mass Spectrometer) and the UVIS (Ultraviolet Imaging Spectrograph) collected and analysed in situ the plume of subsurface material of Enceladus, displayed CH_4 and NH_3 abundances, and small amounts of other species, which include N_2 (Spencer et al., 2006).

The present experiment corresponds to $1\text{-}2 \times 10^4$ years of irradiation of nitrogen-methane ice mixture on icy bodies in the outer Solar System under the action of cosmic rays. This estimation is considering the medium mass ($3 < Z < 11$) ion flux (Solar energetic particles and galactic cosmic rays) taken from Pilling et al. (2011), 5.6×10^{-1} and 6.5×10^{-1} ions $\text{cm}^{-2}\text{ s}^{-1}$ in Saturn and Neptune orbits, respectively, 7.2×10^{-1} ions $\text{cm}^{-2}\text{ s}^{-1}$ for Pluto and other KBOs (average distance of ~ 40 AU), and considering the data obtained in the present experiment (final fluence of 3×10^{13} ion cm^{-2}). Energetic ions simulating cosmic ray and energetic particle bombardment of N_2 - CH_4 ices mixtures can be an important source for the production of hydrocarbons, nitriles/compounds containing C-N bonds in astrophysical environments. It suggests that the set of reactions suggested in this work could contribute to the build up of the N_2/CH_2 -rich organics that cover these icy worlds. Consequently, the scenario of ices processing by energetic ions is of fundamental importance in the synthesis of key precursors of biomolecules in space, including amino acids, and nucleobases i.e., the building blocks of RNA and DNA.

Different reaction pathways leading to these compounds are imaginable, but most probable are those involving abundant astrophysical organic species. For example, CH_2NH is related to a formation path for glycine, when HCN (or HNC) is added to CH_2NH , forming aminoacetonitrile ($\text{NH}_2\text{CH}_2\text{CN}$) (Danger et al. 2011),



which via hydrolysis, yields glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) (Peltzer et al., 1984). Where H_2O molecules are relatively abundant on the above-mentioned icy bodies, we can expect to observe $\text{NH}_2\text{CH}_2\text{COOH}$. Glycine is

the simplest amino acid, used by living organisms to make proteins. No amino acid has been detected in interstellar space. On the other hand, several amino acids and their precursors have been detected in comets and meteorites, such as the Murchison meteorite (Glavin et al., 2010; Kayanuma et al., 2017). For example, glycine has been found in comet 67P/Churyumov-Gerasimenko (Altwegg et al., 2016), supporting the idea that the fundamental building blocks of life may be present in large abundance on frozen moons and cold objects in the outer Solar System.

Alternatively, $\text{NH}_2\text{CH}_2\text{CN}$ may react with NCCN (cyanogen) to produce diaminomaleonitrile ($\text{C}_4\text{H}_4\text{N}_4$), which subsequently reacts with HCN to produce adenine ($\text{C}_5\text{H}_5\text{N}_5$), as follows:



In relation to the reaction (13) to form DAMN (diaminomaleonitrile), we believe that cyanogen can be a precursor of this molecule from the chemical study to understand the reaction mechanism involving HCN and CN radicals from literature. Since $\text{NH}_2\text{CH}_2\text{CN}$ originates from of a reaction involving HCN (Danger et al. 2011), we suggested the role of NCCN to provides a simpler route to the formation of $\text{C}_4\text{H}_4\text{N}_4$. This is also supported by studies of Gupta et al. (2012) which discusses the possibility of formation of DAMN from H and CN radicals, which has been explored on the basis of radical–radical and radical–molecule interaction schemes using quantum chemical methods. The authors record that cyanogen may give rise to the formation of a neutral intermediates molecules in the formation of DAMN, which lead to the formation of adenine. Theoretical calculations will help to clarify this issue.

We also propose a mechanism of formation of adenine in which cyanogen may react with Cyanomethanimine, forming Aminomethanetricarbonitrile ($\text{C}_4\text{H}_2\text{N}_4$), than reacts with methylenimine:



Thus, our data indicate that NCCN might be an important intermediate in the production of more complex nitrile dimers, as those proposed as precursor of adenine, which was always presumed to be the product of HCN pentamerization. Previous experiments (Pilling et al., 2009), employing soft X-rays (broadband photons with energies between 0.5-3 keV) on similar $\text{N}_2\text{-CH}_4$ ice at 14K, showed the formation of adenine (identified by GCMS and ^1H -RMN techniques) after 73 h of continuous exposure to radiation (corresponding to a fluence of 3×10^{21} photons cm^{-2} or an energy fluence of $\sim 10^{12}$ erg cm^{-2}). Both experiments confirm previous results which showed that the organic chemistry on the other solar system bodies can be very complex and extremely rich in prebiotic compounds. Such molecules on early earth have found a place to flourish, leading to the emergence of life as we know.

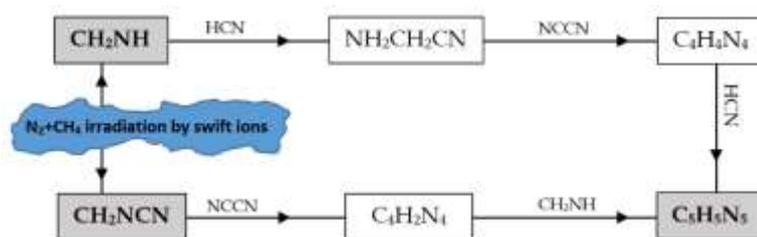


Fig. 6. Possible formation mechanisms of Adenine ($\text{C}_5\text{H}_5\text{N}_5$) based on the Methylenimine e Cyanomethanimine species, observed in this study as result of radiolysis of $\text{N}_2\text{-CH}_4$ ice by swift ions.

5. Conclusions

In this work, a $\text{N}_2\text{-CH}_4$ (90:10) ice mixture was irradiated by 38.4 MeV $^{40}\text{Ca}^{9+}$ (0.96 Mev/u) at 9K in attempt to simulate the role of medium mass cosmic rays and energetic solar particles in the processing of nitrogen-rich ices and the production of organic species in cold astrophysical environments, such as those found in the outer region of the Solar System. The experiment was performed at the GANIL facility in Caen/France and

the sample was analysed by in-situ FTIR technique. The total experiment time was around 25 h and the employed maximum ion fluence was 3×10^{13} ion cm^{-2} . Some of our more important conclusions are summarized below:

1. Bombardment of $\text{N}_2 + \text{CH}_4$ ices produce methylenimine and cyanomethanimine, which of interest in prebiotic chemistry.
2. HCN, HNC, CH and NH radicals are important species in reaction pathways to the production of Methylenimine, while CH_2N_2 and C_2H_2 are key ingredients in the cyanomethanimine production.
3. The results from the IR (estimated) spectra of volatiles species produced during irradiation might help to understand the role of these species in the surface chemistry when these ices are exposed to external or internal heating process, such as cometary and meteoritic impacts, lightning or corona discharges, tidal forces into icy objects of outer Solar System.
4. Methylenimine and cyanomethanimine can participate in reaction pathways, with Aminomethanetricarbonitrile ($\text{C}_4\text{H}_2\text{N}_4$) and Cyanogen (NCCN), which may lead to the formation of Adenine ($\text{C}_5\text{H}_5\text{N}_5$), one of the building blocks of the DNA molecule.

Additional support from the recent analysis of prebiotic species on the surface of icy objects in the outer Solar System by space missions will reveal evidence of organic materials and thus, the formation and origin of biomolecules of particular interest for understanding the steps that led to the appearance of life.

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