Thermal reaction and luminescence of long-lived N ^{2}D in N$_2$ ice

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Photochemistry of an N$_2$ ice and thermal reaction of the irradiated sample were studied with vacuum-ultraviolet (VUV) light from a synchrotron. Concurrent detection of infrared absorption and visible emission spectra provide evidence for the generation of energetic products N (^{2}D) and N (^{2}P) atoms, N$_2$ (A) molecule and linear-N$_3$ (*l*-N$_3$) radical after excitation of icy N$_2$ at 121.6 nm. Irradiation at 190 nm is shown to be an effective way to eliminate the *l*-N$_3$ radical. After the photolysis and photoelimination of the *l*-N$_3$, we initiate synthesis of *l*-N$_3$ via the thermal ramping of the sample in temperature range 3.5 to 20 K. In addition, the emission from the N (^{2}D) atom was observed during the thermal ramping process. These behaviors indicate that a long-lived N (^{2}D$_{long}$) atom is generated in the VUV-photolyzed N$_2$ ice. A comparison of the variations of the visible emission of N (^{2}D) and the infrared absorption of *l*-N$_3$ with time indicates that the long-lived N (^{2}D$_{long}$) dominated the thermal synthesis of *l*-N$_3$. The results have enhanced suggestion and understanding of the conversion for nitrogen species in cold astrophysical environments with VUV irradiation.

atomic N (^{2}D) | azide radical | icy N$_2$ | photochemistry | vacuum-UV radiation

N$_2$ is a fundamental molecule widely distributed in space but is perceived to be a volatile substance above 77 K; however, it is able to exist as an amorphous solid in cold environments below 60 K. Beyond Uranus, N$_2$ ice is observed on many objects such as Triton (1–3), which is the largest satellite of Neptune, the dwarf planet Pluto and its satellite Charon, etc. (3–6). These icy objects continuously undergo photolysis and radiolysis to produce active atoms or radicals which may react to form *N*-bearing complex molecules. In addition, those active nitrogen species might be subject to temperature variations according to daily or seasonal patterns, and endogenic activity. Coupled with these variations, active species in N$_2$ ice could interact with contaminants to synthesize an *N*-bearing complex observed in space.

Although N$_2$ is recognized to be a primary source for the synthesis of much more complicated *N*-containing complexes in astroenvironments, its large dissociation energy, 9.75 eV (7, 8), in the gaseous phase provides a great potential barrier to be overcome. The first excited state, A, of N$_2$ has a long lifetime, on the order seconds (9), and seems to serve as a steppingstone of energy for further reactions, or an energy reservoir to transfer its energy to its surroundings (10–13). Although the lowest resonance absorption of N$_2$ is the Lyman–Birge–Hopfield system (9), for a N$_2$ ice at 145.6 nm (8.52 eV) (14), the measured threshold of emission for A → X, the Vegard–Kaplan system (VK) (9), extends to 175 nm (7.08 eV) (15). With this steppingstone in state A, the dissociation barrier of icy N$_2$ becomes greatly decreased; the important evidence is that emission from the photofragment N (^{2}D → ^{4}S) (16, 17) has a threshold energy of 8.52 eV (18). The energetics and transitions of the photolysis of icy N$_2$ are summarized in Fig. 1.

Other than the nitrogen atom, the azide radical, linear-N$_3$ (*l*-N$_3$), is the other nitrogen complex able to be synthesized from photolysis of the N$_2$ ice in the laboratory; this radical and excited N atom seem active so as to be readily able to induce other reactions with their surroundings (19). In icy N$_2$, the N and *l*-N$_3$ are hence the only products that can be identified from photolysis,

but their identifications differ. The presence of *l*-N$_3$ can be directly verified through absorption spectra in the mid-infrared (IR) (19–23) and UV (24, 25) spectral ranges, whereas, the N can be identified through a visible emission spectrum, like the luminescence from the transition N (^{2}D → ^{4}S) observed in photolysis (18) and radiolysis (16) experiments.

In this work, we applied vacuum-ultraviolet (VUV) light at 121.6 nm from a synchrotron (see *SI Appendix* for experiments) to synthesize *l*-N$_3$ and atomic N in a N$_2$ ice and then used light at 190 nm to irradiate the ice to eliminate *l*-N$_3$ so that the ice contained only *N*-atom doping (26). Our recorded absorption and emission spectra served to monitor the temporal variations of *l*-N$_3$, N$_2$, and N. During the variation of temperature of the *N*-atom–doped ice after in darkness 1 h, α-lines of transition N (^{2}D → ^{4}S) were observed again, indicating that N (^{2}D) still existed in the N$_2$ ice. After that heating, the absorption of *l*-N$_3$ was observed again in the IR spectrum. This long-lived N in state ^{2}D seems to have played a major role in the thermal-activated emission and thermal-activated synthesis of *l*-N$_3$; it seems that whereby raising the temperature can induce further reactions in the irradiated icy environment.

Icy N$_2$ upon 121.6-nm Illumination

Fig. 2 shows the experimental procedure; the horizontal axis indicates a timescale representing the sequence of the experiment. The graphic trend, shown in Fig. 2*A*, indicates variations of the photocurrent of the VUV light and symbols beside the trend indicate the time to record spectra–"IR-#", "iEm-#," and "Em-#"; Fig. 2*C* shows the temperature of the N$_2$ ice. Fig. 2*B*

Significance

N$_2$ is present as ice in cold outer space. In this work, photochemical experiments with concurrent detection of infrared absorption and visible emission spectra provide evidence for the generation of energetic products N ^{2}D atom and *l*-N$_3$ radical after photolysis of icy N$_2$ with vacuum-ultraviolet radiation. We found that the photolysis of icy N$_2$ may also produce the long-lived N ^{2}D$_{long}$ atom which can be triggered to release emission or to induce the synthesis of *l*-N$_3$ upon raising of the temperature. This work enhances our understanding of the transformation of nitrogen species in cold astroenvironments; the results also open a window into photochemical processes in solid state.
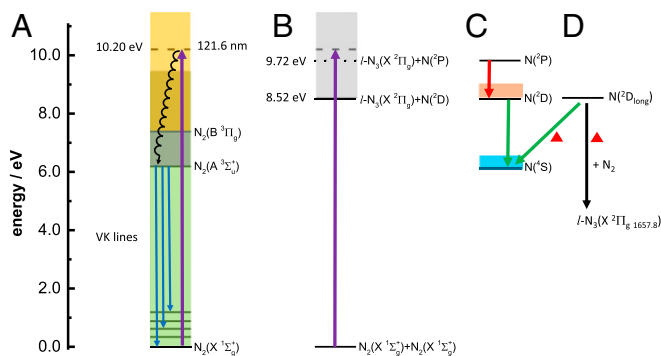
Fig. 1. (A) Scheme of energetics and transitions for excitation of icy N_2 at 121.6 nm, 10.20 eV. (B) Scheme of energetics and generation l-N_3 for excitation of icy N_2 at 121.6 nm. (C) Scheme of N (^{2}P) and N (^{2}D) atoms relax to their lower states N (^{2}D) and N (^{4}S), respectively, through emissions. (D) During thermal ramping (marked with symbols ▲), scheme of conversion and reaction of N ($^2D_{long}$) atoms.

shows temporal profiles of the peak height of emission ("iEm" and "Em") at 522.6 nm. After recording an IR absorption spectrum labeled "IR-1" for the deposited icy N_2 as a basic reference, we irradiated the N_2 ice with VUV light at 121.6 nm, Lyman-α line of atomic H.

Upon 121.6-nm illumination, we simultaneously recorded series emissions, labeled "iEm-1.#" from the icy N_2; for examples, the spectra labeled "iEm-1.1" and "iEm-1.45" in Fig. 3 A and B were recorded as the 1st and 45th of the set of "iEm-1" emission spectra, respectively. These emissions show abundant and complicated features identified as transitions of N_2 (A → X, VK series) (9, 15), N (^{2}D → ^{4}S, α series) (16), N (^{2}P → ^{2}D, δ series) (17) and impurity O [^{1}S → ^{1}D (27), β series (16)]; the details of identifications were presented in our previous work (26).

Excitation at 121.6 nm (10.20 eV) could pump ground-state N_2 to state B $^3\Pi_g$; which rapidly crossed to state A $^3\Sigma_u^+$ with radiationless transition, then relaxed to its ground state X $^1\Sigma_g^+$ through the luminescent process with emissions of VK lines as shown in Fig. 1A. According to previous work (14), the formation of threshold wavelength for N (^{2}D) and l-N_3 from the icy N_2 is 145.6 nm, 8.52 eV, as Eq. 1.

$$N_2(X) + N_2(X) + hv \rightarrow N(^2D) + l\text{-}N_3(X^2\Pi_g)\, \lambda_{th} = 145.6\ nm. \quad [1]$$
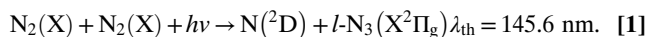
Generation of N (^{2}D) and l-N_3 could occur and the emission from the excited N (^{2}D) hence appeared upon 121.6 nm as displayed in Fig. 1 B and C. In addition, considering that the energy of N (^{2}P) is about 1.2 eV greater than that of N (^{2}D), the formation of N (^{2}P) from photolysis of the icy N_2 at 121.6 nm might also be possible as summarized in Eq. 2.

$$N_2(X) + N_2(X) + hv \rightarrow N(^2P) + l\text{-}N_3(X^2\Pi_g). \quad [2]$$
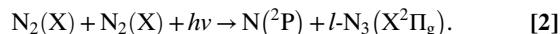
In addition, the N (^{2}D) might be pumped to the N (^{2}P) by light. The above discussion explains observations of emissions from N (^{2}D), N (^{2}P), and N_2 (A $^3\Sigma_u^+$) in Fig. 3. Among these emissions, the most intense emission of atomic N was the α-line from ^{2}D at 522.6 nm as depicted in Fig. 3; details of spectral profiles are shown in Fig. 4. Their identifications were discussed in our previous work (26). Subsequently, the atomic N (^{2}D) might play an important role in the photochemical system of icy N_2; we thus primarily monitored its emission and display the intensity profiles in the Fig. 2B.

After irradiation with VUV light at 121.6 nm, we recorded an IR absorption spectrum labeled "IR-2" in Fig. 5; "IR-1" is the spectrum of precursor N_2 before irradiation. Due to inactive

absorption of N_2, the curve IR-1 shows only background. Two sites of characteristic absorption of l-N_3 were observed at 1,652.6 and 1,657.8 cm^{-1} in IR-2; this result reflects the formation of l-N_3 from the reaction Eqs. 1 or 2 upon 121.6 nm. Two characteristic lines may represent either the same l-N_3 molecule with different vibrational quantum numbers or the different l-N_3 molecules associated with the different structural arrangements stored in icy N_2. There is no other evidence for the ν_3 mode of l-N_3 possessing different vibrational quantum numbers in this work. More likely, considering the host molecule N_2 is not spherical that may result in different structural sites for store the l-N_3 molecules in icy N_2.

Icy N_2 Containing As-Generated l-N_3 Irradiated at 190 nm

To engage the photochemical system simply, we intended to eliminate the as-generated l-N_3 at this stage. The vibronic absorption progression of l-N_3 in the icy N_2 was measured by Chin et al. in wavelength region 190 to 225 nm (28); therefore, we photolyzed the target icy sample containing the as-generated l-N_3 upon light at 190 nm for 1 h. Also, because the threshold wavelengths of emission of the N α-line and N_2 (A → X) are 145.6 and 175 nm (16), respectively, we used VUV light at 190 nm, which initiates no reaction of N_2 ice, to irradiate the icy N_2 containing as-generated l-N_3 radicals. After we irradiated at 190 nm, we then recorded the IR spectrum of the icy sample shown as spectrum "IR-3" in Fig. 5 which discloses only background curve without signal of l-N_3. This result indicates that as-generated l-N_3 radicals were totally dissociated upon 190 nm (26). During upon 190 nm, we could only detect the emission of the N α line as displayed in Fig. 2B. These observations combined allow us to conclude that the photodissociation of l-N_3 generates N_2 (X $^1\Sigma_g^+$) and atomic N (^{2}D) as Eq. 3 (26).

$$l\text{-}N_3(X^2\Pi_g) + hv \rightarrow N(^2D) + N_2(X). \quad [3]$$
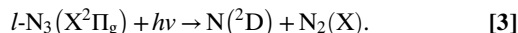
At that point in the experiment the as-generated l-N_3 radicals were eliminated; the target ice contained only N and N_2, which might be not all in their ground states. Considering that the decay lifetimes of N (^{2}D) and N_2 (A) are 25 and 2.5 s due to parity-forbidden transitions (15, 17), we thus waited 1 h with the icy
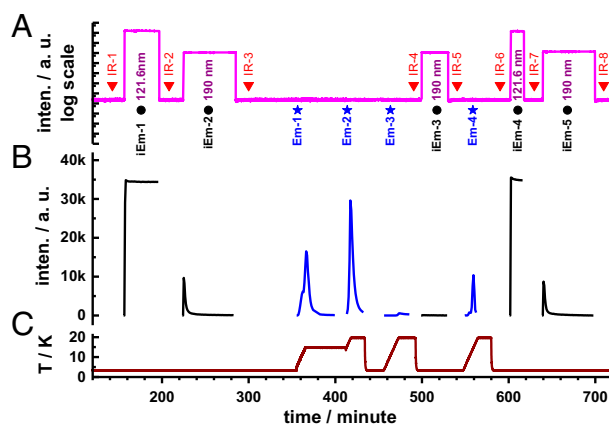

Fig. 2. Experimental procedure related to the photon current of irradiation, temporal profiles of the N α-line and temperature of the N_2 ice. The graphic trend in A shows photon currents (logarithmic scale) of irradiated light; the scatters show the time line of recording various spectra, in which the triangle (▼), circle (●) and star (★) indicate when recording spectra IR, iEm, and Em, respectively. B shows temporal profiles of the height of the atomic N α-line monitored at 522.6 nm; both temporal profiles of iEm-1 and iEm-4 are flat because of saturation of the charge-coupled device (CCD) detector. C shows the variation of temperature of the N_2 ice.
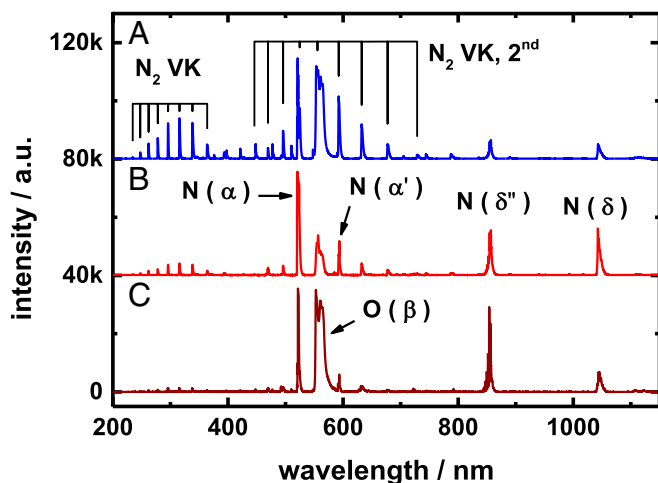
Fig. 3. Emission spectra during irradiation at 121.6 nm. *A* and *B* are spectra of the 1st (recorded at 157 min) and 45th (recorded at 194 min) measured spectra in series spectra of iEm-1; both are labeled as "iEm-1.1" and "iEm-1.45," respectively. *C* indicates the 7th spectrum (recorded at 607 min) in series spectra of iEm-4; it is labeled as "iEm-4.7". The notations "N_2 VK" and "N_2 VK, 2nd" represent the first- and second-order lines of N_2 VK transition (26). The notations N (α) and N (α') indicate lines of (0,0) and (0,1) from transitions N (^{2}D → ^{4}S), whereas N (δ) and N (δ'') indicate lines of (0,0) and (n,n-1) from transitions N (^{2}P → ^{2}D) (26). The notation O (β) represents lines due to O (^{1}S → ^{1}D) from impurity O_2.

sample (after irradiated at 190 nm) in darkness at 3.5 K to ensure that those 2 species had relaxed to their ground states; we hence supposed that there was nearly no excited-state species in the target N_2 ice at this stage due to no emission observed at all.

Thermal Ramping of the Target Ice and Observation of the Long-Lived N (^{2}D)

The target ice was then subjected to a series of temperature variations and concurrently recorded emission spectra labeled "Em-1" to "Em-3," of which temporal and spectral profiles of the α-line from N (^{2}D) are shown in Figs. 2*B* and 4, respectively. Sequentially, we raised the temperature of the icy sample from 3.5 to 15 K over a period of 8.5 min and maintained it at 15 K for 45 min (Em-1), raised from 15 to 20 K over a period of 5 min and maintained it at 20 K over a period of 15 min (Em-2), cooled to 3.5 K again for 20 min, and raised from 3.5 to 20 K over a period of 16.5 min and maintained it at 20 K for 20 min (Em-3).

From spectra Em-1 to Em-3, the observation of N α-line emission indicated that some portion of N was still in state ^{2}D and not all in ground state as previously supposed. After elimination of l-N_3, we waited until no emission of the α-line was measurable as "iEm-2" in Fig. 2; this result indicates that no N was in state ^{2}D. But, the temporal profiles of Em-1 to "Em-3" in Fig. 2 recorded the α line, the results indicate that the target ice still contained N in an excited state ^{2}D which might be different from N (^{2}D) in emissions of "iEm-1" and iEm-2. To distinguish the N (^{2}D) with a lifetime of 25 s, we thus label this long-lived state as N (^{2}D$_{long}$).
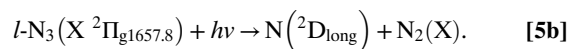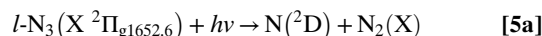
After the thermal ramping and recording visible spectra Em-1 to Em-3, we then recorded the IR spectrum "IR-4" in Fig. 5, in which the absorption of l-N_3 appeared again at 1,657.8 cm^{-1}, but notably corresponding to only 1 site, whereas, the other site of feature absorption at 1,652.6 cm^{-1} is absent here. Considering the nascent threshold wavelengths of l-N_3 and N to be 145.6 nm, we reasonably suppose that l-N_3 was synthesized from N_2 combining with atomic N that might be in an excited state. First considering N_2, no trace of N_2 (A) was found as the A-X emission was not observed; it is hence reasonable to exclude the

effect of N_2 (A) in further formation of l-N_3 and thermal warming. For atomic N, emissions of series of N α-lines were observed. N might hence be present in configuration $2s^2 2p^3$ with ^{4}S, ^{2}D, or other terms. According to a calculation of Galvão (29), a synthesis of l-N_3 has a greater probability from N (^{2}D) than from N (^{4}S). We thus suggest that the formation of l-N_3 at 1,657.8 cm^{-1} in the warming process follows Eq. **4**.

$$N\left(^2D_{long}\right) + N_2(X) \rightarrow l\text{-}N_3\left(X \ ^2\Pi_{g1,657.8}\right). \qquad [4]$$
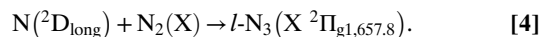
Comparison between the VUV-Synthesized *l*-N₃ with the Thermal-Synthesized *l*-N₃

At this stage in our experiment, we had found 2 methods to synthesize l-N_3; one was VUV irradiation and the other was warming the ice containing atomic N. Only one method, VUV irradiation, can decompose l-N_3 into N and N_2, which could be in their ground states, N (^{4}S) and N_2 (X), or in excited states, N (^{2}D, ^{2}P) and N_2 (A). In the elimination of l-N_3, if its fragments of decomposition are in luminescently excited states, we have the possibility to observe these emissions. Upon 190-nm illumination, we observed strong emission of N (^{2}D → ^{4}S) as in iEm-2 and "iEm-5" shown in Fig. 2*B*, but not in "iEm-3;" these phenomena indicate the states produced were different. The IR absorption spectra might provide some information of states in the icy N_2 at 3.5 K. For the VUV-synthesized l-N_3 with 121.6 nm light, the l-N_3 was formed in 2 sites corresponding to absorption lines at 1652.6 and 1657.8 cm^{-1} as "IR-2" and "IR-7", but only one site, corresponding to 1657.8 cm^{-1}, was observed for the thermal synthesis of l-N_3 as "IR-4". Therefore, we suppose that there are 2 channels for the reaction Eq. **3** as follows:

$$l\text{-}N_3\left(X \ ^2\Pi_{g1652.6}\right) + hv \rightarrow N\left(^2D\right) + N_2(X) \qquad [5a]$$

$$l\text{-}N_3\left(X \ ^2\Pi_{g1657.8}\right) + hv \rightarrow N\left(^2D_{long}\right) + N_2(X). \qquad [5b]$$

The decomposed fragment N (^{2}D) from the reaction Eq. **5a** for l-N_3 at the site corresponding to 1652.6 cm^{-1} luminescently relaxes to ^{4}S with lifetime 25 s, but not that of the N (^{2}D$_{long}$) associated with 1657.8 cm^{-1} from reaction Eq. **5b**. According to these schemes we were able to observe strong emissions from
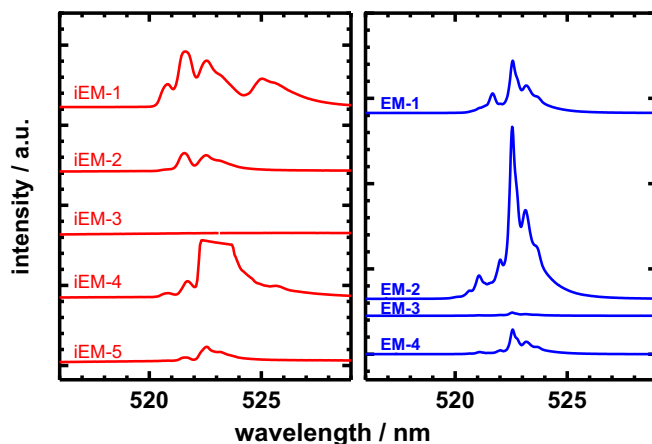

Fig. 4. Profiles of emissions near N α-line region for spectra iEm-# and Em-#. The iEm-# were the 1st of serial emission spectra, in which iEm-1 to iEm-5 were recorded at 155, 222, 497, 600, and 637 min, respectively. Em-# were averaged spectra from serial emission spectra, in which the 1st spectra of Em-1 to Em-4 were recorded at 354, 412, 456, and 550 min, respectively.
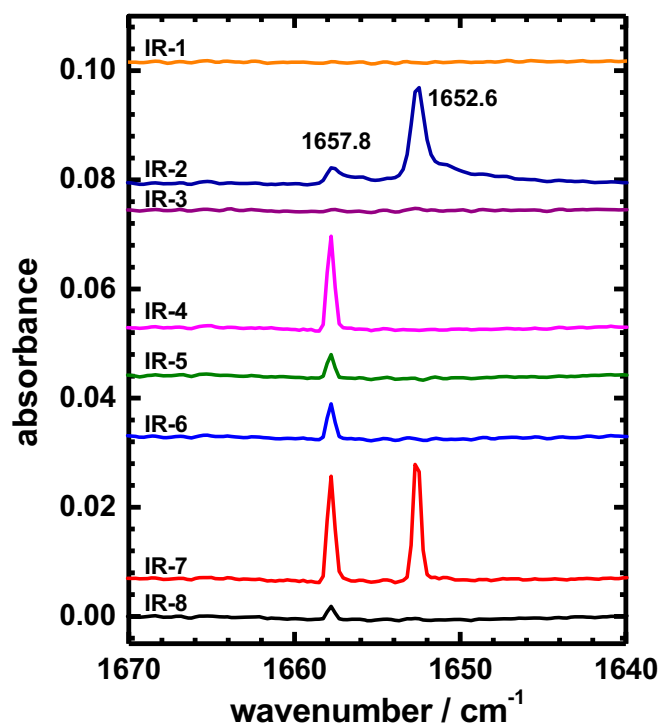
Fig. 5. IR absorption spectra. The labels are those used in Fig. 1; the direct times of IR-1 to IR-8 were recorded at 142, 208, 300, 495, 540, 590, 630, and 710 min, respectively. The IR-1 is the spectrum of precursor N_2 before irradiation, the IR-2 is the spectrum after irradiated 121.6 nm, the IR-3 is the spectrum after irradiated 190 nm, the IR-4 is the spectrum after thermal ramping, the IR-5 is the spectrum after irradiated 190 nm again, the IR-6 is the spectrum after thermal ramping again, the IR-7 is the spectrum after irradiated 121.6 nm again, and the IR-8 is the spectrum after irradiated 190 nm finally. The area ratios are among IR-2: IR-4: IR-5: IR-6: IR-7: IR-8 = 33: 7.8: 2: 3: 22: 1.

the N (^{2}D) at the beginning of "iEm-2" and "iEm-5" but not "iEm-3" in the VUV elimination of as-synthesized l-N$_3$.

Due to thermal effect, 2 excited N atoms in ^{2}D may involve the translation between them; the conversion of N (^{2}D$_{long}$) to N (^{2}D) may proceed during thermal ramping. Upon 121.6-nm irradiation, the reaction Eq. **1** produces not only 2 sites of l-N$_3$ in $^2\Pi_{g1,657.8}$ and $^2\Pi_{g1,652.6}$ but also 2 excited N atoms in ^{2}D and ^{2}D$_{long}$ at low temperature. The excited N (^{2}D) atom luminescently relaxes to ground-state N (^{4}S) with lifetime about 25 s, whereas N (^{2}D$_{long}$) keeps stable for a long time in N$_2$ ice. Induced by thermal, the long-lived N (^{2}D$_{long}$) can convert to N (^{2}D), which subsequently relaxes to N (^{4}S) with emission as described in Eq. **6**:

$$N\left(^2D_{long}\right) \rightarrow N\left(^2D\right) \rightarrow N\left(^4S\right) + h\nu. \qquad [6]$$
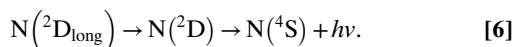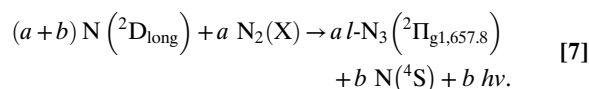
In this process, the conversion of N (^{2}D$_{long}$) to N (^{2}D) can thus be indirectly monitored by the emission of N α-line, as recorded in Fig. 2B. When the temperature of icy sample containing the N (^{2}D$_{long}$) raised from 3.5 to 15 K, the emission of N α-line appeared above 3.5 K, its intensity kept increasing until reaching the final temperature 15 K; then, the intensity of N α-line decayed to none at 15 K in 45 min, shown as Em-1 in Fig. 2B. In the next step, the temperature of target icy sample raised from 15 to 20 K, the N α-line emitted again above 15 K and increased to a maximum until 20 K; after that, the intensity decreased to almost none at 20 K in 20 min as shown in Em-2 profile. From profiles of "Em-1" and "Em-2," the curves demonstrate that the conversion rate from N (^{2}D$_{long}$) to N (^{2}D) increased during

temperature ramping from 3.5 to 20 K. This phenomenon hints that the stability of N (^{2}D$_{long}$) may relate to temperature; it becomes more stable at lower temperature. Interestingly, the conversion of N (^{2}D$_{long}$) to N (^{2}D) is an irreversible process. When the target icy sample cooled from 20 to 3.5 K, and then raised from 3.5 to 20 K again, almost no emission was observed as depicted in Em-3. Combined, these results suggest that N (^{2}D$_{long}$) atoms persist in stable sites of the icy N$_2$. The sites may depend on temperature; the more sites possibly exist at lower temperature. When the temperature of icy N$_2$ goes up, either the sites of store for N (^{2}D$_{long}$) atoms are disrupted by thermal energy irreversibly or the N (^{2}D$_{long}$) atoms have enough thermal energy to physically translocate from these sites irreversibly is possible.

Considering that the relaxations of N (^{2}D) and N$_2$ (A) to ground states involve parity-forbidden transitions (17), the processes of deexcitations may be strongly perturbed from the inter- and intramolecular environments; thus, the unusually long lifetime of N (^{2}D$_{long}$) may be related to a physical character of the N$_2$ ice lattice and could also be influenced by the temperature. It is also possible that the process of conversion from N (^{2}D$_{long}$) to N (^{2}D) depends on temperature; the less active process may occur at lower temperature but that is faster at higher temperature.

To further consider that thermally synthesized l-N$_3$ is dominated by N (^{2}D$_{long}$), one portion of which relaxes to ^{4}S and another portion of which reacts with N$_2$ to synthesize l-N$_3$. This assumption is provable from a comparison of the ratio between the total amount of emission ^{2}D → ^{4}S and the yield of l-N$_3$. For the emission part, we integrated the temporal profiles and obtained (Em-1 to Em-3)/(Em-4) = 6.3; for yields of l-N$_3$, we integrated the IR absorptions of l-N$_3$ and made a comparison of ("IR-4" − "IR-3")/("IR-6" − "IR-5") = (7.8−0)/(3.2−2) = 6.5; these 2 ratios of emission (N α line) and IR absorption (l-N$_3$) are nearly the same. This correlation indicates that the thermal synthesis of l-N$_3$ can be represented with this equation:

$$(a+b)\,N\left(^2D_{long}\right) + a\,N_2(X) \rightarrow a\,l\text{-}N_3\left(^2\Pi_{g1,657.8}\right)$$
$$+ b\,N\left(^4S\right) + b\,h\nu. \qquad [7]$$

The reactions of Eq. **7** involved are displayed in the diagrams of Fig. 1D.

Implication to Astroscience

The mid-UV reflectance spectra of Pluto and Charon were recorded by the *Hubble Space Telescope* Cosmic Origins Spectrograph (*HST*/COS); Stern et al. (30) reported the Pluto's spectrum contains a strong mid-UV absorption feature. Recently, Chin et al. (28) suggested that the carrier of absorption feature of Pluto's surface observed by HST/COS might be l-N$_3$. According to this work, the photochemical process of icy N$_2$ upon VUV light may possibly produce l-N$_3$ and N (^{2}D) in the outer Solar System. For evolution of nitrogen species in cold astroenvironments, the reactive l-N$_3$ radical and N (^{2}D) atom may initiate many chemical reactions to form complicated N compounds at low temperature. For example, the l-N$_3$ radical can react with hydrocarbons like CH$_4$ and ultimately form HCN and HNC in the icy N$_2$ (18). Therefore, these reactive nitrogen species l-N$_3$ and N (^{2}D) may play important roles in the chemical reactions of the nitrogen-ice analogs. Understanding the formation and elimination of N (^{2}D) and l-N$_3$ in icy N$_2$ are thus important and urgent. In this work, our results demonstrate that photolysis of icy N$_2$ with VUV light can produce reactive nitrogen species N (^{2}D) and l-N$_3$. Other than photogeneration of the excited N (^{2}D) with definite lifetime about 25 s, formation of the long life of excited N (^{2}D$_{long}$) has been first confirmed in icy N$_2$; remarkably, the N (^{2}D$_{long}$) can react with N$_2$ to produce l-N$_3$ by thermal-activated reaction. On the contrary,

photodissociation of l-N_3 can generate N (^2D) in icy N_2. Hence, the transformation between these 2 nitrogen species can occur in photochemical process and thermal reaction. The universe is full of VUV source including the Lyman-α 121.6 nm; in addition, the icy N_2 may exist in cold interstellar medium. Our results have thus opened a window to understand the nitrogen transformation in cold astrophysical environments.

Summary

In summary, photolysis of a N_2 ice with VUV light at 121.6 nm produced N and l-N_3; VUV light at 190 nm eliminated l-N_3 leaving the N_2 ice with only N-doping. During VUV synthesis of l-N_3, emissions in the VK series of N_2, α, and δ lines of N and the β-line of O from impurity O_2 were observed. In the elimination of l-N_3, only the α-line was observed; also, the α-line was recorded in the thermal synthesis l-N_3. Although 1 h of darkness prevented N_2 and N from existing in their excited states A and ^2D, respectively, observing the α-line during warming indicated that there existed long-lived N ($^2D_{long}$), having a lifetime much greater than 25 s, which dominated the thermal synthesis of l-N_3. This long-lived N ($^2D_{long}$) was stored in the N_2 ice and could be triggered to release emission or to induce a reaction on raising the temperature.

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