as a gas. With theoretical calculations and measured absorption spectra, many properties, including electronic states and vibrational wavenumbers, of N (^{2}D), N_2^+, N_3 and N_3^+ are revealed. The potential role of N_3 was much less pronounced, but it has been proposed as a specific oxidant to remove electrons from aromatic hydrocarbons. N_3 might hence play an important role as electron scavenger in Titan's upper atmosphere.

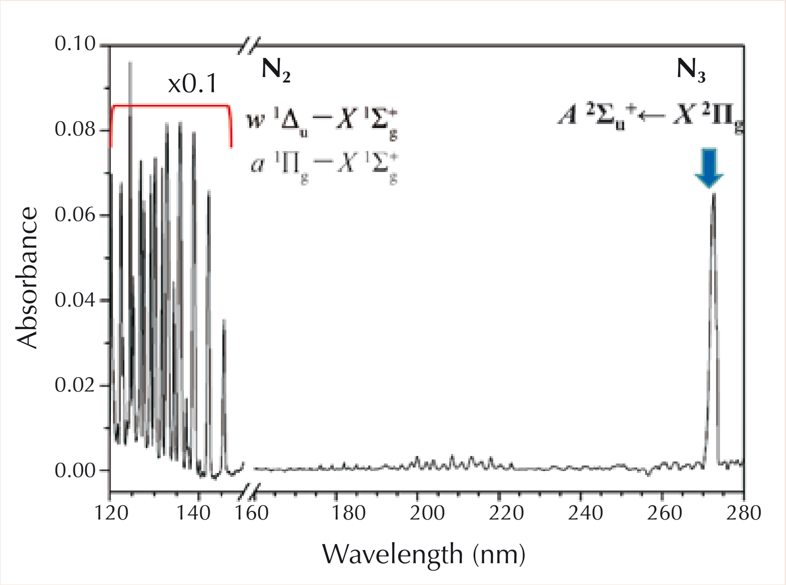

Fig. 3: UV absorption spectrum of N_2 ice subjected to electron irradiation during deposition for 1 h with electron energy 250 eV and current 200 μA.

References

1. Y.-J. Wu, R. C. Y. Wu, S.-L. Chou, M.-Y. Lin, H.-C. Lu, J.-I. Lo, and B.-M. Cheng, Astrophys. J. **746**, 175 (2012).
2. Y.-J. Wu, H.-F. Chen, S.-J. Chuang, and T.-P. Huang, Astrophys. J. **768**, 83 (2013).
3. Y.-J. Wu, H.-F. Chen, S.-J. Chuang, and T.-P. Huang, Astrophys. J. **779**, 40 (2013).

Photochemistry of the Most Abundant Gaseous Element N_2 in the Solid Phase

This report features the work of Bing-Ming Cheng and his co-workers published in Angew. Chem. Int. Ed. ***53****, 738 (2014).*

Dinitrogen N_2 is the most abundant molecule in the terrestrial atmosphere. The photochemistry of nitrogen retains the attention of scientists because of its importance in the atmosphere of earth and other astronomical environments. The photodissociation of gaseous N_2 as well as the succeeding chemistry was thus investigated intensively, whereas the corresponding properties of N_2 in a solid phase are still lacking. To initiate the chemical reactions of N_2, the first step is to break the N-N bond; in the gaseous phase, its dissociation energy is 9.798 eV. Bing-Ming Cheng and his co-workers discovered a smaller energy, 8.63 ± 0.11 eV, that suffices to initiate the chemistry of solid N_2.[1]

In Cheng's research, N_2 was condensed on a surface at 3 K. Beamlines **BL03A1** and **BL21A2** at the TLS, with a VUV source and a FTIR spectrometer respectively, served for the energy of excitation energy and a means of detection. These scientists reasonably began the experiment with an excitation energy greater than the dissociation energy of the N-N bond, 9.798 eV. After the irradiation, evidence for the existence of N_3 was observed, namely the infrared absorption lines at 1657.8 and 1652.7 cm^{-1}. These absorption lines in the infrared region are like a fingerprint because every molecule has its own infrared absorption spectrum. Cheng hence believes that they did observe the formation of N_3 according to the infrared absorption lines reported as the IR absorption spectra of N_3.

The fascinating discovery arose when Cheng and co-workers varied the photon energy to find the energy level at the dissociation threshold. Shown in

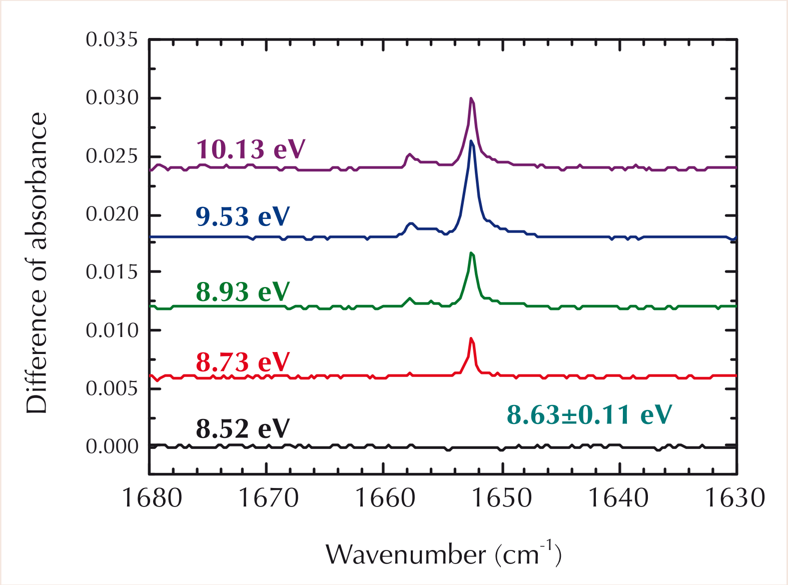

Fig. 1: Infrared spectra of solid dinitrogen at 3 K after phtolysis for 30 min at photon energies of 10.13, 9.53, 8.93, 8.73, and 8.52 eV with corresponding wavelengths 122.4, 130.0, 138.7, 142.0, and 145.5 nm, respectively.

Fig. 1 are the infrared spectra of solid dinitrogen after photolysis at various wavelengths. Wavelength 122.4 nm was the initial choice as that photon energy is greater than the energy to break the bond of N_2. When the wavelength was greater, i.e. the excitation energy was less, evidence for the existence of N_3 was observed, for even a wavelength as large as 142.0 nm (photon energy 8.731 eV). The photochemistry of solid N_2 was therefore definitely not initiated by breaking the N-N bond.

To solve this non-intuitive mechanism of reaction, a theoretical calculation was made utilizing software Gaussian 09 as depicted in Fig. 2. The energy level of solid nitrogen in the ground state is set as zero. The energy necessary to form transition complexes (TS1 and TS2 in Fig. 2), with formula N_4, is about 8.5 eV less than the experimental energy 8.63 ± 0.11 eV at the threshold to form N_3. The complex could then further react after absorbing another photon to form N + N_3. The products formed from TS1 and TS2 are linear N_3 and cyclic N_3, respectively. The infrared spectra of the products of the photochemical reaction demonstrate the character of linear N_3, not cyclic N_3. Cheng and co-workers hence concluded that solid N_2 absorbs one VUV photon to form a complex, linear N_4 (TS1 in Fig. 2), which in turn dissociates to form linear N_3 after absorbing another VUV photon. The threshold energies from these experiments in accordance with calculation and the measured IR absorption character of linear N_3 both confirm this new mechanism in solid N_2.

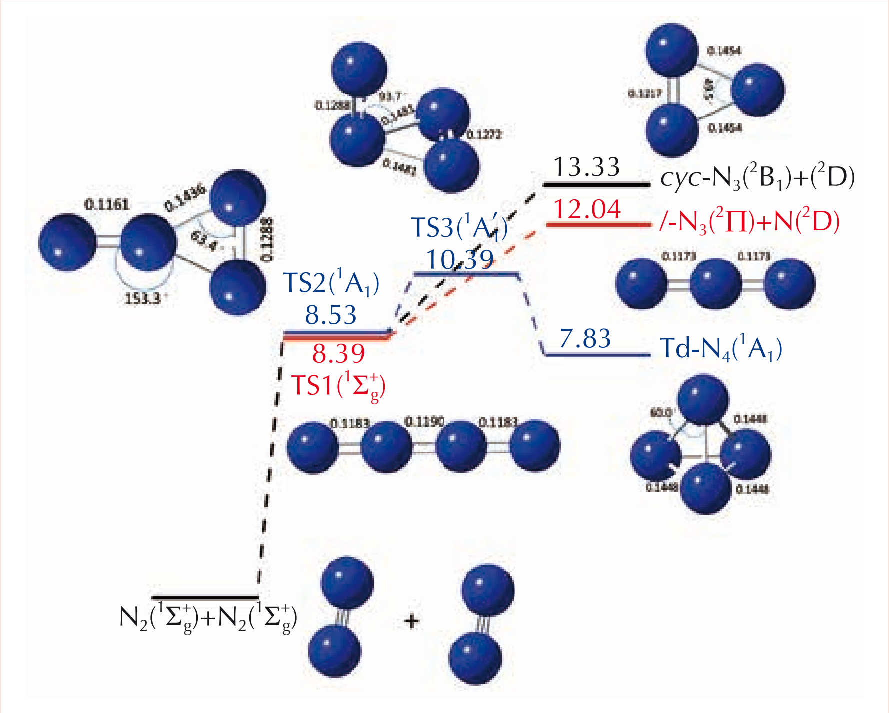

Fig. 2: Energies /kJ mol^{-1} and eV along reaction paths for the reaction N_2 + N_2. The energies calculated at the stationary points are indicated in the figure. The calculated geometries of TS1, TS2, TS3, cyclic N_3, linear N_3, and tetrahedral N_4 are displayed.

Reference

1. S.-L. Chou, J.-I. Lo, M.-Y. Lin, Y.-C. Peng, H.-C. Lu, and B.-M. Cheng, Angew. Chem. Int. Ed. **53**, 738 (2014). (Paper first published online: Nov. 29, 2013.)