Infrared study of ion-irradiated N$_2$-dominated ices relevant to Triton and Pluto: formation of HCN and HNC

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Abstract

Infrared spectra and radiation chemical behavior of N$_2$-dominated ices relevant to the surfaces of Triton and Pluto are presented. This is the first systematic IR study of proton-irradiated N$_2$-rich ices containing CH$_4$ and CO. Experiments at 12 K show that HCN, HNC, and diazomethane (CH$_2$N$_2$) form in the solid phase, along with several radicals. NH$_3$ is also identified in irradiated N$_2$ + CH$_4$ and N$_2$ + CH$_4$ + CO. We show that HCN and HNC are made in irradiated binary ice mixtures having initial N$_2$/CH$_4$ ratios from 100 to 4, and in three-component mixtures have an initial N$_2$(CH$_4$ + CO) ratio of 50. HCN and HNC are not detected in N$_2$-dominated ices when CH is replaced with C$_2$H$_2$, C$_2$H$_4$, or CH$_3$O.

The intrinsic band strengths of HCN and HNC are measured and used to calculate G(HCN) and G(HNC) in irradiated N$_2$+CH$_4$ and N$_2$+CH$_4$+CO ices. In addition, the HNC/HCN ratio is calculated to be ~1 in both icy mixtures. These radiolysis results reveal, for the first time, solid-phase synthesis of both HCN and HNC in N$_2$-rich ices.

We examine the evolution of spectral features due to acid–base reactions (acids such as HCN, HNC, and HNCO and a base, NH$_3$) triggered by warming irradiated ices from 12 K to 30–35 K. We identify anions (OCN$^-$, CN$^-$, and N$_3^-$) in ices warmed to 35 K. These ions are expected to form and survive on the surfaces of Triton and Pluto. Our results have astrobiological implications since many of these products (HCN, HNC, HNCO, NH$_3$, NH$_4$OCN, and NH$_4$CN) are involved in the syntheses of biomolecules such as amino acids and polypeptides.

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1. Introduction

Near-infrared (IR) observations reveal that nitrogen-rich ice containing small amounts of methane (CH$_4$) and carbon monoxide (CO) is abundant on the surfaces of Pluto and Triton, a moon of Neptune (Cruikshank et al., 1993, Owen et al., 1993). Detailed comparisons between observations and laboratory spectra indicate an N$_2$ + CH$_4$ + CO mixture on Triton of 100:0.1:0.05 (Quirico et al., 1999). Frequencies of the observed CH$_4$ bands confidently indicate that this molecule exists in a diluted state in solid nitrogen at or above 35.6 K, although some regions of pure CH$_4$ are consistent with bidirectional reflectance models for the surface. Also observed on Triton, separated from the nitrogen-rich regions, are terrains containing H$_2$O + CO$_2$ ices. For Pluto, which has a surface temperature of ~40 K, similar detailed comparisons between observations and laboratory spectra indicate an N$_2$ + CH$_4$ + CO mixture of 100:0.5:0.25 (Doute et al., 1999). Here the CH$_4$ is diluted in N$_2$, but it is not as segregated as on Triton. IR signatures of either pure CH$_4$ or CH$_4$ with a small fraction of nitrogen are also detected, as are regions of nearly pure N$_2$, and dark regions possibly from processed organics (Grundy and Buie, 2001). Although not excluded from reflectance models fitting Pluto’s spectrum, H$_2$O does not seem to be necessary. For both Pluto and Triton, N$_2$, CH$_4$, and CO sublime and condense in a complex manner during their seasonal cycles (Grundy and Stansberry, 2000).
Although both Triton and Pluto are at 35–40 K, their surface ices can still undergo chemical alterations due to the presence of various ionizing radiations. Solar UV photons, the solar wind plasma, and cosmic rays are all present, but it is the cosmic ray source that dominates at the surfaces of Triton and Pluto. The solar UV and wind fluxes are greatly diminished at the distances of Triton and Pluto (30.1 and 39.4 AU, respectively), and any UV photons that do interact with these worlds are absorbed in their tenuous atmospheres (rough UV penetration depth of about 3 μm-atm or less). Ignoring the expected deflection of solar wind plasma (e.g., Bagental and McNutt, 1989), keV ions will deposit their energy in the upper atmospheres. As a result, some atmospheric chemistry will be induced by the solar UV and wind fluxes, and by Neptune’s magnetospheric electron flux as well, in the case of Triton (see discussion by Delitsky and Thompson, 1987, and Krasnopolsky and Cruikshank, 1995).

Although products formed from atmospheric photolysis and radiolysis may precipitate onto ice surfaces, influencing the ices’ reflectance, the ice chemistry of Triton and Pluto is dominated by the more penetrating radiations, namely the galactic cosmic rays (GCR). Johnson (1989) examined the radiation environment of Pluto and showed that surface doses from cosmic ray bombardment were small per orbit (∼9 × 10⁻⁶ eV molecule⁻¹ in the top 10 g cm⁻² layer) for MeV protons. The same GCR flux at Triton would result in ∼6 × 10⁻⁶ eV molecule⁻¹ in the top 10 g cm⁻² layer per orbit. Over 4.6 billion years, the accumulated dose for Pluto and Triton is ∼165 eV molecule⁻¹. For Triton, more complete modeling by Delitsky and Thompson (1987) examined how the GCR dose in the surface depends on the density of the atmosphere. They calculated that over 4.6 billion years, 167–293 eV molecule⁻¹ is deposited in the upper ∼10 m. For comparison, ices irradiated with only a few eV molecule⁻¹ are expected to form detectable IR signatures of C₂H₂, based on 1-MeV proton radiolysis of H₂O + CH₄ (7:1) (Moore and Hudson, 1998) and 7.3-MeV proton radiolysis of pure CH₄ ice (Kaiser and Roessler, 1998). Typically, organics mixed with ices become “red” after a dose of ∼100 eV molecule⁻¹ (e.g., Andronico et al., 1987). It is the long-term accumulation of organic radiation products that can alter the average reflectance of icy surfaces and produce detectable IR features of radiation products.

From laboratory studies of energetically processed C- and N-containing ices (e.g., Allamandola, 1988; d’Hendecourt et al., 1986; Foti et al., 1984; Hagen et al., 1979; Johnson, 1989; Khare et al., 1989; Lanzerotti et al., 1987; Moore et al., 1983; Strazzulla et al., 1984; Thompson et al., 1987; and references therein) we know that there is a net loss of hydrogen, and complex and often colored and/or dark organic products are formed. The formation of several CN-bonded species has been documented in IR spectra of a few ion-irradiated N₂-containing ices (Strazzulla and Palumbo, 2001; Hudson et al., 2001). Irradiated N₂ + H₂O + CH₄ (1:1:1) and N₂ + CH₃OH (1:1) ices mixtures formed new features at 2260, 2168, and 2085 cm⁻¹, which were attributed to HNCO, and OCN species, and HCN, respectively (Strazzulla and Palumbo, 2001). Similarly a more nitrogen-rich mixture, N₂ + H₂O + CH₄ (100:4:10), showed the same CN features after irradiation (Strazzulla and Palumbo, 2001; Satorre et al., 2001). Hudson et al. (2001) identified the 2168-cm⁻¹ feature as the OCN⁻ ion in both N₂ + H₂O + CH₄ (1:1:1) and N₂ + H₂O + CO (1:5:1). HNCO was shown to form in irradiated N₂ + H₂O + CO. Only one report (Bohn et al., 1994), however, focuses on energetically processed N₂-rich mixtures relevant to the segregated ices of Triton and Pluto. In that paper, IR spectra of UV-photolyzed N₂ + CH₄ (200:1) and N₂ + CH₄ + CO (200:1:1) were measured. The formation of CH₂N₂, CH₃, and C₂H₂ was reported for N₂ + CH₄ ice, along with weaker features characteristic of alkynes and amines. In UV-photolyzed N₂ + CH₄ + CO ice, CH₂N₂, CH₃, C₂H₂, HCO, H₂CO, and (CHO)₂ were identified.

In the present paper, we describe the first systematic IR study of proton-irradiated N₂-rich ices relevant to Triton and Pluto. We chose the mid-IR spectral region since it contains strong diagnostic infrared absorptions of molecules making it the prime region for identification of species, as opposed to the near-IR region, which contains weaker overtone absorption bands. We include results on pure N₂, CH₄, and CO, along with the binary mixtures CO + CH₄, N₂ + CO, and N₂ + CH₄ and the three-component mixture N₂ + CH₄ + CO. These ices were ion-irradiated at 12 K to study the formation and stability of new species. Important goals were to identify new products, to investigate pathways for the synthesis of CN-bonded species, and to consider complications introduced by the presence of CO. To determine likely products participating in pathways, it was necessary to examine 12-K spectra where radicals and other reactive species were isolated prior to their diffusion and reaction as the temperature was raised. In N₂-rich ices containing CH₄ we observed the formation of HCN, HNC, and NH₂. The evolution and stability of these products were followed by warming to T = 35 K, where OCN⁻, CN⁻, N₃⁻, and NH₃⁺ were identified. We discuss the importance of N₂-rich mixtures containing CH₄ and show that radiation chemistry results in a condensed-phase pathway for the synthesis of several species containing CN bonds. We conclude that similar species are likely to exist on the surfaces of Triton and Pluto and review the current detection of such species in both interstellar and cometary environments. A condensed-phase route to such CN-bonded species (e.g., HCN, HNC, OCN⁻, and CN⁻) has astrobiological significance since similar molecules have been used as precursors for the abiotic synthesis of compounds such as amino acids and the nucleic acid adenine (Oro, 1960).

2. Experimental methods

Details of the experimental setup, ice preparation, IR spectral measurements, cryostat, UV lamp, and proton beam
source have been published (Moore and Hudson, 1998, 2000; Hudson and Moore, 1995). In summary, ice samples were formed by condensation of gas-phase mixtures onto a precooled aluminium mirror at \(-12\) K, although some experiments were performed at slightly higher temperatures. Compositions of the resultant ices were determined from the partial pressures of gases in the original mixtures. The vapor deposition technique produces an intimately mixed ice dominated by \(N_2\). Most ice films were several micrometers thick, as determined by a laser interference fringe system. IR spectra were recorded as a function of temperature in some experiments, as the ice temperature could be maintained between 12 and 300 K.

Mid-IR spectra (4000 to 400 cm\(^{-1}\)) were taken before and after energetic processing of ices by diverting the beam of an FTIR spectrometer (Mattson Instruments) toward the ice-covered mirror, where it passed through the ice before and after reflection at the ice-mirror interface. Typically 60-scan accumulations were used for 4-cm\(^{-1}\) resolution spectra and 120-scan accumulations for 1-cm\(^{-1}\) spectra.

Ices were processed by turning them to face either a beam of 0.8-MeV protons, generated by a Van de Graaff accelerator, or UV photons from a microwave-discharged hydrogen flow lamp. The use of proton irradiation to simulate cosmic-ray bombardment has been discussed in other papers (e.g., Moore et al., 2001; Moore et al., 1983). We used standard relations to estimate a stopping power of 323 MeV cm\(^{-1}\) (Chatterjee, 1987) and a range of \(\sim 20\) \(\mu\)m (\(\sim 0.5 \times 10^{20}\) molecule cm\(^{-2}\)) for 0.8-MeV protons in solid \(N_2\) (see www.srim.org). Based on this range, we know that incident protons in our experiment passed through the ices and came to rest in the substrate mirror. Dominant radiative-chemical reactions triggered by laboratory 0.8-MeV protons are the same as those triggered by a range of higher MeV GCR protons (up to \(\sim 110\) MeV) that penetrate the top 10 cm (\(\sim 10^{22}\) molecule cm\(^{-2}\)) of the surfaces of Triton and Pluto. Unless otherwise noted, dose calculations are specific to the mass of the dominant molecule in the ice mixture, \(N_2\) (1 eV molecule\(^{-1}\) = 1 eV (28 amu molecule\(^{-1}\)).

Results from several UV-photolysis experiments are included to show similarities to and differences from proton bombardment experiments. Our recent lamp calibrations show that the average incident photon’s energy is 7.41 \(\pm\) 0.23 eV and the flux is 3.1 \(\times\) \(10^{18}\) photons cm\(^{-2}\) s\(^{-1}\). Gerakines et al. (2000) described in detail the methods by which photolytic and radiation doses can be calculated and compared.

Band strengths of HCN and HNC were needed to determine column densities and yields in different radiation experiments. The intrinsic band strength, \(A(\nu)\), in cm molecule\(^{-1}\) was determined from the band area \(\int \tau(\nu) d\nu\), in cm\(^{-1}\), using

\[
A = \frac{\int \tau(\nu) d\nu}{N},
\]

where \(N\), the column density (molecule cm\(^{-2}\)), was calculated from the total film thickness, the gas-phase ratio of \(N_2/\text{HCN}\), and the density of \(N_2\) ice (1.027 g cm\(^{-3}\), Scott, 1976). We found \(A(\nu_1 \text{ HCN}) = 1.1 \times 10^{-17} (\pm 0.46, -0.29) \text{ cm molecule}^{-1}\) in \(N_2\) at 12 K.

\(A(\text{HNC})\) was estimated indirectly. We observed that during irradiation (or UV photolysis) at 12 K, HCN isomerized to HNC. Assuming each HNC comes from the rearrangement of one HCN, the decrease in band intensity of HCN is directly proportional to the increase in band intensity of HNC. This assumption results in a calculation of a lower limit for \(A(\text{HNC})\). A plot of the decreasing area of an HCN band against the increasing area of an HNC band has a slope equal to \(A(\text{HNC})/A(\text{HCN})\). Taking \(A(\nu_1 \text{ HCN}) = 1.1 \times 10^{-17} (\pm 0.46, -0.29) \text{ cm molecule}^{-1}\), we found \(A(\nu_1 \text{ HNC}) = 5.1 \times 10^{-18} (\pm 5.1, -2.2) \text{ cm molecule}^{-1}\). The average and uncertainty are calculated for \(A(\text{HNC})\) from four spectra in one experiment and for \(A(\text{HNC})\) from four spectra in two different experiments.

Initial yields of HCN and HNC were calculated by determining the slope of the linear portion of a plot of column density vs energy dose (eV cm\(^{-2}\)). Initial yields, as opposed to equilibrium abundances, are given since we are interested in product formation from direct interaction of the radiation with the original reactant molecules, and not yields averaged over the course of the entire radiation experiment (see discussion in Gerakines and Moore 2001). The production yield is given as a \(G\)-value, the number of molecules formed per 100 eV of energy deposited. We calculated \(G(\text{HCN}) = 0.066 \pm 0.014\) and \(G(\text{HNC}) = 0.067 \pm 0.007\) in \(N_2 + \text{CH}_4 (100:1)\) ices; \(G(\text{HCN}) = 0.023 \pm 0.002\) and \(G(\text{HNC}) = 0.025 \pm 0.001\) in \(N_2 + \text{CH}_4 + \text{CO (100:1:1) ices after a dose of \(\sim 2\) eV molecule\(^{-1}\). The uncertainty is the error in the slope of a linear fit to the data.

Most ice mixtures were irradiated or photolysed at 12 K, a temperature below the expected surface temperatures of 30–35 K for Triton and Pluto. \(N_2\) and CO sublime rapidly in our \(10^{-8}\)-torr vacuum when warmed to 35 K since their vapor pressures are in the ranges 10\(^{-3}\) and 10\(^{-4}\) torr, respectively (Honig and Hook 1960). \(\text{CH}_4\) is less volatile at 35 K, with a vapor pressure in the range \(10^{-7}\) torr. After processing, our ices were warmed and spectra were recorded at 30–35 K. In some cases spectra of less volatile species were recorded up to room temperature.

Reagents used and their purities are as follows: \(N_2\) (Air Products research grade, 99.9995%), \(^{15}\)N\(_2\) (Aldrich, 98%), CO (Matheson, 99.99%), \(\text{CH}_4\) (Matheson, 99.99%), \(\text{CD}_4\) (MSD Isotopes, 99.2% atom D), \(^{13}\)CH\(_3\) (Monsanto Research Corp., 99% atom \(^{13}\)C), \(\text{C}_2\text{H}_2\) (Matheson, purified using appropriate ice bath to remove acetone), \(\text{C}_2\text{H}_6\) (Air Products, CP grade), \(\text{C}_3\text{H}_4\) (Matheson, 99.99%), \(\text{CH}_3\text{OH}\) (Aldrich, HPLC grade). HCN was synthesized in a vacuum manifold by combining KCN and stearic acid (both from Eastman Kodak) in nearly equal molar ratios and heating to approximately 353 K. The gases released were collected in a glass bulb cooled by liquid \(N_2\). An acetone slush bath at
178 K was used to separate the HCN from impurity gases such as CO₂.

3. Results

3.1. Results at low temperature (T = 12 K)

Presentation of our results begins with experiments involving pure N₂, CO, and CH₄ ices. Next, we consider the binary mixtures CO + CH₄, N₂ + CO, and N₂ + CH₄. Finally we examine the more complex three-component mixture, N₂ + CO + CH₄. This provides a self-consistent approach to understanding the chemical results. Experiments comparing IR products in proton-irradiated and UV-photolyzed pure N₂- and CO-ice have been published, as have studies of ion irradiation and UV-photolysis products in pure CH₄. Therefore we combine here our new observations with those previously reported for pure ices to lay the foundation for understanding the mixtures examined.

3.1.1. Pure N₂

Since N₂ has no permanent dipole moment, it has no IR-allowed features. However, the mid-IR spectrum of solid N₂ at 12 K shows a weak forbidden transition at 2328.2 cm⁻¹ that is significantly enhanced by the presence of CO₂ (Sandford et al., 2001, and Bernstein and Sandford, 1999). It is also known that bombardment of pure solid N₂ with either 4 keV Ne/Ne²⁺ (Tian et al., 1988) or 120 eV N atoms (Khabashesku et al., 1997) produces the N₁ radical (1657 cm⁻¹), an electrically neutral species with an unpaired electron in its outer orbital. N₁, like many free radicals, can be stabilized in low-temperature matrices, but reacts quickly during warming. In our experiments, the N₁ radical was observed after proton bombardment of solid N₂, but not after UV photolysis. Thus N₁ is a signature of radiolysis. In a recent paper (Hudson and Moore, 2002) N₁ radical formation in both pure N₂ and N₂-rich ices is examined. The N₂-rich ices studied in our current experiments are listed in Table 1 along with the positions of the observed N₁ band.

Green luminescence was observed from N atoms during radiolysis of pure N₂, and on warming irradiated N₂. This luminescence has been characterized through many experiments (e.g., Peyron and Broida, 1959). No luminescence was detected during UV photolysis experiments or on warming UV-photolyzed N₂ ices.

3.1.2. Pure CO

Major products identified in proton-irradiated CO ice were CO₂ at 2343 cm⁻¹ and C₃O₂ at 2242 cm⁻¹. In UV-photolyzed CO, the major product was CO₂ (spectra not shown). Table 1 lists major radiation products and their peak positions. In a recent paper by Gerakines and Moore (2001), a detailed comparison of mid-IR spectra of pure CO before and after radiolysis and photolysis was presented. Included were details of the formation and thermal stability of C₂O₂, a molecule that can polymerize to form a more stable dark reddish-brown material. Formation yields for C₂O₂ were G(C₂O₂) radiolysis = 0.2 and G(C₂O₂) photolysis = 0.01.

3.1.3. Pure CH₄

Figure 1 shows the mid-IR spectrum of pure solid CH₄ at 12 K before and after processing with both protons and UV photons. Bands of CH₄ at 3011 cm⁻¹ (ν₃) and 1298 cm⁻¹ (ν₁) dominate the spectrum of the freshly deposited ice. After processing, dominant new IR features are due to C₂H₆, C₂H₄, and C₂H₂. Also detected was a weak band at 3269 cm⁻¹, attributed to C₂H₂. Each numbered feature in Fig. 1 is identified in Table 1. Identifications were made by matching the position and relative intensity of each product band with appropriate solid-phase reference spectra.

We compared our results with earlier work on processed CH₄ ice. Kaiser and Roessler (1998) studied solid methane after irradiation with 9-MeV α-particles and 7.3-MeV protons. They analyzed irradiated CH₄ using mid-IR spectroscopy and probed gases released during warm-up through mass spectrometry. New molecules were identified in the IR (e.g., C₂H₆, C₂H₄, and C₂H₂), along with some less abundant, larger mass species. Gerakines et al. (1996) used IR to examine the complex photochemistry of pure CH₄ at 10 K and identified C₂H₆, C₂H₄, and C₂H₂ as major products. Baratta et al. (2002) compared the loss of CH₄ after UV photolysis and 30-keV He⁺ bombardment. They showed that at <20 eV (16 amu⁻¹) both processes give similar results, but at higher doses, impinging ions modify the entire sample while UV photons cause fewer modifications since they are absorbed at increasingly smaller depths. Other studies, e.g., Davis and Libby (1964) and Calcagno et al. (1985), formed and analyzed room-temperature residues from processed CH₄ ice. These last two studies are less relevant to our low-temperature radiation chemistry focus, but are important for documenting the overall loss of H and the evolution of pure CH₄ toward a dark, carbon-rich film.

3.1.4. CO + CH₄

Experiments were performed on CO + CH₄ ice mixtures and are included here for the sake of completeness (spectra not shown). A CO + CH₄ (100:1) mixture was ion-irradiated, and a 50:1 CO + CH₄ ice was photolyzed. Interestingly new observations were of bands at 1380 and 1127 cm⁻¹, probably from ketene (Moore et al., 1965), at 619 cm⁻¹ for CH₂ (Milligan and Jacox, 1967a), at 2026 cm⁻¹ for HCCO (Forney et al., 1995), and at 2489, 1859, and 1090 cm⁻¹ for the formyl radical, HCO (Milligan and Jacox, 1964). Table 1 lists major products and their peak positions.

3.1.5. N₂ + CO

New features appearing in processed solid N₂ + CO (100:1) at 12 K are shown in Fig. 2. The spectrum before processing contains only the bands of CO at 2139 cm⁻¹ and ¹³CO at 2092 cm⁻¹. Comparing results from proton-irradi-
ated and UV-photolyzed ices shows that both processes form CO$_2$ efficiently. Products N$_2$O, NO$_2$, and NO are numbered in Fig. 2 and identified in Table 1. N$_3$ and OCN radicals were formed only in ion-irradiated N$_2$ + CO. Major features identified in our UV-photolyzed ice (spectra not shown) are consistent with those reported by Elsila et al. (1997). Although C$_3$O$_2$ was efficiently formed in pure, irradiated CO ices, in N$_2$-rich ices only a weak feature at 2253 cm$^{-1}$ is identified with matrix-isolated C$_3$O$_2$. This feature at 2253 cm$^{-1}$ and other weak features in the region 2200 cm$^{-1}$ agree in position with a more intense complex band formed in irradiated N$_2$ + CO (1:1), attributed to C$_3$O$_2$.

3.1.6. N$_2$ + CH$_4$

Mid-IR spectra of N$_2$ + CH$_4$ (100:1) before and after processing are shown in Figs. 3 and 4. In the unprocessed ice, the bands of CH$_2$ at 3014 cm$^{-1}$ ($v_6$) and 1302 cm$^{-1}$ ($v_4$) dominate. Small features were detected due to the forbidden transition of N$_2$ (2328 cm$^{-1}$) and to H$_2$O (3726 and 1598 cm$^{-1}$) and CO$_2$ (2349 cm$^{-1}$) impurities. New features (e.g., HNC, HCN, NH$_3$, and the N$_3$ radical, along with diazometh-
1.2

1.0

Cs

uO 0.8

C

Cs

-2

0.6

-0.4

Cs

0.2

0.0

Wavelength (m)

3.5 4.0

10 15 20

2000

3000 2750 2500 1500 1000 500

Wavenumbers (cm-1)

Fig. 1. Mid-IR spectrum of pure CH4 (thickness ~4 μm) deposited at 12 K, compared with the same ice after proton irradiation to a dose of ~1 eV (16 amu molecule)-1. The spectrum of photolyzed CH4 at 12 K from Gerakines et al. (1996) is included for comparison. Positions and identifications of numbered features are listed in Table 1. New molecules identified after processing are C2H2, C2H6, C2H4, and C3H8.

C2H2 is numbered in Figs. 3 and 4 and identified in Table 1. Although C2H2, C2H6, C2H4, and C3H8 are formed in irradiated pure CH4-ice, only a small signature of C2H6 is detected in the IR spectrum of processed N2 + CH4 (100:1) mixtures, where most CH4 molecules are surrounded by N2.

The spectrum of ion-irradiated N2 + CH4 shows features identified as HNC, HCN, NH3, and the N3 radical, along with CH2N2 (Pacansky et al., 1981) and HCN2 (Ogilvie, 1968) radicals. These results demonstrate a condensed-phase pathway for the formation of acids HNC and HCN and a base (NH3) in N2-rich ices containing CH4.

The spectrum in Figs. 3 and 4 for the UV-processed N2 + CH4 was recorded after simultaneous photolysis and deposition for ~2 h. The resulting ice thickness was ~6 μm. The major products we detected, CH2N2, C2H6, and the CH3 radical, were the same as those reported by Bohn et al.

0.00 0.04 0.08 0.12 0.16 0.20 0.24 0.28 0.32 0.36 0.40 0.44 0.48 0.52 0.56 0.60 0.64 0.68 0.72 0.76 0.80 0.84 0.88 0.92 0.96 1.00 1.04 1.08 1.12 1.16 1.20 1.24 1.28 1.32 1.36 1.40 1.44 1.48 1.52 1.56 1.60 1.64 1.68 1.72 1.76 1.80 1.84 1.88 1.92 1.96 2.00 2.04 2.08 2.12 2.16 2.20 2.24 2.28 2.32 2.36 2.40

Relative Absorbance

Wavelength (μm)

3 4 5

Relative Absorbance

Wavelength (μm)

1 2 3 4 5 6 7

Fig. 2. Mid-IR spectrum from 2500 to 1600 cm-1 of N2 + CO (100:1) (thickness ~3.5 μm) deposited at 12 K, compared with that same ice after proton irradiation to a dose of ~1 eV molecule-1. Identifications and band positions of numbered features are given in Table 1.

Fig. 3. Spectra from 4000 to 2000 cm-1 of N2 + CH4 (100:1) (thickness ~3 μm) before and after processing at 12 K. This spectral region contains the ν4 CH4 band. New features formed in the ice after irradiation (dose of ~1 eV molecule-1) are numbered and identified in Table 1. For comparison, a spectrum of photolyzed N2 + CH4 (100:1) is also shown. New molecules in the irradiated ice include HCN (747 cm-1), CH2N2 (1407 and 881 cm-1), and NH3 (971 cm-1).

Fig. 4. Spectra from 1900 to 400 cm-1 of N2 + CH4 (100:1) (thickness ~3 μm) before and after processing at 12 K. This spectral region contains the ν3 CH4 band. New features formed in the ice after irradiation (dose of ~1 eV molecule-1) are numbered and identified in Table 1. For comparison, a spectrum of photolyzed N2 + CH4 (100:1) is also shown. New molecules in the irradiated ice include HCN (747 cm-1), CH2N2 (1407 and 881 cm-1), and NH3 (971 cm-1).
Bohn et al., 1994). Solid solutions of HzI was observed and attributed to acetylene feature of HCN was easily detected in irradiated of the strongest band of HCN since its position was near the intensities at 3286 cm\(^{-1}\). For an HCN is also the most intense band when it is diluted in strongest band was at 3130 cm\(^{-1}\). Masterson and Khanna (1990) reported \(n\) and \(k\) values for pure solid HCN at 60 K and showed that its band positions were consistent with those reported in matrix isolation studies by King and Nixon (1968) and Milligan and Jacox (1967a, 1967b). These assignments are facilitated by the well-separated IR positions of DCN, DNC, and \(\text{C}_2\text{D}_2\). Good evidence that acetylene is not a major contributor in an irradiated \(\text{N}_2 + \text{C}_4\) mixture is the presence of only a very weak \(v_5\) \(\text{C}_2\text{D}_2\) feature at 2435 cm\(^{-1}\) (Bagdanskis and Bulanin, 1972) in Fig. 5. This point is important because it implies that HCN is the major source of the 3286 cm\(^{-1}\). Further support of the HNC and HCN identifications comes from our examination of an irradiated mixture of \(^{15}\text{N}_2 + \text{CH}_4\) (100:1) (spectrum not shown) and the identification of \(^{15}\text{N}\) at 3553 cm\(^{-1}\) and \(^{13}\text{C}\) at 3285 cm\(^{-1}\) (i.e., \(^{15}\text{N}\)-shifts of -12 and -1). Similarly, irradiated \(\text{N}_2 + ^{13}\text{CH}_4\) (100:1) showed the formation of \(^{13}\text{N}\) and \(^{13}\text{C}\) at 3562 and 3268 cm\(^{-1}\), respectively, \(^{13}\text{C}\)-shifts of -3 and -18 cm\(^{-1}\). All shifts observed in the hydrogen isocyanide and hydrogen cyanide isotopomers are consistent with those found in an argon matrix (Mickle and Andrews, 1990) \(^{15}\text{N}\)-shifts of -12 and -1 \(^{13}\text{C}\)-shifts of -1 and -17 cm\(^{-1}\).

Fig. 6 shows that HCN and HNC were detected in irra-

\(\nu_5\) fundamental at 748 and 743 cm\(^{-1}\) (Bagdanskis et al., 1970). However, nearly identical positions are found for the 3286 cm\(^{-1}\) \((v_3)\) and 746 cm\(^{-1}\) \((v_5)\) bands of HCN. Therefore, it was necessary to explore in more detail the HCN identification using various isotopomers.

A comparison of irradiated \(\text{N}_2 + \text{CH}_4\) and \(\text{N}_2 + \text{C}_4\) (100:1) is shown in Fig. 5, along with the spectrum of photolyzed \(\text{N}_2 + \text{C}_4\). Features identified with HNC and HCN are at 3565 and 3286 cm\(^{-1}\) (respectively) in the \(\text{N}_2 + \text{CH}_4\) ice. Both irradiated and photolyzed \(\text{N}_2 + \text{C}_4\) had features at 2728 and 2616 cm\(^{-1}\) assigned to DNC and DCN, respectively (Milligan and Jacox, 1967a; King and Nixon, 1968). These assignments are facilitated by the well-separated IR positions of DCN, DNC, and \(\text{C}_2\text{D}_2\).

Fig. 5. The mid-IR spectrum of irradiated \(\text{N}_2 + \text{CH}_4\) (100:1) at 12 K shows formation of HNC and HCN at 3565 and 3286 cm\(^{-1}\), respectively. Both irradiated and UV-photolyzed \(\text{N}_2 + \text{CD}_4\) (100:1) shows formation of DNC and DCN at 2726 and 2615 cm\(^{-1}\), respectively. (MeV proton dose was \(-1 eV\) molecule\(^{-1}\), UV exposure was \(-7 \times 10^{17}\) UV photons cm\(^{-2}\)) The \(v_5\) \(\text{CD}_2\) band lies at 2258 cm\(^{-1}\), outside the region of this plot. A feature due to \(\text{C}_2\text{H}_2\) is also identified.

(1994) for an \(\text{N}_2 + \text{CH}_4\) ice (200:1). After photolysis we also identified \(\text{C}_2\text{H}_6\) in the 100:1 mixture at 12 K. Weak features in the Bohn et al. (1994) experiment also point to the possible presence of HNC and HCN, but it is difficult to interpret the presence or absence of such weak signatures without additional work. Our photolyzed \(\text{N}_2 + \text{CH}_4\) sample was also examined for the formation of HCN and HNC, but potential signatures were very weak.

Identification of the \(v_5\) bands of HCN and HNC in \(\text{N}_2\) matrices was made by comparison to an \(\text{N}_2 + \text{HCN}\) (200:1) ice, which had been proton-irradiated to form HNC (reference spectrum shown in Fig. 6). Our HNC and HCN band positions were consistent with those reported in matrix isolation studies by King and Nixon (1968) and Milligan and Jacox (1967a, 1967b).

The relative intensities of different HCN bands have been studied in the past and are relevant to our work. For example, Masterson and Khanna (1990) reported \(n\) and \(k\) values for pure solid HCN at 60 K and showed that its strongest band was at 3130 cm\(^{-1}\) \((v_3)\). The \(v_5\) feature of HCN is also the most intense band when it is diluted in \(\text{N}_2\). For an \(\text{N}_2/\text{HCN}\) ratio of 100, we measured the relative intensities at 3286 cm\(^{-1}\) \((v_5)\), 2096 cm\(^{-1}\) \((v_1)\), and 747 cm\(^{-1}\) \((v_2)\) as 1.0:3:0.8.

One problem encountered was the secure identification of the strongest band of HCN since its position was near the \(v_5\) band of \(\text{C}_2\text{H}_2\). As already mentioned, the 3286 cm\(^{-1}\) \((v_3)\) feature of HCN was easily detected in irradiated \(\text{N}_2 + \text{CH}_4\) ice spectra. In photolyzed \(\text{N}_2 + \text{CH}_4\) a weak band at 3270 cm\(^{-1}\) was observed and attributed to acetylene \(\text{C}_2\text{H}_2\) (Bohn et al., 1994). Solid solutions of \(\text{C}_2\text{H}_2\) in an \(\text{N}_2\) matrix showed the \(v_5\) monomeric \(\text{C}_2\text{H}_2\) band at 3282 cm\(^{-1}\) and the
radiated N$_2$ + CH$_4$ for three different N$_2$/CH$_4$ ratios: 100, 50, and 4. Also detected at all ratios were two features of CH$_3$N$_2$, at 2096 and 1406 cm$^{-1}$. The strengths of the aliphatic hydrocarbon features due to C$_2$H$_6$ and C$_2$H$_8$ increased as the initial concentration of CH$_4$ increased. The C$_2$H$_2$ absorption at 3273 cm$^{-1}$ was best seen in the experiment with an N$_2$/CH$_4$ ratio of 4, although its presence in more dilute mixtures is seen as a shoulder of the HCN absorption at 3286 cm$^{-1}$.

In irradiated N$_2$-rich ices, HCN and HNC did not form when CH$_4$ was replaced by other simple aliphatic hydrocarbons. A comparison of products in irradiated 100:1 mixtures of N$_2$ with CH$_4$, C$_2$H$_6$, C$_2$H$_4$, or C$_2$H$_2$ is presented in Fig. 7. Irradiated $^{13}$N$_2$ + C$_2$H$_6$ ($\nu_1$ C$_2$H$_2$ at 2986 cm$^{-1}$) and $^{13}$N$_2$ + C$_2$H$_2$ (spectrum not shown) both formed a band at 3282 cm$^{-1}$ attributed to C$_2$H$_2$. Other products detected between 2600 and 400 cm$^{-1}$ were C$_2$H$_4$ and CH$_4$. Irradiated N$_2$ + C$_2$H$_4$ ($\nu_0$ C$_2$H$_2$ at 3104 cm$^{-1}$) formed C$_2$H$_2$, along with C$_2$H$_6$, C$_2$H$_4$, and CH$_4$. Irradiated N$_2$ + C$_2$H$_2$ ($\nu_3$ C$_2$H$_2$ at 3282 cm$^{-1}$) formed several new weak bands.

To determine trends in product formation, we examined N$_2$ + CD$_4$ (100:1) ices as a function of radiation dose. These experiments were done with CD$_4$, as opposed to CH$_4$, to remove the problem of confusing adjacent IR features (e.g., overlapping HCN and C$_2$H$_2$ bands in the region 3290–3270 cm$^{-1}$), so that band areas could be determined without curve fitting. Fig. 8 plots trends in product formation and loss of CD$_4$ over an extended dose period.

The band areas of DCN, DNC, and CD$_3$N$_2$ showed growth and saturation with increasing radiation dose. The $\nu_4$ band of CD$_4$ (at 993 cm$^{-1}$) decreased with increasing dose as CD$_4$ was destroyed. Based on our 12-K experiment, about half of the CD$_4$ was destroyed after a dose of ~3 eV molecule$^{-1}$. A similar dose on Triton and Pluto would accumulate after ~80 million years of exposure (Johnson, 1989). However, due to the complex transport of volatiles on these icy objects, there may be no stable CH$_4$ so that application of these results is not straightforward.

Finally, in addition to the acids HNC and HCN, the base NH$_3$ was detected at 971 cm$^{-1}$ ($\nu_2$). This is the strongest band of NH$_3$ isolated in an N$_2$ matrix. Its band position and intensity in our work are consistent with matrix isolation studies (Lundell et al., 1998 and references therein) and our own reference spectrum of N$_2$ + NH$_3$ (100:1) (not shown).

3.1.7. N$_2$ + CH$_4$ + CO

HNC and HCN also were detected at 3565 and 3285 cm$^{-1}$, respectively, in irradiated N$_2$ + CH$_4$ + CO (100:1:1), demonstrating formation of these products in the presence of CO. Fig. 9 shows the mid-IR spectrum in the range 3600–2600 cm$^{-1}$ for N$_2$ + CH$_4$ + CO, for N$_2$ + CH$_2$ and for two other ices (discussed in Section 3.1.8.).

After irradiation of N$_2$ + CH$_4$ + CO, the N$_1$ radical was detected at 1656 cm$^{-1}$, and CH$_2$N$_2$ bands were seen at 2096 and 1407 cm$^{-1}$. Table 1 lists observed features from 4000 to 400 cm$^{-1}$, which includes radiation products from both N$_2$ + CO and N$_2$ + CH$_4$ ices along with NH$_3$ and isocyanic acid, HNCO. This acid formed only when both CH$_4$ and CO were present in an N$_2$-rich ice. Spectral features of HNCO and CH$_3$N$_2$ in the region 2275–1975 cm$^{-1}$ are shown in Fig. 10.

Other products from photolyzed N$_2$ + CH$_4$ + CO (100:1:1) (spectrum not shown) included CH$_3$N$_2$, C$_2$H$_6$, HCO, and CO$_2$. These are the same products reported by Bohn et al. (1994) for a UV-photolyzed 200:1:1 mixture. Band positions and identifications of UV-products given in Table 1 come from both our results and those of Bohn et al. (1994).
the spectral range from 3600 to 2600 cm$^{-1}$ and 1499 cm$^{-1}$ and CO at 2140 cm$^{-1}$ showed that the major species detected in CH$_3$OH after irradiation.

Ion-irradiated N$_2$ + CH$_4$ + CO ices for three N$_2$/CH$_4$ + CO ratios (50, 5, and 0.5) showed HNC and HCN only when the initial ratio was 50. When the ratio was 5 or 0.5, the dominant products included aliphatic hydrocarbons, CO$_2$, C$_2$O$_3$, and a molecule with a C==O bonded feature at 1720 cm$^{-1}$, probably acetaldehyde.

3.1.8. Other routes to HCN and HNC

Although irradiated N$_2$ ices containing CH$_4$ led to HNC, HCN, and CH$_3$N$_2$, other routes to these species were investigated. As mentioned before, irradiated N$_2$ + C$_2$H$_6$ did not produce HNC, HCN, or CH$_3$N$_2$. Instead, the observed major reaction was the synthesis of C$_2$H$_4$ and C$_2$H$_2$ as hydrogen was lost, with a change from C==C to C==C bonding: H$_2$C==CH$_2$ $\rightarrow$ H$_2$C==CH$_2$ $\rightarrow$ HCC$_2$H.

Since in the search for formation pathways we were not limited by the requirement that the ice composition be relevant to Triton or Pluto, we examined the possible synthesis of HNC and HCN in dilute N$_2$ matrices containing methanol (CH$_3$OH) and methylene (CH$_2$NH$_2$). First we examined CH$_3$OH, a relatively abundant molecule in comets and interstellar ices. CH$_3$OH has one CH$_3$ group connected to OH through a C==O bond. Previously the 2096 cm$^{-1}$ band of HCN was reported in the IR spectrum of irradiated N$_2$ + CH$_3$OH (1:1) (Strazzulla et al., 2001). However, in the dilute mixtures studied in this paper, irradiated N$_2$ + CH$_3$OH (100:1) ice did not show IR features of HNC, HCN, or CH$_3$N$_2$. Instead, bands for H$_2$CO at 1738 and 1499 cm$^{-1}$ and CO at 2140 cm$^{-1}$ showed that the major reaction was the loss of hydrogen and the accompanying change from C==O to C==O to C==O bonding: H$_2$C==OH $\rightarrow$ H$_2$C==O $\rightarrow$ H$_2$C==O. Fig. 9 compares the mid-IR spectrum (in the spectral range from 3600 to 2600 cm$^{-1}$) of protonated N$_2$ + CH$_3$OH (100:1) at 12 K with that of irradiated N$_2$ + CH$_4$ and N$_2$ + CH$_4$ + CO.

The other molecule examined was CH$_3$NH$_2$, which has a CH$_3$ group bonded to an NH$_2$ group through a C==N bond. After irradiation of N$_2$ + CH$_3$NH$_2$ (100:1), HNC and HCN were identified (see Fig. 9). The reaction path probably led from C==N to C==N to C==N bonding: H$_2$C==NH$_2$ $\rightarrow$ H$_2$C==NH $\rightarrow$ HNC $\rightarrow$ HNC and HCN (and HNC==N). Weak signatures of the intermediate product, CH$_3$NH$_2$, detected near 1066, 1129, 1354, 1452, and 1639 cm$^{-1}$ (spectra in this range is not shown) are consistent with this proposed reaction path.

3.2 Results at T $\approx$ 30 K

The ion-irradiation studies of N$_2$ + CH$_4$ (100:1) and N$_2$ + CH$_4$ + CO (100:1:1) described above were performed at $\sim$12 K, below the 35–40 K thought to be relevant for Triton and Pluto (Quirico et al., 1999; Doute et al., 1999). Table 1 lists all of the new products trapped in the N$_2$ matrix at 12 K. The list includes four CN-bonded species, six radicals, NH$_2$, and hydrocarbons. This group contains both acids and bases. Knowing the identity of these reactive species provides important clues for understanding possible chemical reaction pathways during diffusion, as the matrix becomes less rigid with warming. In our experiments, the intensities of sharp IR features of molecules such as HNC, HCN, and HNCO were diminished greatly at 30 K, which is evidence for chemical reactions triggered by warming.

Fig. 10 compares spectra in the ranges 3600–3200 and 2300–1950 cm$^{-1}$ for irradiated N$_2$ + CH$_4$ + CO (100:1:1)
and N$_2$ + CH$_4$ (100:1) ices at 12 K and the same ices warmed to 30–35 K. Sharp features at 12 K attributed to HNCO (3565 and 2030 cm$^{-1}$) and HCN (3285 cm$^{-1}$) and the 2096 cm$^{-1}$ feature attributed to both HCN and CH$_2$N$_2$ were not seen after warming. In addition, features at 2266 cm$^{-1}$ (HNCO), 2040 cm$^{-1}$ (the CN radical), and 2003 cm$^{-1}$ (the free azide ion, N$_3^-$ (Tian et al., 1988)) disappear after warming.

The relatively sharp feature of HNCO was detected in the N$_2$ + CH$_4$ + CO irradiated ice at 12 K. A small feature attributed to HNCO in the N$_2$ + CH$_4$ ice comes from CO formation from a CO$_2$ impurity in the original ice mixture. At 35 K, HNCO is replaced by a broad weaker feature at $\sim$2257 cm$^{-1}$ and the 2166 cm$^{-1}$ band of the OCN$^-$ ion. The formation of OCN$^-$ is consistent with a reaction involving HNCO and NH$_3$, and is direct evidence of an acid–base reaction triggered by raising the temperature.

The 2083 cm$^{-1}$ band formed in irradiated N$_2$ + CH$_4$ (100:1) and N$_2$ + CH$_4$ + CO (100:1:1) ices warmed from 12 to 35 K is evidence of a second acid–base reaction. In this case, HCN and most likely NH$_3$ react to form ammonium cyanide, NH$_4^+$, and CN$^-$. Fig. 11 compares the 2083 cm$^{-1}$ band of irradiated N$_2$ + CH$_4$ (100:1) at 30 K with a spectrum of NH$_2$CN produced by warming an HCN + NH$_3$ ice from 13 K to 50 K (P.A. Gerakines, private communication). The CN-stretch feature of NH$_2$CN is a good match to our 2083 cm$^{-1}$ band. Spectral studies of pure NH$_2$CN at 77 K list a $\equiv$CN stretch at 2095 cm$^{-1}$ (Kanesaka et al., 1984). Furthermore, our identification of the 2083 cm$^{-1}$ band with the CN$^-$ ion is supported by isotopic substitution experiments. Fig. 11 shows that irradiated N$_2$ + CD$_4$(100:1) ice, warmed to 35 K, formed a band at 2084 cm$^{-1}$ with essentially no shift in position from the CH$_4$-containing ice. This implies that the vibration corresponding to the 2083 cm$^{-1}$ band has no contamination from hydrogen. Fig. 11 also shows that similarly irradiated and warmed ice containing $^{13}$CH$_4$ forms a band near 2041 cm$^{-1}$, a shift of $\sim$42 cm$^{-1}$ from the $^{12}$C position. An $^{15}$N$_2$ + CH$_4$ irradiated and warmed ice (spectrum not shown) formed a new band near 2047 cm$^{-1}$, a shift of $\sim$36 cm$^{-1}$ from the $^{14}$N position. These shifts are consistent with those found for CN$^-$ ions in neon matrices by Forney et al. (1992) ($^{15}$CN$^-$ shift of $\sim$42 cm$^{-1}$ and $^{15}$N$^-$ shift of $\sim$31 cm$^{-1}$). In summary, the 2083 cm$^{-1}$ band is attributed to the CN$^-$ ion (most likely NH$_3$ is the cation).

The weak broad feature at 2038 cm$^{-1}$ in irradiated N$_2$ + CH$_4$ (100:1) and N$_2$ + CH$_4$ + CO (100:1:1) ices, warmed to 30–35 K (Fig. 10), is evidence for an azide ion, N$_3^-$. The azide band is weaker than the OCN$^-$ or CN$^-$ bands, and therefore its identification is not as secure. The free (isolated) azide anion can be identified at 2003 cm$^{-1}$ in both 12-K irradiated ice mixtures (Fig. 10), based on IR studies of bombarded N$_2$ ice by Tian et al. (1988). (An anion is an atom or group of atoms that carries a negative charge.) They observed that during annealing, the peak at 2003 cm$^{-1}$ decreased as the matrix warmed and sublimed. We observed the same trend during warming along with the formation of a broad weak band at 2038 cm$^{-1}$, a position consistent with the 2037 cm$^{-1}$ frequency of azides in a KBr lattice (Theophanides and Turrell, 1967). The difference of 39 cm$^{-1}$ between CN$^-$ and N$_3^-$. peak positions increases to 73 cm$^{-1}$ for the $^{15}$N-labeled ions and is consistent with the increase for these species calculated from matrix experiments. (See Forney et al. (1992) for CN$^-$ values and Tian et al. (1988) for N$_3^-$ values.) These identifications are consistent with formation of the azide anion in an irradiated N$_2$ + NH$_3$ ice where the cation, NH$_4^+$, is easy to identify (Hudson et al., 2001). Our observation that a band grows in intensity near 1460 cm$^{-1}$ during the warming of irradiated N$_2$ + CH$_4$ ice is also consistent with NH$_4^+$, but since the region 1460 cm$^{-1}$ overlaps with the $\nu_3$ band of C$_2$H$_4$, the NH$_3^+$ identification is less firm. To summarize, the feature 2038 cm$^{-1}$ is assigned to the N$_3^-$ ion.

Results obtained after warming irradiated ices of N$_2$ + CH$_4$ + CO (100:1:1) show that OCN$^-$, CN$^-$, and N$_3^-$ are part of the residual material above the sublimation temperatures of N$_2$, CH$_4$, and CO. The infrared positions and FWHM of these anions is given in Table 2. Fig. 12 shows spectra (in the region 2150–1925 cm$^{-1}$) of irradiated N$_2$ + CH$_4$ + CO (100:1:1) warmed from 30 to 200 K after irradiation at 12 K. The ion OCN$^-$ is at 2163 cm$^{-1}$, CN$^-$ at 2083 cm$^{-1}$, and N$_3^-$ at 2038 cm$^{-1}$. We show the warm-up of this ice to demonstrate the higher temperature stability of these ions. All three were detected at 150 K; OCN$^-$ is still detected at 200 K. The relative intensities of these ions are affected by initial concentrations of CH$_4$ and CO in the ice, the thickness of the ice, and the warming rate. The role that
4. Discussion

4.1. Mechanisms

We have shown that HCN and HNC form in irradiated N$_2$ + CH$_4$ where the N$_2$/CH$_4$ ratio varied from 100 to 4, and in irradiated N$_2$ + CH$_4$ + CO (100:1:1) ices. N$_2$ ices containing other aliphatics such as C$_2$H$_6$, a longer saturated hydrocarbon, or C$_2$H$_4$ and C$_2$H$_2$, doubly- and triply-bonded molecules respectively, did not show HCN and HNC after irradiation.

Several explanations can be conceived for the production of HCN and HNC in our N$_2$ + CH$_4$ experiments. It might be possible that CH radicals, formed on radiolysis of CH$_4$, could react with N atoms, made from N$_2$, as follows:

$$\text{CH}_4 \rightarrow \text{CH} \quad \text{(by several steps)}$$

$$\text{N}_2 \rightarrow \text{N} + \text{N}$$

$$\text{CH} + \text{N} \rightarrow \text{HCN}.$$  

Some of the HCN produced could then isomerize to give the observed HNC. The main problem with this mechanism is that only small concentrations of CH and N radicals are expected in our experiments. This means that it is unlikely that CH and N would ever encounter one another in an ice, so that the radical–radical reaction leading to HCN will be unimportant.

A second possible mechanism for HCN formation is suggested by the work of Moore and Pimental (1965) who observed HCN after photolysis of N$_2$ + CH$_3$N$_2$ mixtures. Their reaction pathway involved formation of CH$_3$ from CH$_2$, and their subsequent “attack” on CH$_2$N$_2$ in the following sequence:

$$\text{CH}_2 + \text{CH}_3\text{N}_2 \rightarrow \text{HCN} + \text{H}_2\text{C} \equiv \text{NH}$$

$$\text{H}_2\text{C} \equiv \text{NH} \rightarrow \text{H}_2 + \text{HNC}.$$  

These reactions explained the presence of both HCN and HNC in photolyzed N$_2$ + CH$_3$N$_2$ mixtures. To search for these reactions in our experiments, we first checked that ion-irradiated methylamine (CH$_3$NH$_2$) would form CH$_3$NH and that CH$_3$NH would then be a source for both HNC and HCN. Fig. 9 shows the detection of HNC and HCN in the spectrum of irradiated of N$_2$ + CH$_3$N$_2$ (100:1). This experiment supports the role played by CH$_3$NH. However, in our irradiated N$_2$ + CH$_4$ (100:1) ices CH$_2$N$_2$ is itself a reaction product, not a starting material. As such it is unlikely that CH$_2$ and CH$_2$N$_2$, both at low concentrations, would encounter each other. As before, we expect little, if any, HCN from these reactions, with any contribution certainly diminishing as the N$_2$/CH$_4$ ratio increases.

As an alternative to these two mechanisms for HCN formation, we offer the work of Maier et al. (1996). In a comprehensive study, they probed the potential energy surface of CH$_2$N$_2$ isomers using both experimental and theoretical methods. Diazomethane was shown to rearrange to nitrilimine (HCNNH), and from there to a loose HN···HCN complex. As this complex can decompose to NH radicals and HCN, we are led to an intramolecular pathway from CH$_2$N$_2$ to HCN. The sequence is as follows:

$$\text{CH}_2 \rightarrow \text{CH}_2 + \text{H}_2$$

$$\text{CH}_2 + \text{N}_2 \rightarrow \text{CH}_2\text{N}_2$$

$$\text{CH}_2\text{N}_2 \rightarrow \text{HCNNH} \rightarrow \text{HN} \cdots \text{HCN} \rightarrow \text{NH} + \text{HCN}$$

$$\text{HCN} \rightarrow \text{HNC}.$$  

Because this sequence is intramolecular, once CH$_2$N$_2$ is reached the subsequent reactions will occur regardless of the initial N$_2$/CH$_4$ ratio. Thus we fully expect HCN and HNC formation on Solar System objects, such as Pluto and Triton, where the N$_2$/CH$_4$ ratio may be far higher than in our experiments.

Fig. 12. Infrared spectra in the region 2100 cm$^{-1}$ show the stability of bands of OCN$^-$, CN$^-$, and N$_3^-$ as a function of temperature. These ions form at 30–35 K in N$_2$ + CH$_4$ + CO (100:1:1) ice irradiated to ~1 eV molecule$^{-1}$. The OCN$^-$ band is still seen at 200 K.
In passing we note that this last set of reactions does not apply to the other hydrocarbons we studied. For example, spectra of proton-irradiated $N_2 + C_2H_6$ ices failed to show IR features of $CH_3CHN_2$, diazoethane, whose spectrum is known (Seburg and McMahon, 1992). As the diazo compound did not form, the above reactions imply that no rearrangement to HCN is expected, and indeed no HCN (or HNC) was seen. The observed reaction sequence for $C_2H_4$ in $N_2 + C_2H_4$ ices appeared to be hydrogen loss as $C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$.

4.2. Temperature effects

IR spectra of 12-K irradiated ices warmed to $\sim$30 K showed that relatively sharp features of acids (HCN, HNC, and HNCO) decreased, and bands of OCN$^-$ and CN$^-$ grew, along with a broad feature consistent with NH$_4^+$ near 1460 cm$^{-1}$. These changes support the following acid–base reactions:

$$\text{HCN} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{CN}^-$$
$$\text{HNC} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{CN}^-$$
$$\text{HNCO} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{OCN}^-.$$

A broad band for $N_2^+$ was also observed to form when irradiated ices were warmed. One source is the pairing of free $N_2^+$ ions as the matrix material is diminished and diffusion occurs. In addition, a likely reaction occurs in the presence of hydrazoic acid (HN$_3$) to form $N_3^-$:

$$\text{HN}_3 + \text{NH}_3 \rightarrow \text{NH}_4^+ + N_3^-.$$

Currently we have only a tentative identification of HN$_3$ in our irradiated ices, since its strongest band in $N_2$ matrices lies under the CO band.\(^1\) In summary, we observe extensive acid–base chemistry triggered by warming.

Finally, we note that in contrast to these results for warmed $N_2 + CH_4$ ices, our $N_2 + CO$ mixtures (N$_2$/CO ratios of 100 or 1) did not form cyanate, cyanide, azide, or ammonium ions when warmed to 35 K. This was not surprising since neither an acid nor a base, like NH$_4^+$, was observed in irradiated $N_2 + CO$ mixtures. Rather than ions, it was carbon suboxide, $C_4O_2$, that remained during warming of $N_2 + CO$ samples to $T > 100$ K.

5. Relevance to icy surfaces

A highlight of our study of low-temperature, $N_2$-dominated chemistry is the radiation synthesis of nearly equal concentrations of HCN and HNC when $CH_4$ is present or when both $CH_4$ and CO are present. This is the first demonstration of condensed-phase pathways to these molecules in realistic Triton/Pluto surface ices. The icy origin of these acids, along with HNCO and possibly HN$_3$, sets the stage for reactions with NH$_3$ to form NH$_4^+$, OCN$^-$, CN$^-$, and $N_3^-$ as diffusion occurs during warming. Since these ions are thermally more stable than the volatile reactants ($N_2$, $CH_4$, and CO), they may accumulate on the surfaces of Triton and Pluto and be good candidates for future mid-IR observations. Similar laboratory radiolysis studies are currently underway to identify products in CH$_4$ and CO-riche ices with varying concentrations of $N_2$ (work in progress in our laboratory), and in $N_2$-rich ices containing both CH$_4$ and H$_2$O (Satorre et al., 2001; Strazzulla and Palumbo, 2001), since terrains on Pluto and Triton may also include these ices.

The radiation chemistry we observed in $N_2$-rich laboratory ices may also be relevant to the chemistry expected in some interstellar ices. $N_2$ forms most efficiently in interstellar regions where H$_2$ rather than atomic H exists. Theoretical models of interstellar ice grain chemistry (Tielens and Hagen, 1982; d’Hendecourt et al., 1985) also predict that molecules such as CO, O$_2$, and some CO$_2$ will form and condense along with $N_2$. This apolar ice may form as a separate layer on grains (Ehrenfreund et al., 1998). Another likely nonpolar species is CH$_4$. Currently, only indirect evidence exists for condensed $N_2$ mixed with CO, O$_2$, and CO$_2$ (Elsla et al., 1997). Plausible interstellar ratios of $N_2$/CO, $N_2$/O$_2$, etc. associated with a range of possible environments include $N_2$-rich ices.

Observational evidence exists for the presence, in both interstellar regions and comets, of some of the molecular products we report in this paper. Considering first the acids, HCN is one of the more abundant nitrogen-bearing species detected in dense interstellar clouds. In addition, cold interstellar molecular clouds have large HNC/HCN ratios (0.2–1, Ohishi and Kaifu, 1998). In comets, a typical HCN abundance relative to water is $2 - 10 \times 10^{-3}$, and HCN is considered a parent species. The HNC/HCN ratio ranges from 0.06 to 0.2 (Irwin, 1996, 1999; Biver et al., 1997; Hirota et al., 1999) depending on the comet and its distance from the Sun. The origin of HNC may be a combination of a native and an extended source (see, e.g., Rodgers and Charnley, 1998). HNCO and NH$_3$ are detected in both interstellar hot core regions and in cometary comae; NH$_3$ is also found in dense clouds surrounding protostars (see, e.g., review by Ehrenfreund and Charnley, 2001). These species, identified from gas-phase observations, are expected to condense as icy mantles on cold grain surfaces. Our experimental results demonstrate that in addition to any gas-phase source, a condensed-phase pathway to the formation of these species exists in $N_2$-rich ices containing CH$_4$ and CO. In particular, HNC and HCN form in nearly equal concentrations.

Observations of cold icy grains of embedded protostars show several condensed-phase products we report in this paper. Solid NH$_3$ is one definite candidate (Gibb et al.,

\(^1\) Confirmation of $HN_3$ synthesis using appropriate isotopically labeled starting materials is in progress.
2001, Dartois and d’Hendecourt, 2001, and references therein). But detecting NH$_3$ ice is difficult since its major features overlap with those of H$_2$O and the silicate band. Of 16 sources, Gibb et al. (2001) showed that 4 have a change in slope at 8.5 μm and peak at 9 μm that could be attributed to ammonia (the remaining sources have only upper limits). In addition, the prominent feature at 2165 cm$^{-1}$ in IR spectra is assigned to the OCN$^-$ ion (see, e.g., Hudson et al., 2001, and references therein). It is also possible that a contributor to the unidentified absorption band of 1460 cm$^{-1}$ observed toward embedded protostars is the ion NH$_5^+$ (see, e.g., Demyk et al., 1998). Although the actual N$_2$ or NH$_3$ budget in molecular clouds is not well determined; the existence of OCN$^-$ ion supports the idea that low-temperature pathways, similar to those we describe in this paper, occur on cold icy grains.

Radiation processing of N$_2$-rich ices on Triton and Pluto could provide an endogenous source of HNC, HCN, HNCO, NH$_3$, NH$_5^+$, OCN$^-$, CN$^-$, and N$_2$. The presence of these molecules would suggest the possibility of interesting prebiotic chemistry. It is well known that many of these species are involved in reactions producing biomolecules. The role of HCN and its derivatives in prebiotic evolution has been discussed by many authors (see, e.g., Matthews, 1995, Oro and Lazcano-Araujo, 1981). Wöhler (1828) and Dunitz et al. (1998) studied the instability of NH$_2$OCN and its conversion to urea. Draganic et al. (1985) studied the radiation chemistry of solutions of HCN and NH$_2$CN and the formation of amino acids. More recently, the instability of NH$_2$CN, in the presence of H$_2$O and NH$_3$ was examined by Levy et al. (2000). They found that adenine, guanine, and a set of amino acids dominated by glycine are formed after storage for 25 years at temperatures as low as −78 C. Because it is not clear to what extent any of these prebiotic syntheses would progress at temperatures relevant to Triton and Pluto, this area requires more work.

Evidence for CN-bonded species exists for a variety of other Solar System objects. Along with observed HNC and HCN in cometary coma, there is the detection of a 2.2-μm feature on outer Solar System surfaces, which is suggested to be evidence for the overtone mode of C≡N. For example, this feature is seen on some D-class asteroids, in the dust of some comets, on Iapetus, and in the rings of Uranus (Cruikshank et al., 1991). If a condensed-phase route to HCN, HNC, and other CN-bonded species plays a significant role in Solar System objects, then our work implies a formation region rich in N$_2$ ices containing CH$_4$, but devoid of H$_2$O.

An opportunity to look closely at Triton and Pluto for evidence of HCN, HNC, and the more stable ion signatures of OCN$^-$, CN$^-$, N$_2^+$, and NH$_5^+$ will require the resolution and wavelength coverage proposed for NGST, a future IR mission. Detecting and mapping these species may help determine if Pluto and Triton will be targets of future astrobiology missions. The New Horizons Mission is scheduled to make the first reconnaissance of Pluto as early as 2015. However, its proposed spectroscopy is shortward of 2.5 μm. Therefore, future laboratory work on the near-IR band positions and band strengths of cyanates, cyanide, azides, and polymers of hydrogen cyanide is needed. Understanding the radiation chemistry of remote worlds with N$_2$-rich icy surfaces may provide support for the icy origin of HCN and HNC from similarly processed N$_2$-rich segregated cometary ices. This scenario would strengthen the idea that comets contain interesting biomolecules.

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References


