

Isotopic study of the formation of the azide radical (N_3)

Corey S. Jamieson, Ralf I. Kaiser *

Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA

Received 11 February 2007; in final form 10 April 2007

Available online 18 April 2007

Abstract

Solid molecular nitrogen (N_2) may exist in large abundances in various low-temperature interstellar and solar system environments. Intense radiation fields can cause molecular nitrogen ice to undergo chemical alterations by cleaving the nitrogen–nitrogen triple bond. We have simulated this chemical processing by carrying out radiolysis experiments using energetic electrons on molecular nitrogen ice at 10 K that has been labeled with different isotopes. We have identified four isotopologues of the azide radical (N_3) via infrared spectroscopy. The $^{14}N_3$ radical was detected by a doublet that has peaks centered at 1657 and 1652 cm^{-1} . The formation dynamics are also investigated.

© 2007 Published by Elsevier B.V.

1. Introduction

In order to study the chemistry of ices that are exposed to the harsh radiation environments in space, it has been useful to send spacecraft to objects to spectroscopically investigate their surfaces. For example, the Galileo spacecraft observed Europa (one of Jupiter's moons) to find that the radiation-induced decay of water can produce hydrogen peroxide [1]. This technique works well for water, carbon dioxide, and other molecules that are in reach of spacecraft. However, volatile molecules like molecular nitrogen only exist in the solid state in the outskirts of the solar system where the temperature is low enough and they are therefore very difficult to observe. Additionally, molecular nitrogen has no dipole moment and so determining its chemical properties and abundance is spectroscopically difficult. This makes laboratory studies of chemically processed molecular nitrogen extremely important.

Ground based observations have confirmed that nitrogen ice is the dominant component of the surfaces of Triton [2] (Neptune's largest moon) and Pluto (ex-planet)

[3]. Nitrogen ice may also be present in large abundances in comets, Kuiper Belt Objects (KBOs), and trans-Neptunian objects [4] (TNOs), although this has not been spectroscopically confirmed. Since molecular nitrogen is a homonuclear diatomic molecule with a strong triple bond (9.8 eV), its radiation-induced chemistry would not intuitively seem very interesting. However, the full potential of nitrogen chemistry is only starting to come into view.

The linear azide molecule has long been known and has been extensively studied both experimentally and theoretically [5–10]. Hudson and Moore [7] have previously proposed using the linear azide radical as a tracer molecule to follow the abundance of molecular nitrogen in space. Its formation may also indicate the type of radiation environment in which molecular nitrogen exists since, in their experiments, the azide radical was found to form under proton irradiation of low-temperature molecular nitrogen ice but not by photolysis.

More recently, photodissociation of CIN_3 has provided experimental evidence for the production of the cyclic N_3 isomer, identified by its predicted photoionization potential [11] and also by photofragment translational spectroscopy [12]. Theoretical work has also predicted the stability of several N_4 and N_6 isomers [13–16] and possible experimental identifications of one N_4 isomer (azidonitrene) [17] and one N_6 isomer (hexaazabenzene) [18] have been proposed.

* Corresponding author. Fax: +1 808 956 5908.

E-mail addresses: cjamieso@hawaii.edu (C.S. Jamieson), kaiser@gold.chem.hawaii.edu (R.I. Kaiser).

These higher order nitrogen molecules, if confirmed, could prove to be extremely useful high energy density materials by storing large amounts of internal energy, especially if ring structures exist [19]. Secondly, molecular nitrogen byproducts are in line with the general trend for green chemistry desired in energy sources. Here we carry out irradiation experiments of different isotopologues (molecules of the same isomeric form but differing in isotopic composition) of molecular nitrogen. We identify the linear azide radical (N_3) via infrared spectroscopy and investigate the mechanism(s) of its formation.

2. Materials and methods

The experiments were carried out in an ultra high vacuum stainless steel chamber [20]. The chamber can reach pressures as low as 5×10^{-11} Torr by use of a magnetically suspended turbo molecular pump that is backed by a scroll pump. All pumps used are oil-free to ensure no hydrocarbon contaminants enter the system. Temperatures as low as 10 K are reached using a two-stage closed-cycle helium refrigerator that is interfaced directly to a polished single crystal silver mirror onto which the ices are condensed. The silver substrate is suspended by a differentially pumped rotatable feedthrough, which aligns the wafer in the center of the main chamber. Gas condensation is carried out at 10 K where the pressure is regulated by a thermovalve that lets gas through the linear transfer mechanism and to the gas capillary array which evenly disburses the gas. The gases were condensed for 30 min at a pressure of 1.0×10^{-7} Torr at 10 K to give an amorphous molecular nitrogen ice with a total thickness of 1 μm . The ice thickness was derived using an equation provided in Bennett et al., [20] where the column density of the initial ice was calculated by integrating the ν_1 absorption feature of molecular nitrogen ($^{14}\text{N}_2$, 2328 cm^{-1}) and dividing by the absorption coefficient for molecular nitrogen in pure nitrogen ice ($1.8 \times 10^{-22} \text{ cm molecule}^{-1}$) [21]. The ice sample was then irradiated isothermally with 5 keV electrons to cleave the N–N triple bond. The experiments were also carried out at three different electron beam currents of 1.0, 0.1, and 0.01 μA . The beam has an extraction efficiency of 78.8% and is scanned over the sample area $1.8 \pm 0.3 \text{ cm}^2$ to avoid heating the ice. The sample was irradiated for one hour, which exposed the target to 1.8×10^{16} electrons in the 1 μA experiment. In this work, three molecular nitrogen irradiation experiments were performed using (a) $^{14}\text{N}_2$, (b) $^{15}\text{N}_2$, and (c) $^{14}\text{N}_2$: $^{15}\text{N}_2$ (1:1). The progress of the reaction was monitored using a Nicolet 510 DX Fourier Transform Infrared Spectrometer (FTIR). The spectrometer has a wavenumber range of 6000–500 cm^{-1} and operates in absorption–reflection–absorption mode with a reflection angle of 75° with respect to the surface normal relative to the silver mirror. The infrared spectra of the ice were recorded online and in situ at an integrated time of 2.5 min (242 scans) and at a resolution of 2 cm^{-1} . The column densities of a molecule (or abundance, in units of mol-

ecules cm^{-2}) can be calculated according to Bennett et al. [20]. A quadrupole mass spectrometer (Balzer 420) with electron impact ionization was attached directly to the reaction chamber to detect molecules liberated into the gas phase.

3. Results

The experiments were carried out in three phases. First, the nitrogen ices were irradiated for one hour while the experiment was monitored by infrared spectroscopy. The temporal developments of the infrared bands of the azide radical were quantified to help us understand the kinetics of the reactions that occur. Next, the electron beam was turned off and the ice was left at 10 K to check the stability and/or reactivity of the molecular species produced. Finally the ice was warmed at a rate of 0.5 K min^{-1} to observe any reaction, dissociation, and/or sublimation of the products.

In the rather featureless infrared absorption spectrum of molecular nitrogen, a small peak was observable before irradiation at 2327 cm^{-1} corresponding to $^{14}\text{N}_2$. In the $^{15}\text{N}_2$ experiment, the fundamental mode of nitrogen was shifted to 2249 cm^{-1} . The samples were then irradiated for one hour.

In the $^{14}\text{N}_2$ experiment, the $^{14}\text{N}_3$ radical was observed by a doublet with peaks at 1657 and 1652 cm^{-1} (Table 1, Fig. 1). Comparing these absorptions to previous work by Tian et al., both peaks of the doublet seem to correspond to the ν_3 vibrational mode of the azide radical that are in different sites in the nitrogen matrix [6]. In their experiment, Tian et al. found a triplet of peaks in this spectral region centered at 1657.5 , 1654.5 , and 1652.6 cm^{-1} (we, therefore, did not observe this middle absorption). They gave three lines of argument that justify that these three absorptions resulted from the ν_3 vibration of the $^{14}\text{N}_3$ radical occupying different sites in their matrix ice. First, reducing the deposition rate or increasing the deposition temperature during the formation of their molecular nitrogen ice matrix had the effect of only producing one N_3 absorption feature (1657.5 cm^{-1}) after the N_2 ice was irradiated, rather than the three peaks in their original experiment. This could be explained by a more homogeneous crystal structure that is formed at higher deposition temperatures or slower deposition rates resulting in fewer

Table 1

The infrared absorption positions are give for the ν_3 vibrational mode of the azide radical

| Isotopologue | Peaks positions (cm^{-1}) |
|---|--------------------------------------|
| $^{14}\text{N}_3$ | 1657, 1652 |
| $^{15}\text{N}^{14}\text{N}^{14}\text{N}$ | 1648, 1643 |
| $^{14}\text{N}^{15}\text{N}^{15}\text{N}$ | 1612, 1607 |
| $^{15}\text{N}_3$ | 1603, 1598 |

The wavenumbers are reported for both peaks of the doublet observed for each isotopologue although Tian et al. [6] have considered the higher wavenumber peak the most stable site.

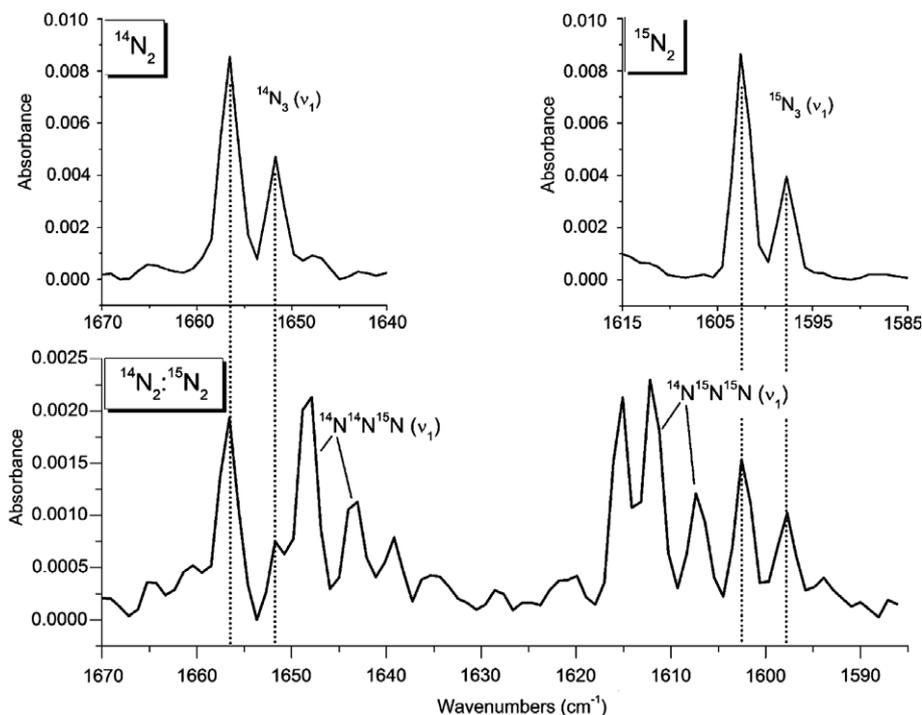


Fig. 1. The infrared spectra are shown for the different azide radical isotopologues after irradiating a molecular nitrogen ice for 1 h. The initial molecular nitrogen isotopologue is boxed in the upper left corner of each graph. The only absorption features that were observed after irradiation were due to the azide radical. Doublets are observed for each azide radical isotopologue due to their occupation of different sites in the ice thereby affecting their absorption character [6].

unique sites in the ice in which the azide radical could vibrate. This argument was also confirmed by creating a more uniform crystal structure by repeatedly annealing the ice once the triplet of peaks had been produced by irradiation. The result was that the two lower energy peaks (1654.5 and 1652.6 cm^{-1}) began to disappear while the intensity of the high energy peak (1657.5 cm^{-1}) increased. This confirmed that the 1657.5 cm^{-1} peak is due to the azide radical in its most stable site in the nitrogen matrix and that the three peaks are likely correlated. Lastly, to further confirm that the three peaks are due to the same molecule, isotopically labeled nitrogen ice was irradiated where identical shifts in the peak positions were observed.

The doublet absorption features due to N_3 were the only peaks found to result from irradiation in our experiments. When the $^{15}\text{N}_2$ ice was irradiated, the azide radical peaks shifted to 1603 and 1598 cm^{-1} due to the formation of $^{15}\text{N}_3$ [6]. Lastly, a 1:1 ice mixture containing two nitrogen isotopologues ($^{14}\text{N}_2$: $^{15}\text{N}_2$) was irradiated. Peaks were observed that correspond to $^{14}\text{N}_3$ and $^{15}\text{N}_3$ as previously found but also peaks for the isotopologues $^{15}\text{N}^{14}\text{N}^{14}\text{N}$ and $^{14}\text{N}^{15}\text{N}^{15}\text{N}$ with absorptions centered at 1648 and 1643 cm^{-1} and 1612 and 1607 cm^{-1} , respectively. From Fig. 1 the doublets of the four isotopologues of the azide radical are clearly marked, however, the nondetection of the remaining two isotopologues, $^{14}\text{N}^{15}\text{N}^{14}\text{N}$ and $^{15}\text{N}^{14}\text{N}^{15}\text{N}$, is interesting. From Tian et al. [6], the expected peaks positions for the ν_3 vibrations of these isotopologues are centered at 1621.4 and 1639.7 cm^{-1} , respectively. This

gives clues into the formation of the azide radical as will be discussed in the next section.

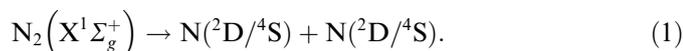
In comparison with previous works investigating the radiation-induced decomposition of molecular nitrogen ice at low-temperatures, our results compare well. Hudson and Moore [7] carried out proton irradiation of solid N_2 at 12 K to find N_3 as their only irradiation product. They observed peak positions of 1657, 1649, 1615, and 1603 cm^{-1} for $^{14}\text{N}_3$, $^{15}\text{N}^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}_2$ and $^{15}\text{N}_3$, respectively, compared with our peak positions of 1657, 1648, 1612, and 1603 cm^{-1} , respectively for the high energy band of our observed doublets. The interesting difference here is that Hudson and Moore observed only a single band while our experiment showed doublets and, as previously mentioned, Tian et al. observed a triplet of peaks corresponding to N_3 absorptions. This is not too surprising since, as Tian et al. have found, the number of peaks observed for the N_3 radical is very sensitive to the experimental conditions such as deposition rate, deposition temperature, and possibly other factors like radiation source or the type of substrate onto which the nitrogen ice is condensed. Evidence that altering the radiation source may play a role in altering the formation of the azide radical is well provided by Hudson and Moore where they found photolysis of solid nitrogen by Ly α photons (10.6 eV) to be inefficient at producing the azide radical and it was not detected (in contrast to their proton irradiation experiments).

This last significant difference between the current work and past experiments is that Tian et al. report the detection

of two more N_3 isotopologues ($^{15}N^{14}N^{15}N$ and $^{14}N^{15}N^{14}N$) as well as the $v_1 + v_3$ and v_2 vibrations for several of the isotopologues. For example, for $^{14}N_3$, they observed three different absorption features including peaks at 2944.9 ($v_1 + v_3$), 472.7 (v_2), and 1657.5 cm^{-1} (v_3). In the current experiment, only the v_3 absorption was detected and four of the six possible isotopologues were observed.

4. Discussion

We will now investigate the formation pathways of the azide radical. First it would be useful to understand the irradiation effects within the ice. As the electrons enter the sample, they may interact with the N_2 molecules causing electronic excitations and/or ionizations. If ions were produced in our 10 K ice, they could be stabilized. However, there was no evidence of ionized species in the infrared spectra and so they may not play a large role influencing the observed chemistry. Instead, to initiate reactions, a molecule may be electronically excited to a dissociative state where it may then fragment. For example, radiation-induced dissociation of molecular nitrogen may take place within the ice to produce two nitrogen atoms (Eq. (1)).



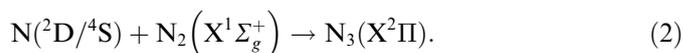
Upon direct dissociation, where spin conversion should occur, the nitrogen atoms would either both be in the doublet D or both in the quartet S states. However, if a predissociative mechanism were followed, the most likely electronic states of the fragments would be 2D for one atom and 4S for the other [22]. The branching ratios of these dissociation pathways in our ice is not currently known. Dissociation into two ground state nitrogen atoms (4S) requires at least 941 $kJ\ mol^{-1}$ of energy to be absorbed by molecular nitrogen and an electronically excited nitrogen atom (2D) lies 231 $kJ\ mol^{-1}$ above the ground 4S state. Consequently, to produce two excited nitrogen atoms in the 2D state would require 1403 $kJ\ mol^{-1}$ of total energy, just below the ionization limit of molecular nitrogen (1503 $kJ\ mol^{-1}$) [23]. The excess energy absorbed by the nitrogen molecule, beyond what is needed to break the bond, is channeled into translational degrees of freedom of the fragment species.

Previous experiments using ion irradiation to dissociate molecular nitrogen indicate the observation of the $N(^2D) \leftarrow N(^4S)$ emission in their ices and that, consequently, the previously mentioned, direct dissociation pathway occurs [6,7]. However, we cannot discount the possibility that different energy transfer processes using electron radiation exist that may result in different pathways to initiate reactions. For example, an ' $N_2 + N_2^* \rightarrow N + N_3$ ' type reaction could occur where an electronically excited nitrogen molecule reacts with another nitrogen molecule to produce a nitrogen atom and the azide radical. This has been found to be the case for the dissociation of carbon monoxide [24–26]. One argument against this pro-

cess in our experiment is that in the photolysis experiments by Hudson and Moore using 10.6 eV photons to irradiate molecular nitrogen, the azide radical was not produced [7]. These photons should be energetic enough to excite molecular nitrogen into a reactive state, assuming one existed (note the carbon monoxide dissociation reaction requires much less energy than the direct dissociation reaction). The lack of observable chemistry at these excitation energies seems to suggest that direct dissociation by higher energies is necessary to initiate nitrogen chemistry.

Secondly, we have carried out electron radiation experiments on $N_2:CO_2$ ice mixtures where the nitrogen molecule was found to dissociate producing two nitrogen atoms that reacted with carbon dioxide to produce the OCNO molecule [27].

Assuming the reactions in our ice are initiated by the direct dissociation of molecular nitrogen, the nitrogen atoms that are produced may be either electronically excited and/or suprathermal (with an excess kinetic energy), and can then react with molecular nitrogen to form the azide radical (Eq. (2)).



This reaction was calculated to be slightly endoergic by 0.96 $kJ\ mol^{-1}$ at 0 K relative to the ground state reactants (Fig. 2, adapted from Zhang et al. [10]). However, intersystem crossing is required where a barrier of 219 $kJ\ mol^{-1}$ to reach the minimum on the seam of crossing (MSX) has been calculated [10]. On the other hand, reaction initiated by $N(^2D)$ on the doublet potential energy surface would require a barrier of only 13.2 $kJ\ mol^{-1}$ to open this channel where the reaction is exoergic by 236 $kJ\ mol^{-1}$. Since, in this reaction, the nitrogen atom approaches molecular nitrogen at $C_{\infty v}$ symmetry, the attacking nitrogen atom would be incorporated into the azide radical as one of the terminal nitrogens. This is consistent with the detection of $^{15}N^{14}N^{14}N$ and $^{14}N^{15}N^{15}N$ in our $^{14}N_2:^{15}N_2$ experiment.

Theoretical work has proposed the formation of a stable and long-lived cyclic N_3 molecule [10]. Energetically this molecule exists 127 $kJ\ mol^{-1}$ higher in energy than the linear isomer but lies well below (118 $kJ\ mol^{-1}$) the minimum on the crossing seam from the $N_2 + N(^4S)$ reaction at C_{2v} geometry (Fig. 2). This suggests that although the reaction between $N(^2D)$ and molecular nitrogen likely has sufficient energy to proceed to the lowest energy isomer (linear- N_3) by immediate isomerization of the cyclic structure, reaction between $N(^4S)$ and N_2 where the nitrogen atom approaches at C_{2v} geometry should produce the stable cyclic N_3 molecule. This cyclic structure may subsequently isomerize to the linear conformation by passing a barrier of 133 $kJ\ mol^{-1}$ where there should be an equal probability of opening at any of the three N–N bonds, assuming complete intramolecular vibrational redistribution (IVR). This would result in isotopic scrambling in the linear isomer if different isotopes were being used. However, from our experiment there is no spectroscopic evidence for the

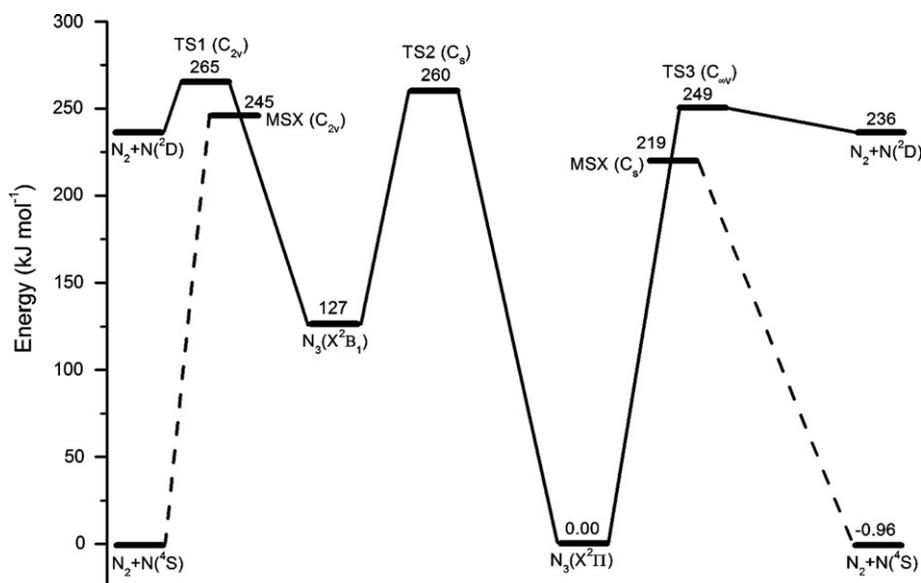


Fig. 2. This potential energy surface relates the $N_2 + N(^4S/^2D)$ reactions with the cyclic $N_3(X^2B_1)$ and linear- $N_3(X^2II)$ products. It was adapted from Zhang et al. [10].

formation of the cyclic structure. Also, the nondetection of $^{14}N^{15}N^{14}N$ and $^{15}N^{14}N^{15}N$ indicates that the isotopes in the linear azide radical are not scrambled. In summary, there is no evidence that the cyclic isomer has been produced or even accessed at any point during our experiment.

In order to gain an understanding of the evolution of the abundance of the azide radical over the course of the experiment, the column density has been quantified and plotted versus time (Fig. 3). This graph was derived by integrating each peak of the doublet corresponding to $^{14}N_3$ for three different irradiation currents. Column densities were calculated according to a Beers law derived method provided in Bennett et al. [20] where the absorption coefficient for the ν_3 band of N_3 has been previously calculated by our group at the B3LYP/6-311G(d) level of theory using the GAUSSIAN 98 programming package [28]. The calculated value was found to be 4.00×10^{-17} cm molecule $^{-1}$. This compares with an experimentally estimated value of

7.2×10^{-20} cm molecule $^{-1}$ that was found by Hudson and Moore [7]. These two values are obviously in conflict with each other, however, assumptions are made in each case. For example Hudson and Moore set the N_3 concentration at 1% of the N_2 abundance which surely is an overestimate resulting in the low absorption coefficient. Our calculated result also has errors associated with it since the calculations assume gas phase vibrations which may be inaccurate in describing vibrational frequencies in our ice. These gas phase calculations can be 20–30% off from the solid state values. We have decided to use our calculated absorption coefficient for determining the N_3 column densities. Following the development of the column densities in Fig. 3, we can begin to understand the evolution of the abundance of the azide radical over time.

During irradiation ($t = 0$ –3600 s) the bands of the azide radical (1657 and 1652 cm $^{-1}$) increased at each of the three irradiation currents where, as expected, the higher currents

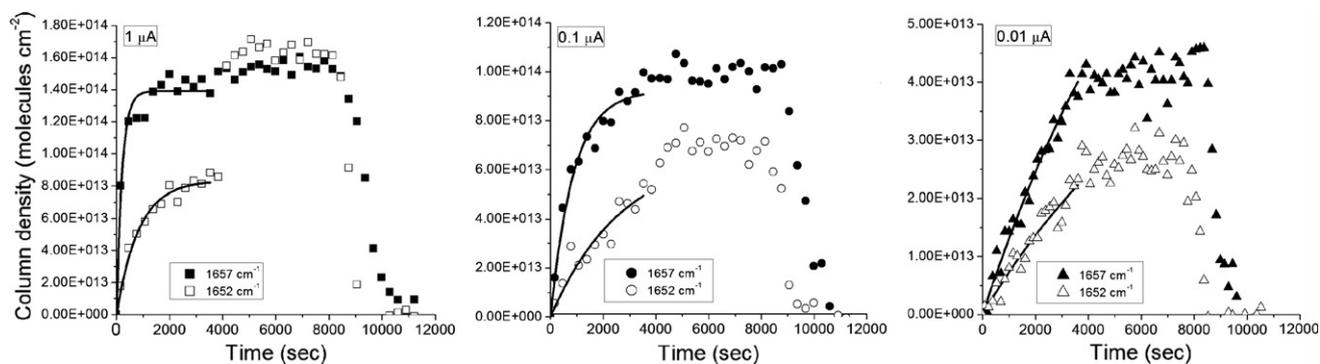


Fig. 3. The abundances (column density with units of molecules cm $^{-2}$) of the azide radical (N_3) are shown over the course of the $^{14}N_2$ irradiation experiments for three different irradiation currents. Each peak of the doublet (see Fig. 1) resulting from N_3 was individually integrated for each experiment and the abundances were kinetically fit using pseudo-first order kinetics for the irradiation phase of the experiment (see text and Table 2). Irradiation was stopped after 3600 s and warmup began at 7200 s.

Table 2

The integrated absorption of the observed peaks of N₃ were fit with the pseudo-first order kinetic equation $[N_3] = a(1 - e^{-kt})$, where a is in units of molecules cm⁻² and k is in s⁻¹

| Current (μA) | Peak center (cm ⁻¹) | a (molecules cm ⁻²) | k (s ⁻¹) | k' (s ⁻¹ μA ⁻¹) |
|--------------|---------------------------------|-----------------------------------|------------------------------|--|
| 1.0 | 1657 | $1.4 \pm 0.3 \times 10^{14}$ | $4.8 \pm 0.7 \times 10^{-3}$ | $4.8 \pm 0.7 \times 10^{-3}$ |
| | 1652 | $8.3 \pm 0.2 \times 10^{13}$ | $1.2 \pm 0.1 \times 10^{-3}$ | $1.2 \pm 0.1 \times 10^{-3}$ |
| 0.1 | 1657 | $9.2 \pm 0.3 \times 10^{13}$ | $1.2 \pm 0.1 \times 10^{-3}$ | $1.2 \pm 0.1 \times 10^{-2}$ |
| | 1652 | $7 \pm 2 \times 10^{13}$ | $3.7 \pm 0.2 \times 10^{-4}$ | $3.7 \pm 0.2 \times 10^{-3}$ |
| 0.01 | 1657 | $1.1 \pm 0.4 \times 10^{14}$ | $1.3 \pm 0.6 \times 10^{-4}$ | $1.3 \pm 0.6 \times 10^{-2}$ |
| | 1652 | $6 \pm 3 \times 10^{13}$ | $1.0 \pm 1.0 \times 10^{-4}$ | $1.0 \pm 1.0 \times 10^{-2}$ |

The effective rate constant (k') which takes into account the irradiation current was calculated where $k' = k/I$, I is the irradiation current in microamps. These values (a , k , and k') are reported for both N₃ peaks of the doublets (1657 and 1652 cm⁻¹) that were observed in the nitrogen experiments using different irradiation currents.

formed the azide radical more quickly and at a higher abundances. The developments of the N₃ bands in each experiment were quantified using pseudo-first order kinetics (Table 2). More specifically, the column densities of each peak of the azide radical were best fit using the equation: $[N_3] = a \times (1 - e^{-kt})$ where a is the pre-exponential factor in units of molecules cm⁻² and k is the rate constant in s⁻¹. The effective rate constant for the development of these bands (k') was calculated where $k' = k/I$. Here, I is the irradiation current in μA and k is the observed rate constant. It is most useful to compare the effective rate constants since it accounts for the irradiation current.

In the 1.0 μA experiment, the peak centered at 1657 cm⁻¹ was found to form at four times the rate of the formation of the 1652 cm⁻¹ peak ($k' = 4.8 \pm 0.7 \times 10^{-3}$ and $1.2 \pm 0.1 \times 10^{-3}$ s⁻¹ μA⁻¹, respectively). This same trend was also found in the 0.1 μA experiment, where the 1657 cm⁻¹ peak was found to form three times faster than the 1652 cm⁻¹ peak ($k' = 1.2 \pm 0.1 \times 10^{-2}$ and $3.7 \pm 0.2 \times 10^{-3}$ s⁻¹ μA⁻¹, respectively). However, comparing the two peaks of N₃ molecule in the 0.01 μA experiment, the rate constants are nearly identical ($k' = 1.3 \pm 0.6 \times 10^{-2}$ and $1 \pm 1 \times 10^{-2}$ s⁻¹ μA⁻¹, respectively), although the errors present in these rate constants detract from the importance of this result. Comparing between the experiments, the development of the N₃ bands in the 0.1 μA experiment were found to occur at about three times the rate as in the 1.0 μA experiment, although the reason for this is unclear (remember these rate constants account for the irradiation current).

The most interesting part of Fig. 2 graphs is the marked increase in the area of the 1652 cm⁻¹ peak but not the 1657 cm⁻¹ peak immediately after the irradiation was stopped. This increase is most evident for irradiation at 1 μA, still significant at 0.1 μA, but within the error limits at 0.01 μA. There are a few possible scenarios in considering what could cause this increase in the N₃ abundance. One explanation could be that residual reactions in the ice are still occurring after the irradiation has ended thereby forming more azide radical. For example, nitrogen atoms could still be present in the ice and react with molec-

ular nitrogen. However, as evident in Fig. 2, reaction of ²D nitrogen atoms with molecular nitrogen would still need to surpass a minimum barrier of 13.2 kJ mol⁻¹ and N(⁴S) reactions would require 219 kJ mol⁻¹. This energy is not available in the 10 K ice once the nitrogen atoms have thermalized. Additionally, the lifetime of the electronically excited nitrogen atom is not long, only several seconds [29]. This seems to eliminate the N + N₂ reaction as a source of the delayed N₃ production. Another possibility could be from the decay of either an N₅ or N₆ molecule that may have been produced in the ice. For example, two C_{2v} symmetric isomers of N₅ exist that are metastable with a dissociation barrier of only a few kJ mol⁻¹ to molecular nitrogen and an azide radical [30,31]. This low barrier should have a non-negligible rate constant even at 10 K and may therefore be responsible for producing the azide radical after completion of irradiation. However, it is noted that no other observable bands were found in the infrared spectra to confirm the presence of higher order nitrogen compounds.

Another explanation for the increase in the azide band may be due to relaxation effects that may take place in the nitrogen ice after irradiation had ended. Irradiation often has the effect of destroying ordered regions within the ice creating a more amorphous ice. During the isothermal phase of the experiment, disordered regions of the ice may be relaxing into a more ordered or even crystalline state. This would influence the infrared absorption coefficient since the N₃ radical resides in distinct lattice environments. This explanation seems to agree with the fact that only one of the N₃ bands changes in intensity after irradiation since these bands likely arise from the azide radical in different matrix sites in the nitrogen ice [6].

After leaving the irradiated ice at 10 K for 1 h, the temperature of the sample was slowly raised at a rate of 0.5 K min⁻¹. The N₃ peaks began to decrease in intensity concurrently with the sublimation of the molecular nitrogen matrix (~30 K). This indicates that the azide radical was stable up to the temperature at which the N₂ ice started to disappear. It is therefore difficult to comment on the cause of the disappearance of the N₃ molecule since it

could be explained by sublimation, reaction, or dissociation. However, no signal was detected at $m/z = 42$ in the mass spectrometer during warmup and so sublimation and survival of the azide radical in the gas phase is not likely.

5. Conclusions

Due to the large abundance of molecular nitrogen on Triton, Pluto, and possibly Kuiper belt objects in the outer solar system, understanding its radiation-induced chemistry is extremely important. We have carried out irradiation experiments of molecular nitrogen ice at 10 K that has been labeled with different isotopes and at various irradiation currents. We have identified four isotopologues of the azide radical (N_3) via infrared spectroscopy. The $^{14}N_3$ radical was detected by a doublet that has peaks centered at 1657 and 1652 cm^{-1} . No evidence could be found to confirm the presence of the cyclic N_3 structure; by either its vibrational features or by the detection of two azide radical isotopologues, $^{14}N^{15}N^{14}N$ and $^{15}N^{14}N^{15}N$. Summarized, energetic processing of low-temperature solar system ices is expected to produce solely the azide isomer.

Acknowledgement

This material is based upon work supported by the Air Force Office of Scientific Research (W911NF-05-1-0448).

References

- [1] R.W. Carlson et al., *Science* 283 (1999) 2062.
- [2] T.C. Owen et al., *Science* 261 (1993) 745.
- [3] D.P. Cruikshank, R.H. Brown, R.N. Clark, *Icarus* 58 (1984) 293.
- [4] J. Licandro, N. Pinilla-Alonso, M. Pedani, E. Oliva, G.P. Tozzi, W.M. Grundy, *Astron. Astrophys.* 445 (2006) L35.
- [5] J.I. Bryant, *Spectrochim. Acta* 22 (1966) 1475.
- [6] R. Tian, J.C. Facelli, J. Michl, *J. Phys. Chem.* 92 (1988) 4073.
- [7] R.L. Hudson, M.H. Moore, *Astrophys. J.* 568 (2002) 1095.
- [8] R. Prasad, *J. Chem. Phys.* 119 (2003) 9549.
- [9] D.A. Dixon et al., *J. Am. Chem. Soc.* 126 (2004) 834.
- [10] P. Zhang, K. Morokuma, A.M. Wodtke, *J. Chem. Phys.* 122 (2005) 014106.
- [11] P.C. Samartzis, J.J.M. Lin, T.T. Ching, C. Chaudhuri, Y.T. Lee, S.H. Lee, A.M. Wodtke, *J. Chem. Phys.* 123 (2005) 051101.
- [12] N. Hansen, A.M. Wodtke, S.J. Goncher, J.C. Robinson, N.E. Sveum, D.M. Neumark, *J. Chem. Phys.* 123 (2005) 104305/1.
- [13] A. Larson, M. Larsson, H. Ostmark, *J. Chem. Soc., Faraday Trans.* 93 (1997) 2963.
- [14] M. Bittererova, T. Brinck, H. Ostmark, *J. Phys. Chem. A* 104 (2000) 11999.
- [15] R. Engelke, *J. Phys. Chem.* 96 (1992) 10789.
- [16] M. Tobita, R.J. Bartlett, *J. Phys. Chem. A* 105 (2001) 4107.
- [17] M.T. Nguyen, T.L. Nguyen, A.M. Mebel, R. Flammang, *J. Phys. Chem. A* 107 (2003) 5452.
- [18] A. Volger, R.E. Wright, H. Kunkely, *Angew. Chem. Int. Ed. Engl.* 19 (1980) 717.
- [19] L.E. Fried, M.R. Manaa, P.F. Pagoria, R.L. Simpson, *Annu. Rev. Mater. Res.* 31 (2001) 291.
- [20] C.J. Bennett, C. Jamieson, A.M. Mebel, R.I. Kaiser, *Phys. Chem. Chem. Phys.* 6 (2004) 735.
- [21] M.P. Bernstein, S.A. Sandford, *Spectrochim. Acta A* 55 (1999) 2455.
- [22] C.W. Walter, P.C. Cosby, H. Helm, *J. Chem. Phys.* 99 (1993) 3553.
- [23] P.C. Cosby, *J. Chem. Phys.* 98 (1993) 9544.
- [24] P.A. Gerakines, W.A. Schutte, P. Ehrenfreund, *Astron. Astrophys.* 312 (1996) 289.
- [25] H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978.
- [26] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, *Astrophys. J. Supp. Series* 163 (2006).
- [27] C.S. Jamieson, A.M. Mebel, R.I. Kaiser, *Phys. Chem. Chem. Phys.* 7 (2005) 4089.
- [28] C.S. Jamieson, C.J. Bennett, A.M. Mebel, R.I. Kaiser, *Astrophys. J.* 624 (2005) 436.
- [29] K. Takizawa, A. Takami, S. Koda, *J. Phys. Chem. A* 104 (2000) 3693.
- [30] X. Wang, H. Hu, A. Tian, N.B. Wong, S.H. Chien, W.K. Li, *Chem. Phys. Lett.* 329 (2000) 483.
- [31] M.T. Nguyen, *Coord. Chem. Rev.* 244 (2003) 93.