Photocatalysis of a N₂ ice and thermal reaction of the irritated 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 (3D) and N (5P) atoms, N₂ (A) molecule and linear-N₃ (l-N₃) radical after excitation of icy N₂ at 121.6 nm. Irradiation at 190 nm is shown to be an effective way to eliminate the l-N₃ radical. After the photolysis and photoelimination of the l-N₃, we initiate synthesis of l-N₃ via the thermal ramping of the sample in temperature range 3.5 to 20 K. In addition, the emission from the N (3D) atom was observed during the thermal ramping process. These behaviors indicate that a long-lived N (3Dlong) atom is generated in the VUV-photoalyzed N₂ ice. A comparison of the variations of the visible emission of N (3D) and the infrared absorption of l-N₃ with time indicates that the long-lived N (3Dlong) dominated the thermal synthesis of l-N₃. The results have enhanced understanding of the conversion for nitrogen species in cold astrophysical environments with VUV irradiation.

N₂ 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, N₂ 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 N₂ ice could interact with contaminants to synthesize an N-bearing complex observed in space.

Although N₂ 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 N₂ has a long lifetime, on the order seconds (9), and seems to serve as a steppingstone of energy to its surroundings (10–13). Although the lowest resonance absorption of N₂ is the Lyman–Birge–Hopfield system (9), for a N₂ ice at 145.6 nm (8.52 eV) (14), the measured threshold of emission for A → X is the Vergard–Kaplan system (VK) (9), extends to 175 nm (7.08 eV) (15). With this steppingstone in state A, the dissociation barrier of icy N₂ becomes greatly decreased; the important evidence is that emission from the photofragment N (3D → 2S) (16, 17) has a threshold energy of 5.52 eV (18). The energetics and transitions of the photolysis of icy N₂ are summarized in Fig. 1.

Other than the nitrogen atom, the azide radical, linear-N₃ (l-N₃), is the other nitrogen complex able to be synthesized from photolysis of the N₂ 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 N₂, the N and l-N₃ are hence the only products that can be identified from photolysis, but their identifications differ. The presence of l-N₃ 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 (3D → 5S) 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-N₃ and atomic N in a N₂ ice and then used light at 190 nm to irradiate the ice to eliminate l-N₃ so that the ice contained only N atom doping (26). Our recorded absorption and emission spectra served to monitor the temporal variations of l-N₃, N₂, and N. During the variation of temperature of the N–atom–doped ice after in darkness 1 h, a-lines of transition N (3D → 2S) were observed again, indicating that N (3D) still existed in the N₂ ice. After that heating, the absorption of l-N₃ was observed again in the IR spectrum. This long-lived N in state 2D seems to have played a major role in the thermal-activated emission and thermal-activated synthesis of l-N₃; it seems that whereby raising the temperature can induce further reactions in the irritated icy environment.

**Icy N₂ 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. 2A, indicates variations of the photocurrent of the VUV light and symbols beside the trend indicate the time to record spectra—“IR-#”; “Em-#”; “C-#”; “Em-#”; “C-#”; Fig. 2C shows the temperature of the N₂ ice. Fig. 2B

**Significance**

N₂ 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 (3D) atom and l-N₃ radical after photolysis of icy N₂ with vacuum-ultraviolet radiation. We found that the photolysis of icy N₂ may also produce the long-lived N (3Dlong) atom which can be triggered to release emission or to induce the synthesis of l-N₃ 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.
were recorded as the 1st and 45th of the set of previous work (26). Subsequently, the atomic N \( (2D) \) might play an shown in Fig. 4. Their identifications were discussed in our pre-

522.6 nm as depicted in Fig. 3; details of spectral profiles are series emissions, labeled \( iEm-1.45 \) 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 complica-
ted features identified as transitions of \( N_2 \) (\( A \rightarrow X \), VK series) (9, 15), \( N \) \( (\tilde{D} \rightarrow \tilde{S}, \alpha \) series) (16), \( N \) \( (\tilde{P} \rightarrow \tilde{D}, \beta \) series) (17) and impurity O \( [\tilde{S} \rightarrow \tilde{D}, \beta \) 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 \( B \tilde{Π}_L \); which rapidly crossed to state \( A \tilde{Σ}^+ \), with radi-

ationless transition, then relaxed to its ground state \( X \tilde{Σ}^+ \) 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 \( N \) \( (\tilde{D}) \) and \( l-N_3 \) from the icy \( N_2 \) is 145.6 nm, 8.52 eV, as Eq. \( 1 \).

\[
N_2(X) + N_2(X) + hν \rightarrow N(\tilde{D}) + l-N_3(X^2Π_g)\lambda_{th} = 145.6 \text{ nm}.
\]

Generation of \( N \) \( (\tilde{D}) \) and \( l-N_3 \) could occur and the emission from the excited \( N \) \( (\tilde{D}) \) hence appeared upon 121.6 nm as displayed in Fig. 1 \( B \) and \( C \). In addition, considering that the energy of \( N \) \( (\tilde{P}) \) is about 1.2 eV greater than that of \( N \) \( (\tilde{D}) \), the for-
mation of \( N \) \( (\tilde{P}) \) from photolysis of the icy \( N_2 \) at 121.6 nm might also be possible as summarized in Eq. \( 2 \).

\[
N_2(X) + N_2(X) + hν \rightarrow N(\tilde{P}) + l-N_3(X^2Π_g).
\]

In addition, the \( N \) \( (\tilde{D}) \) might be pumped to the \( N \) \( (\tilde{P}) \) by light. The above discussion explains observations of emissions from \( N \) \( (\tilde{D}), N \) \( (\tilde{P}) \), and \( N_2 \) \( (A \tilde{Σ}^+ \) ) in Fig. 3. Among these emissions, the most intense emission of atomic \( N \) was the \( \alpha \)-line from \( \tilde{D} \) 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 \( N \) \( (\tilde{D}) \) 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-1” 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 charac-
teristic 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 \( v_1 \) 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 \( l-N_3 \) mol-
ecules 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 ab-
sorption 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 \( N \) \( \alpha \)-line and \( N_2 \) \( (A \rightarrow X) \) 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 \( N \) \( \alpha \) line as displayed in Fig. 2B. These observations combined allow us to conclude that the photodissociation of \( l-N_3 \) generates \( N_2 \) \( (X \tilde{Σ}^+ \) ) and atomic \( N \) \( (\tilde{D}) \) as Eq. \( 3 \) (26).

\[
l-N_3(X^2Π_g) + hν \rightarrow N(\tilde{D}) + N_2(X).
\]

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 \( N \) \( (\tilde{D}) \) 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
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 N2 ice at this stage due to no emission observed at all.

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

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 (2D) are shown in Figs. 2B and 4, respectively. Sequentially, we raised the temperature of the ice 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 2D and not all in ground state as previously supposed. After elimination of l-N3, 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 2D. 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 2D which might be different from N (2D) in emissions of “iEm-1” and iEm-2. To distinguish the N (2D) with a lifetime of 25 s, we thus label this long-lived state as N (2Dlong).

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-N3 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-N3 and N to be 145.6 nm, we reasonably suppose that l-N3 was synthesized from N2, combining with atomic N that might be in an excited state. First considering N2, no trace of N2 (A) was found as the A-X emission was not observed; it is hence reasonable to exclude the effect of N2 (A) in further formation of l-N3 and thermal warming. For atomic N, emissions of series of N α-lines were observed. N might hence be present in configuration 2S with 2P, or 2D, or other terms. According to a calculation of Galvão (29), a synthesis of l-N3 has a greater probability from N (2D) than from N (2S). We thus suppose that the formation of l-N3 at 1,657.8 cm−1 in the warming process follows Eq. 4.

\[
N(2D_{long}) + N_2(X) \rightarrow N_3(X \ 2 \Pi_{g,1657.8}).
\]

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-N3; one was VUV irradiation and the other was warming the ice containing atomic N. Only one method, VUV irradiation, can decompose l-N3 into N and N2, which could be in their ground states, N (4S) and N2 (X), or in excited states, N (2D, 2P) and N2 (A). In the elimination of l-N3, if its fragments decomposition are in luminescently excited states, we have the possibility to observe these emissions. Upon 190-nm illumination, we observed strong emission of N (2D) as in iEm-2 and “iEm-3” shown in Fig. 2B, 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 N2 at 3.5 K. For the VUV-synthesized l-N3 with 121.6 nm light, the l-N3 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-N3 as “IR-4.” Therefore, we suppose that there are 2 channels for the reaction Eq. 3 as follows:

\[
l-N_3(X \ 2 \Pi_{g \lambda 1652.6}) + h\nu \rightarrow N(2D) + N_2(X) \quad [5a]
\]

\[
l-N_4(X \ 2 \Pi_{g \lambda 1657.8}) + h\nu \rightarrow N(2D_{long}) + N_2(X). \quad [5b]
\]

The decomposed fragment N (2D) from the reaction Eq. 5a for l-N3 at the site corresponding to 1652.6 cm−1 luminescently relaxes to 3S with lifetime 25 s, but not that of the N (2Dlong) associated with 1657.8 cm−1 from reaction Eq. 5b. According to these schemes we were able to observe strong emissions from

\[
\begin{align*}
\text{Fig. 3. Emission spectra during irradiation at 121.6 nm. A and B are spectra of the 1st (recorded at 157 min) and 45th (recorded at 194 min) measured spectra in series spectra of iEm-1; both are labeled as iEm-1.1 and “iEm-1.45, respectively.” C indicates the 7th spectrum (recorded at 607 min) in series spectra of iEm-4; it is labeled as “iEm-4.7.” The notations “N (α) and “N (α’), “N (δ), “N (β), and “N (δ’) represent the first- and second-order lines of N2, λ transition (26). The notations N (α) and N (α’) indicate lines of (0,0) and (0,1) from transitions N (2D → 4S), whereas N (δ) and N (δ’) indicate lines of (0,0) and (n,n-1) from transitions N (9P → 3D) (26). The notation O (β) represents lines due to O (5S → 1D) from impurity O2.
\end{align*}
\]

\[
\begin{align*}
\text{Fig. 4. Profiles of emissions near N α-line region for spectra iEm-1 and Em-9. The Em-9 were the 1st of serial emission spectra, in which iEm-1 to iEm-5 were recorded at 155, 222, 497, 600, and 637 min, respectively. Em-9 were averaged spectra from serial emission spectra, in which the 1st spectra of Em-1 to Em-4 were recorded at 354, 412, 456, and 550 min, respectively.}
\end{align*}
\]
temperature ramping from 3.5 to 20 K. This phenomenon hints that the stability of N (^2D\textsubscript{long}) may relate to temperature; it becomes more stable at lower temperature. Interestingly, the conversion of N (^2D\textsubscript{long}) to N (^2D) 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 (^2D\textsubscript{long}) atoms persist in stable sites of the icy N\textsubscript{2}. The sites may depend on temperature; the more sites possibly exist at lower temperature. When the temperature of icy N\textsubscript{2} goes up, either the sites of store for N (^2D\textsubscript{long}) atoms are disrupted by thermal energy irreversibly or the N (^2D\textsubscript{long}) atoms have enough thermal energy to physically translocate from these sites irreversibly is possible.

Considering that the relaxations of N (^2D) and N\textsubscript{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 (^2D\textsubscript{long}) may be related to a physical character of the N\textsubscript{2} ice lattice and could also be influenced by the temperature. It is also possible that the process of conversion from N (^2D\textsubscript{long}) to N (^2D) 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-N3 is dominated by N (^2D\textsubscript{long}), one portion of which relaxes to ^3S and another portion of which reacts with N\textsubscript{2} to synthesize l-N3. This assumption is provable from a comparison of the ratio between the total amount of emission ^2D \rightarrow ^3S and the yield of l-N3. For the emission part, we integrated the temporal profiles and obtained (Em-1 to Em-3)/(Em-4) = 6.3; for yields of l-N3 we integrated the IR absorptions of l-N3 and made a comparison of "IR-4" - "IR-3"/"IR-6" - "IR-5" = (7.8 - 0.0)/(3.2 - 2) = 6.5; these 2 ratios of emission (N \textalpha line) and IR absorption (l-N3) are nearly the same. This correlation indicates that the thermal synthesis of l-N3 can be represented with this equation:

\[(a + b)N\ (^2D\textsubscript{long}) + aN\textsubscript{2}(X) \rightarrow a-l-N3^\textalpha \textsubscript{1\Pi\textsubscript{g}, 657,8} + bN\ (^3S) + bhv.\]  

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\textsubscript{3}. According to this work, the photochemical process of icy N\textsubscript{2} upon VUV light may possibly produce l-N3 and N (^2D) in the outer Solar System. For evolution of nitrogen species in cold astroenvironments, the reactive l-N3 radical and N (^2D) atom may initiate many chemical reactions to form complicated N compounds at low temperature. For example, the l-N3 radical can react with hydrocarbons like CH\textsubscript{4} and ultimately form HCN and HNC in the icy N\textsubscript{2} (18). Therefore, these reactive nitrogen species l-N3 and N (^2D) may play important roles in the chemical reactions of the nitrogen-ice analogs. Understanding the formation and elimination of N (^2D) and l-N3 in icy N\textsubscript{2} are thus important and urgent. In this work, our results demonstrate that photolysis of icy N\textsubscript{2} with VUV light can produce reactive nitrogen species N (^2D) and l-N3. Other than photogeneration of the excited N (^2D) with definite lifetime about 25 s, formation of the long life of excited N (^2D\textsubscript{long}) has been first confirmed in icy N\textsubscript{2}; remarkably, the N (^2D\textsubscript{long}) can react with N\textsubscript{2} to produce l-N3 by thermal-activated reaction. On the contrary,
photodissociation of I-N₃ can generate N (²D) in icy N₂. 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 N₂ 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, photography of a N₂ ice with VUV light at 121.6 nm produced N and I-N₃; VUV light at 190 nm eliminated I-N₃ leaving the N₂ ice with only N-doping. During VUV synthesis of I-N₃, emissions in the VK series of N₂, α, and δ lines of N and the β-line of O from impurity O₂ were observed. In the elimination of I-N₃, only the α-line was observed; also, the α-line was recorded in the thermal synthesis I-N₃. Although 1 h of darkness prevented N₂ 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 (²Dlong), having a lifetime much greater than 25 s, which dominated the thermal synthesis of I-N₃. This long-lived N (²Dlong) was stored in the N₂ ice and could be triggered to release emission or to induce a reaction on raising the temperature.

Data Availability. All data discussed in the paper are presented in the figures and will be made available to readers.

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