

UV and IR Spectra to Determine Simulated Astrophysical Species

*This report features the work of Yu-Jong Wu and his co-workers published in *Astrophys. J.* **768**, 83 (2013) and *Astrophys. J.* **779**, 40 (2013).*

To explore the boundless outer space and the origin of life is a beautiful dream of a human being. Relying on advanced telescopes and measured spectra, these dreams might come true. Nevertheless an explanation of these spectra is sometimes lacking. A trans-Neptunian object (TNO), also known as a Kuiper-Belt object, is any object existing beyond the orbit of Neptune in the Solar System. These objects have received much attention during recent decades because they are remnants of the formation of the Solar System, and carry information about the early stages of its development. The Kuiper Belt, which is the location of these TNO, is proposed to be the main reservoir of the comets of short period that are thought to be carriers of organic molecules to Earth. These organic molecules might be produced by the interaction of sunlight or galactic cosmic rays (GCR) with the surface ices of TNO. These ices on several TNO, such as Triton, Pluto and Eris, contain predominantly N_2 with traces of CH_4 , CO and H_2O .

Recent observations with the Hubble Space Telescope (HST) have found strong absorption in the ultraviolet (UV) region on the surface of Pluto, indicating the presence of complicated hydrocarbons or nitriles. In addition, HCN has been tentatively identified on Triton, and the presence of tholins on Triton and Pluto has been proposed. The temperature of TNO is generally below 40 K; chemical reactions would thus be initiated with solar UV photons, solar wind particles and GCR, but the fluxes of solar winds and solar photons decrease significantly at such large distances, and they might be fully absorbed by the tenuous atmospheres of TNO or interact with only the upper few millimeters of the icy surfaces. In contrast, GCR can penetrate the upper several meters of icy surfaces, and are thought to deliver more energy to the surfaces of TNO than do solar photons. Furthermore, the interaction of GCRs with icy surfaces can gener-

ate secondary electrons, which might have energy sufficient to ionize or to excite nearby molecules and to induce further reactions.

Many experiments have been performed to study the effects of irradiation of N_2 -dominated ices with charged particles or photons. The excitation sources include 0.8-MeV protons, 7.4-eV photons, Lyman- α photons (10.2 eV), 5-keV electrons, 60-keV Ar^{2+} ions and so on. From the existence of CH_4 in N_2 ice, products such as CH_3 , C_2H_2 , HNC, HCN, C_2H_6 , CH_2N_2 , and HCN_2 were identified. Pure N_2 ice and of solid N_2 with dilute CH_4 have been subjected to photolysis at various wavelengths using synchrotron radiation.¹ The formation of nitriles in a series, most of which were identified for the first time in this ice system, were observed. Yu-Jong Wu and his co-workers chose to use electrons of energy 500 eV because a few hundred eV have energies resonant for the ionization or dissociation of molecules caused by electronic excitation of core-level electrons of molecules.² To identify the simulated astrophysical species, absorption spectra in IR and UV regions are measured. A Fourier-transform infrared spectrometer (Bruker, Vertex 80) equipped with a KBr beamsplitter and HgCdTe detector was utilized to record the IR spectra. To measure the UV spectra, UV light was dispersed using a 6-m monochromator on the high-flux beamline (**BL03A1**) at Taiwan Light Source. The measured UV and IR absorption spectra are shown in **Figs. (1) and (2)**, respectively.

In **Fig. 1**, a sharp feature at 272.5 nm is assigned unambiguously to the electronic absorption of N_3 . To assign correctly carriers of the observed broadband is difficult. In general, the products might be classified into two groups: those that contain $-\text{CN}$ (nitriles) and those without the $-\text{CN}$ group. In contrast, the so-called finger-print region in the IR spectrum enables

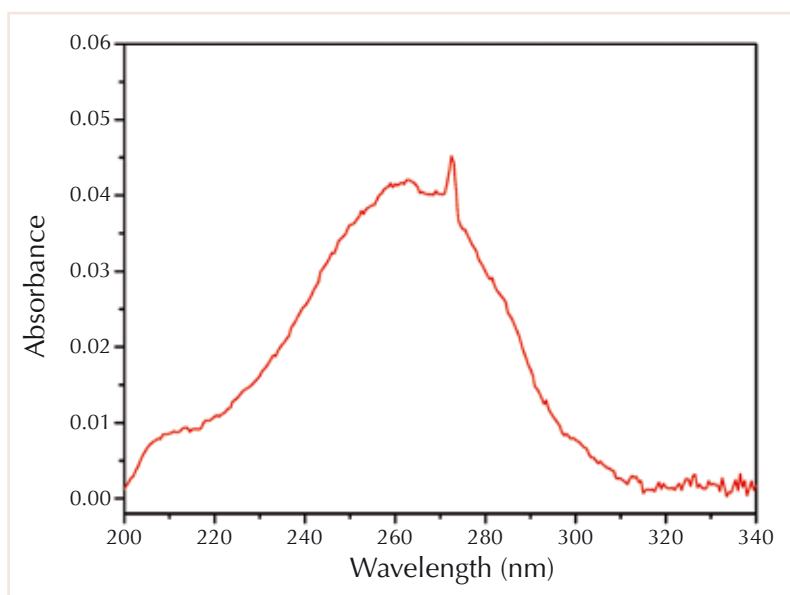


Fig. 1: UV absorption spectrum recorded after irradiation of a CH_4/N_2 (1/100) ice sample with electrons at 500 eV for 1 h.

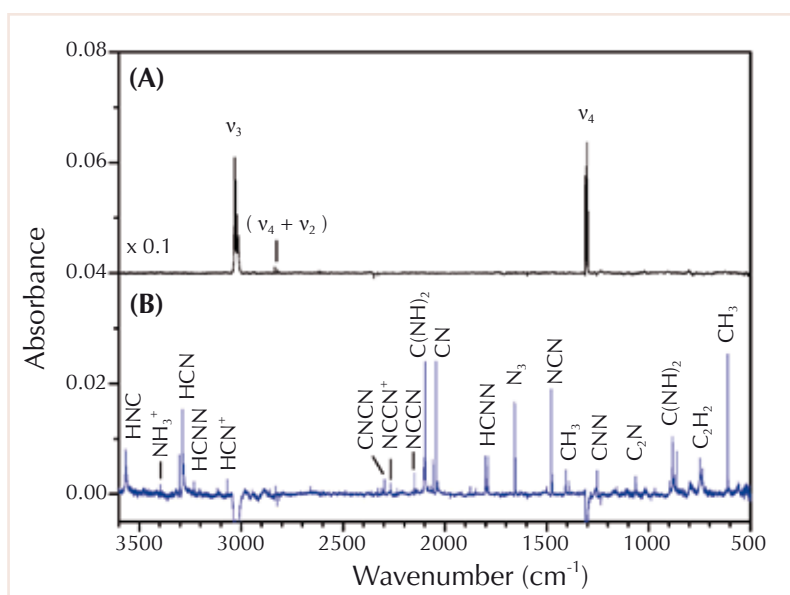


Fig. 2: IR absorption spectra of (A) a sample with CH_4/N_2 (1/100) and (B) the sample in (A) recorded after irradiation with electrons at 500 eV for 1 h.

many products – CH_3 , C_2H_2 , $\text{C}(\text{NH})_2$, CNN, NCN, N_3 , HCNH, CN, $(\text{CN})_2$, HCN, HNC, and so on – formed after irradiation with electrons at 500 eV to be identified. Wu confirmed the formation of various products, including hydrocarbons and nitriles, by IR spectra, and obtained subsequently the UV spectrum of the ice sample. These observations solved an open question about the measurement with the HST of an

absorption feature within 210 – 214 nm from Pluto on which nitrogen ice dominates methane and carbon monoxide.

In our solar system, gaseous dinitrogen (N_2) is abundant in the atmospheres of Earth, Titan, Triton and Pluto. This condition motivates an investigation of the excitation of N_2 , which is crucial for understanding the related nitrogen chemistry of these planetary atmospheres. For instance, Saturn's largest moon, Titan, has a dense atmosphere (160 kPa) composed of $\text{N}_2 \sim 98.4\%$, $\text{CH}_4 \sim 1.6\%$, and other, trace gases. When these trace substances assume a sufficiently large proportion, they form aerosol hazes in Titan's atmosphere, but the composition and the mechanism of formation of these organic layers are poorly understood. These reactions are likely initiated by electronically highly excited N_2 and CH_4 and their fragments; the excitation energy might derive from solar UV, solar wind, or GCR. Emission from excited N_2 was measured and assigned as transition $a^1\Pi_g \rightarrow X^1\Sigma_g$. These observations of the formation of activated nitrogen species in the nitrogen-dominant atmospheres of planets clearly indicate that excitation and de-excitation of N_2 play important roles in planetary atmospheric chemistry.

Wu and his co-workers decided to measure the products formed from the gaseous N_2 excited on electron bombardment.³ An electron gun (Kimball Physics, Model EFG-7) was utilized to generate electron beams of energies 250 eV and 1000 eV and beam current 200 mA, to bombard gaseous N_2 during the deposition of a matrix. A UV absorption spectrum is shown in Fig. 3. The single sharp line at 272.7 nm was readily assigned to the transition of N_3 , providing clear evidence of its formation even when N_2 was excited

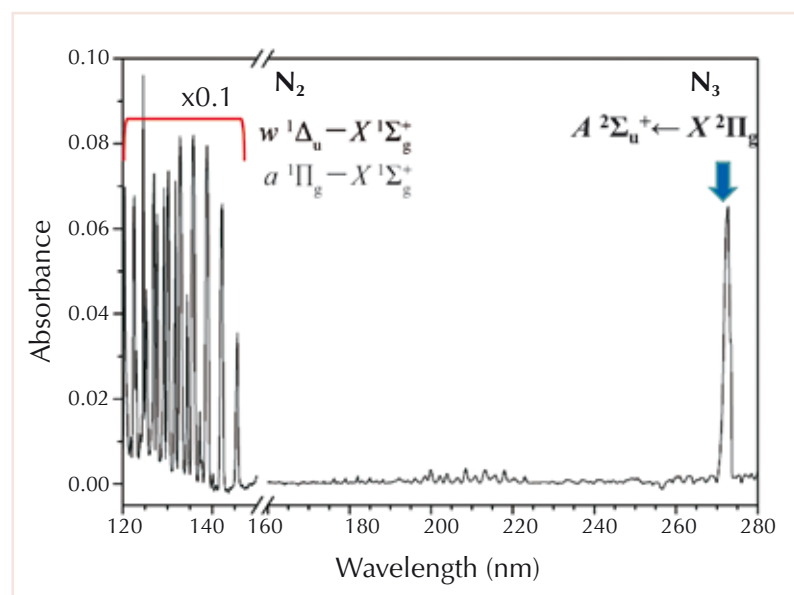


Fig. 3: UV absorption spectrum of N_2 ice subjected to electron irradiation during deposition for 1 h with electron energy 250 eV and current 200 μ A.

as a gas. With theoretical calculations and measured absorption spectra, many properties, including electronic states and vibrational wavenumbers, of $N(^2D)$, 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.

References

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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