Solid-State Nitrogen

DOI: 10.1002/anie.201306876

Production of N_3 upon Photolysis of Solid Nitrogen at 3 K with Synchrotron Radiation[**]

*Sheng-Lung Chou, Jen-Iu Lo, Meng-Yeh Lin, Yu-Chain Peng, Hsiao-Chi Lu, and Bing-Ming Cheng**

Abstract: *The photodissociation of gaseous molecular nitrogen has been investigated intensively, but the corresponding knowledge in a solid phase is lacking. Irradiation of pure solid nitrogen at 3 K with vacuum-ultraviolet light from a synchrotron produced infrared absorption lines of product l-*N_3 *at 1657.8 and 1652.6* cm^{-1}*. The threshold wavelength to generate l-*N_3 *was determined to be (143.7 ± 1.8) nm, corresponding to an energy of (8.63 ± 0.11) eV. Quantum-chemical calculations support the formation of l-*N_3 *from the reaction* $N_2 + N_2$*, possibly through an activated complex l-*N_4 *upon photoexcitation with energy above 8.63 eV. The results provide a possible application to an understanding of the nitrogen cycle in astronomical environments.*

Nitrogen is the most abundant chemical element in the terrestrial atmosphere, comprising approximately four fifths of the total content. The photodissociation of the nitrogen molecule maintains interest because of its importance in the atmosphere of Earth and various other astronomical environments; its photolysis illustrates problems over a range of molecular dynamics. The photochemistry of gaseous nitrogen has been investigated intensively,[1] but a corresponding knowledge of a solid phase is lacking: we extend this acquaintance to the solid state. Herein, the irradiation of pure solid nitrogen at 3 K with vacuum-ultraviolet (VUV) light from a synchrotron produced infrared absorption lines of product *l*-N_3; the threshold energy to generate *l*-N_3 is determined to be 8.63 ± 0.11 eV. Quantum-chemical calculations support the formation of *l*-N_3 from the reaction $N_2 + N_2$, possibly through an activated complex *l*-N_4 upon photoexcitation. Our results are possibly applicable to enhance our understanding of the nitrogen cycle in astronomical environments.

A photochemical reaction of nitrogen is initiated with the breaking of the strong N–N bond; the dissociation energy of gaseous N_2 is 9.798 eV,[2] corresponding to a wavelength of 126.54 nm. Chemical paths in the solid state might differ from those in the gaseous phase because, according to a phenomenon in the solid state known as the cage effect, the separation or migration of a fragment of photolysis from its site of production might be inhibited, so altering the relative efficiencies of the possible reaction paths.[3] As N_2 is stable in the gaseous phase up to the stated large energy, we might wonder whether that condition persists in the solid state. The matrix environment might not only influence the escape of a nitrogen atom but also provide a reaction path to form a polynitrogen species. Three known species of molecular nitrogen include N_2,[4] N_3,[5] and N_4.[6] Can a polynitrogen species containing nitrogen atoms more than two be formed upon photoexcitation in the solid state? The investigation of the photodissociation of N_2 in the solid state is thus of interest.

For photolytic dissociation, it is important to know the electronic state and the extent of the absorption of solid N_2 involved in the radiant excitation. For this purpose, we measured, with a double-beam absorption apparatus coupled to beamline BL03 at Taiwan's National Synchrotron Radiation Research Center (NSRRC),[7] the absorption spectrum of pure solid nitrogen in the vacuum-ultraviolet region to the limit of the transmission of optical components, which is about 105 nm. Figure 1 shows the VUV absorption spectrum of pure solid N_2 at 3 K in the spectral region between 106 nm and 160 nm at spectral resolution 0.1 nm; the thickness of the deposited sample was about 8–10 μm. An inspection of the total absorption profile and an analysis of the observed vibrational progressions reveal that two dominant electronic transitions in this region include the Lyman–Birge–Hopfield

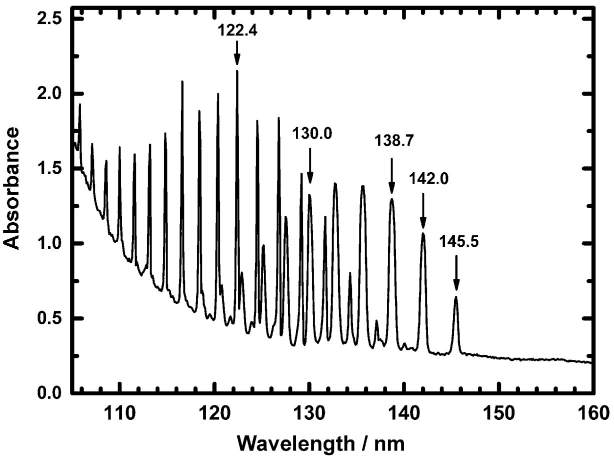

Figure 1. Absorption spectrum (resolution 0.1 nm, step 0.1 nm) of pure solid nitrogen at 3 K in the wavelength range 105–160 nm. The thickness of the nitrogen film is estimated to be 8–10 μm.

---

[*] S.-L. Chou, Dr. J.-I. Lo, M.-Y. Lin, Y.-C. Peng, Dr. H.-C. Lu, Dr. B.-M. Cheng
National Synchrotron Radiation Research Center
No. 101, Hsin-Ann Road, Hsinchu Science Park
Hsinchu 30076 (Taiwan)
E-mail: bmcheng@nsrrc.org.tw

[**] The National Science Council of Republic of China (grants NSC99-2113- M-213-003-MY3 and NSC102-2113-M-213-005-MY3) and the National Synchrotron Radiation Research Center (NSRRC) provided financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306876.

(LBH, $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$) and Tanaka (TA, $w\,^1\Delta_u \leftarrow X\,^1\Sigma_g^+$) systems. A detailed assignment of the transitions has been published;[8] the positions of lines in the LBH and TA progressions are listed in the Supporting Information, Tables S1 and S2.

In relation to the dissociation energy 9.798 eV of gaseous N_2 and its corresponding wavelength 126.54 nm and to the absorption spectrum in Figure 1, it is of interest to investigate the photoexcitation of solid nitrogen in wavelength range 110–150 nm. We selected the radiation from an undulator with periodically spaced permanent magnets (90 mm, U90) attached to beamline BL21A2 at NSRRC. Harmonics from the undulator were suppressed through absorption by Ar at pressure 1.33 kPa and a filter window (LiF for 105–125 nm and CaF_2 for 125–150 nm). Gaseous N_2 was deposited on a CsI window cooled to 3 K in an apparatus similar to that described elsewhere.[9] We recorded the infrared absorption spectrum of the deposited solid samples of nitrogen before and after photolysis with radiation at a selected wavelength. Before photolysis, the absorption spectrum revealed a doublet at 2349.2 and 2347.7 cm^{-1} owing to adventitious CO_2 and weak lines near 3726.8 and 1597.3 cm^{-1} associated with H_2O; both contaminants were present in vestigial proportions after deposition for 2 h or more. Otherwise, only a weak line at 2328.4 cm^{-1} of full width 0.8 cm^{-1} at half maximum (FWHM) was recorded and identified as the absorption of solid N_2.

According to our ultraviolet spectrum, the most intense absorption of solid nitrogen below 126.54 nm (9.798 eV) occurs at 122.4 nm, corresponding to 10.13 eV, which is attributed to the transition (7,0) in the TA progression (see the Supporting Information). We thus initially selected wavelength 122.4 nm (as indicated in Figure 1) to excite the solid nitrogen. After that irradiation, infrared absorption lines appeared at 1657.8 and 1652.7 cm^{-1}; Figure 2a shows the difference of IR absorption after photolysis for 30 min. The line at 1652.7 cm^{-1} is more intense than that at 1657.8 cm^{-1}, which was accompanied on occasion with a small shoulder at 1655.7 cm^{-1}. These features are characteristic of the ν_3 mode of the azide radical, N_3, reported by Tian et al.[10] and by us.[8] Tian et al. recorded lines at 1657.5, 1654.5, and 1652.6 cm^{-1} after bombardment of solid N_2 at 20 K with Ne/He$^+$ particles (energy 4 keV). In contrast, we recorded lines at 1657.8 and 1652.6 cm^{-1} after VUV photolysis at 130 nm (9.5 eV) of solid nitrogen at 20 K, and proposed that N_3 was generated from $N\,^2D$ with $N_2\,X\,^1\Sigma_g^+$. The dissociation energy of ground-state N_2 into $N\,^2D + N\,^4S$ is about 12.14 eV in the gaseous phase; $N\,^2D$ can thus not be generated from photolysis of $N_2\,X\,^1\Sigma_g^+$ at 9.5 eV. That proposed mechanism of formation is therefore questionable.

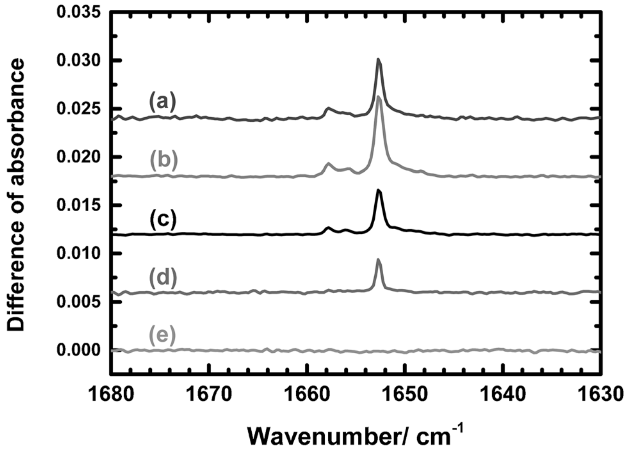

Figure 2. Infrared spectra (resolution 0.5 cm^{-1}) of solid nitrogen at 3 K after photolysis for 30 min at wavelengths a) 122.4, b) 130.0, c) 138.7, d) 142.0, e) 145.5 nm.

In a separate experiment with $^{15}N_2$, we measured absorption lines of $^{15}N_3$ at 1603.6 and 1601.9 cm^{-1}, corresponding to isotopic ratios 0.9673 and 0.9693, respectively. To verify the carrier of these lines based on isotopic shifts and the line splitting, we performed quantum-chemical calculations (Gaussian09 program, basis set B3LYP/6-311G**). The calculated values of l-N_3 and l-$^{15}N_3$ for vibrational mode ν_3 are 1665.2 and 1608.9 cm^{-1}, respectively; these values agree satisfactorily with experimental data (the discrepancies are within 0.8 %). The calculated isotopic ratio, 0.9662, of mode ν_3 similarly agrees satisfactorily with the experimental values. We thus assign unambiguously the specified new lines to the azide radical in mode ν_3; detailed calculations and discussion are presented in the Supporting Information.

Upon excitation at 122.4 nm, nitrogen might dissociate to $N\,^4S + N\,^4S$ according to Equation (1):

$$N_2\,X\,^1\Sigma_g^+ + h\nu \rightarrow N\,^4S + N\,^4S \quad (1)$$

In the solid phase, N atoms might recombine to reform N_2, but another possibility is that $N\,^4S$ might react with N_2 to form N_3 according to Equation (2):

$$N_2\,X\,^1\Sigma_g^+ + N\,^4S \rightarrow N_3\,X\,^2\Pi \quad (2)$$

The production of N_3 thus indicates the photodissociation of N_2 in the solid state. We thereby monitored the infrared absorption of N_3 as an indicator of the photolytic dissociation of solid N_2.

The photon energy, 10.13 eV, at wavelength 122.4 nm is 0.33 eV greater than the threshold energy, 9.798 eV, of gaseous N_2 at 126.54 nm. To discover the threshold for the formation of N_3 upon photoexcitation of solid nitrogen, we tuned the wavelength of radiation beyond 127 nm based on the absorption lines of solid nitrogen, as indicated in Figure 1. We separately selected the lines corresponding to transitions (5,0), (2,0), (1,0), and (0,0) in the progression of the LBH system[8] to irradiate the samples of solid nitrogen at 130.0, 138.7, 142.0, and 145.5 nm, respectively; the corresponding infrared absorption spectra are shown as curves (b), (c), (d), and (e), respectively, in Figure 2. The absorption lines of N_3 clearly appeared after irradiation at wavelengths 130.0, 138.7 and 142.0 nm, but not at 145.5 nm, even for irradiation prolonged beyond 30 min. In these experiments, the VUV radiation was directed from undulator U90 and regulated on adjusting its gap; this mode of operation yields a beam of ultraviolet light of relative width 2 %, corresponding to width 0.175 eV of photon energy at the selected wavelength. According to Figure 2, the threshold for the formation of N_3 is thus between wavelengths 142.0 and 145.5 nm, corresponding to photon energies 8.731 and 8.521 eV, respectively. We hence derive the threshold energy to generate N_3 from photolysis of solid nitrogen at 3 K to be 8.63 ± 0.11 eV (143.7 ± 1.8 nm) as the midpoint of those two energies.

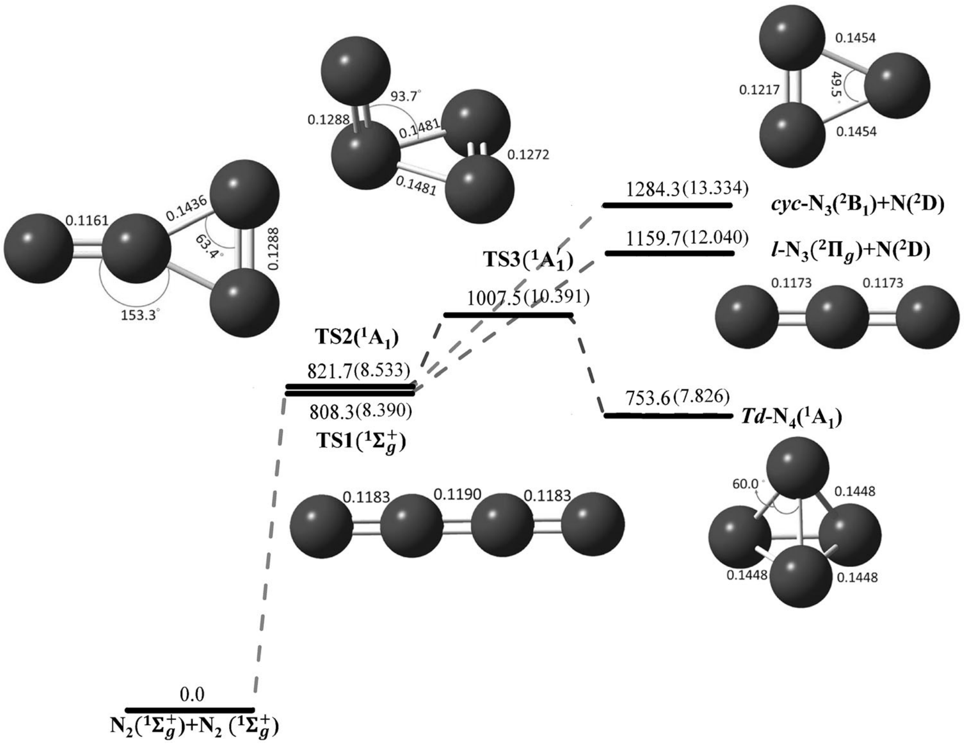

Figure 3. Energies [kJ mol^{-1}, eV in parentheses] along reaction paths for the reaction $N_2 + N_2$. The energies calculated at the stationary points are indicated in the figure. The calculated geometries (bond lengths [nm], angles [°]) of TS1, TS2, TS3, *cyc*-N_3, *l*-N_3, and T_d-N_4 are displayed. The structures were optimized with B3LYP/aug-cc-pVTZ; their energies were calculated with basis set CCSD(T)/aug-cc-pVTZ.

The photochemical behavior of a species in a solid sample differs from that in the gaseous phase: at a small density, gaseous fragments readily move apart after dissociation, whereas a fragment produced in a solid sample might have insufficient energy to escape from its immediate environment. In this case, impeded by the surrounding nitrogen molecules, an N atom as fragment might be constrained typically to remain at or near its site of origin, and to recombine to the original molecule, unless the N atom obtains sufficient kinetic energy to escape its original lattice boundary and thus become isolated from another N atom. If diffusion plays a key role in generating an isolated N atom upon photolytic dissociation of solid nitrogen, excess energy must be provided to facilitate the migration or diffusion of an N fragment through the lattice of solid nitrogen. For this reason, the photodissociation energy of solid nitrogen must exceed its gaseous threshold value, namely 9.798 eV. Induced by photodissociation according to Equation (1), atom $N\,^4S$ might subsequently react with a solid nitrogen molecule to form N_3 according to Equation (2); the reaction might occur at either the original lattice site or elsewhere after migration. In either case, the threshold energy of formation of N_3 through Equation (2) is also 9.798 eV.

The threshold energy that we obtained to form N_3 (8.63 ± 0.11 eV) is less than the dissociation energy of gaseous N_2 (9.798 eV). This result indicates that a mechanism for formation involves other than simply a dissociation of a N atom from one N_2 that reacts with another N_2, according to Equation (2). To understand the potential-energy profiles of the reaction, we calculated the energy along a reaction path for reaction $N_2\,^1\Sigma_g^+ + N_2\,^1\Sigma_g^+$. All of the calculations were performed with the program Gaussian 09; geometric parameters, vibrational wavenumbers, and infrared intensities were initially calculated and subsequently characterized with the B3LYP method and both local and nonlocal terms in conjunction with basis set aug-cc-pVTZ (correlation-consistent polarized-valence triple-zeta). To enhance the reliability of the relative energies, we calculated single-point electronic energies for the stationary points with coupled-cluster theory CCSD (T). By this means, we performed the calculations at points selected to provide a balanced global representation of the potential-energy surface along various reaction paths illustrated in Figure 3. According to our calculations, four reaction products comprise $N\,^2D$, *cyc*-$N_3\,^2B_1$, *l*-$N_3\,^2\Pi_g$, and T_d-$N_4\,^1A_1$. In our experiments recording IR absorption, we detected only *l*-N_3; no absorption line related to either *cyc*-N_3 or T_d-N_4 (see the Supporting Information);[11,12] we thus eliminate the paths related to products *cyc*-N_3 and T_d-N_4. Only one path for the reaction $N_2 + N_2$ remains, involving initial formation of activated complex N_4 as transition structure TS1; its calculated structure is linear, and is denoted *l*-N_4. Excitation of *l*-N_4 with energy about 3.6 eV can dissociate it to $N +$ *l*-N_3. The calculated energy 8.39 eV of the most stable activated complex, TS1 *l*-N_4, is notable; the value is near the threshold energy 8.63 ± 0.11 eV to form N_3. We therefore propose that *l*-N_3 might form from two nitrogen molecules through activated complex *l*-N_4 upon photoexcitation above energy 8.63 eV; this reaction path is supported by our calculations.

Our results open a new window to understand the photochemistry in the solid state. The ramifications of our experiments are applicable to the nitrogen cycle in astrophysical environments. In cold outer space, nitrogen molecules exist in the solid state; the excitation with energetic photons is a driving force to evolve nitrogen species in astronomical environments. We have shown that the exposure of solid nitrogen to energetic radiation forms N_3. The investigation of the formation and chemistry of various nitrogen species enhances our understanding of the evolution of the nitrogen and bio-nitrogen cycles in space.

As further evidence, another product, $\mathrm{N}\,^{2}\mathrm{D}$, was detected from its emission of light near 521 nm (see the Supporting Information). The threshold energy to form nascent $\mathrm{N}\,^{2}\mathrm{D}$ was measured to be 8.61 ± 0.09 eV (144.1 ± 1.6 nm). This value is practically the same as the threshold energy, 8.63 ± 0.11 eV (143.7 ± 1.8 nm), for the production of *l*-N_3 detected with IR absorption; the result supports the proposed mechanism.

In summary, our work demonstrates that photodissociation of solid nitrogen at 3 K with vacuum-ultraviolet light in the wavelength region 105–150 nm yields infrared absorption features 1657.8 and 1652.6 cm^{-1} associated with *l*-N_3, the only nitrogen product detected with IR spectra; for the formation of *l*-N_3, the threshold wavelength, 143.7 ± 1.8 nm, corresponded to energy 8.63 ± 0.11 eV. Quantum-chemical calculations indicate a possible reaction path from the reaction $N_2\,^1\Sigma_g^+ + N_2\,^1\Sigma_g^+$; this reaction recombines a pair of nitrogen molecules to activated complex *l*-N_4 that can in turn dissociate to generate *l*-N_3. The threshold energy 8.63 eV to form *l*-N_3 from solid nitrogen is significantly less than the photodissociation threshold energy 9.798 eV of gaseous nitrogen.

Received: August 6, 2013
Revised: August 27, 2013

Keywords: dissociation energy · nitrogen · photolysis · synchrotron radiation · ultraviolet light

---

[1] a) A. Lofthus, P. H. Krupenie, *J. Phys. Chem. Ref. Data* **1977**, *6*, 113–307; b) H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, **1978**.
[2] http://webbook.nist.gov.
[3] a) L. E. Bruce, V. E. Bondybey, *J. Chem. Phys.* **1976**, *65*, 71–76; b) R. Alimi, R. B. Gerber, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 174–183; c) B.-M. Cheng, W.-J. Lo, L.-H. Lai, W.-C. Hung, Y.-P. Lee, *J. Chem. Phys.* **1995**, *103*, 6303–6304.
[4] J. Priestley, *Philos. Trans. R. Soc. London* **1772**, *62*, 147–264.
[5] B. A. Thrush, *Proc. R. Soc. London Ser. A* **1956**, *235*, 143–147.
[6] a) J. P. Zheng, J. Waluk, J. Spanget-Larsen, D. M. Blake, J. G. Radziszewski, *Chem. Phys. Lett.* **2000**, *328*, 227–233; b) F. Cacace, G. de Petris, A. Troiani, *Science* **2002**, *295*, 480–481.
[7] a) H.-C. Lu, H.-K. Chen, B.-M. Cheng, Y.-P. Kuo, J. F. Ogilvie, *J. Phys. B* **2005**, *38*, 3693–3704; b) H.-C. Lu, H.-K. Chen, B.-M. Cheng, J. F. Ogilvie, *Spectrochim. Acta Part A* **2008**, *71*, 1485–1491.
[8] Y.-J. Wu, C. Y. R. Wu, S.-L. Chou, M.-Y. Lin, H.-C. Lu, J.-I. Lo, B.-M. Cheng, *Astrophys. J.* **2012**, *746*, 175.
[9] a) Y.-J. Wu, M.-Y. Lin, B.-M. Cheng, H.-F. Chen, Y.-P. Lee, *J. Chem. Phys.* **2008**, *128*, 204509; b) Y.-J. Wu, H.-F. Chen, C. Camacho, H. A. Witek, S.-C. Hsu, M.-Y. Lin, S.-L. Chou, J. F. Ogilvie, B.-M. Cheng, *Astrophys. J.* **2009**, *701*, 8–11; c) Y.-J. Wu, H.-F. Chen, S.-L. Chou, M.-Y. Lin, H.-C. Lu, H.-K. Chen, B.-M. Cheng, *Astrophys. J.* **2010**, *721*, 856–863.
[10] R. Tian, J. C. Facelli, J. Michl, *J. Phys. Chem.* **1988**, *92*, 4073–4079.
[11] a) M. Bittererová, H. Östmark, T. Brinck, *Chem. Phys. Lett.* **2001**, *347*, 220–228; b) T. J. Lee, C. E. Dateo, *Chem. Phys. Lett.* **2001**, *345*, 295–302.
[12] M. T. Nguyen, T. L. Nguyen, A. M. Mebel, R. Flammang, *J. Phys. Chem. A* **2003**, *107*, 5452–5460.