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Ultraviolet Absorption Spectra of N_3 in Solid Nitrogen

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[Introduction] Molecular nitrogen (N_2) is known to be abundant in the atmospheres of Earth, Titan, Triton, and Pluto in the solar system and also has been found to dominate as surface ices on several trans-Neptunian objects (TNOs), such as Triton, Pluto, and Eris. The study of excitation of N_2 is particularly important in understanding the related nitrogen chemistry of these planetary atmospheres and icy surfaces. In our previous work, we have investigated the effect of secondary electrons generated by irradiation of pure N_2 ice with 500-eV electrons and the recorded IR and UV spectra clearly showed the formations of N_3 and N_3^+ [1]. In the present work, gaseous N_2 was bombarded with 250 or 1000-eV electrons and then followed by condensation onto the cold target to form a N_2 ice. The IR absorption spectra of the icy sample were recorded to identify the radiolysis products and the UV absorption spectra of the same matrix sample were subsequently recorded for comparison with the recent astronomic observations of Titan and Pluto in the UV spectral region.

[Experiment] A nickel-plated copper flat cooled to 10 K served as a cold substrate for matrix samples. The substrate was cooled with a ARS DE-204 closed-cycle helium refrigerator system and a turbomolecular pump provided the cryo-chamber vacuum, which was backed with a scroll pump, typically yielding a pressure of less than 1×10^{-8} Torr. The IR absorption spectra were recorded with a Fourier-transform infrared (FTIR) spectrometer (Bruker, Vertex 80) equipped with a KBr beamsplitter and a Hg-Cd-Te detector (cooled to 77 K), covering the spectral range of 500–4000 cm^{-1}. For measurement of far-UV spectra of matrix samples covering the spectral region 110-350 nm, the UV light was dispersed with a 6-m monochromator on the high-flux beam line at National Synchrotron Radiation Research Center (NSRRC). A spectral resolution of 0.1 nm was used with an accuracy of ±0.1 nm in the measurements of spectral positions. An electron gun (Kimball Physics, Model EFG-7) generated electron beams with energy of 250 and 1000 eV and beam current of 200 μA for electron bombardment of gaseous N_2 during matrix deposition.

[Result and Discussion] The IR spectra recorded after electron bombardment of gaseous N_2 during deposition show the absorption features of N_3 at 1657.6 and

1652.4 cm^{-1} assigned to the asymmetric stretching (ν_3) mode of N_3 and weak peaks at 2003.3 (2005.7) cm^{-1} corresponding to the asymmetric stretching (ν_3) mode of N_3^-. In addition, green luminescence was observed during matrix deposition indicating the N(^{2}D) atoms were produced via radiolysis and subsequently relaxed to N(^{4}S). We found no absorption appearing around 1170 cm^{-1} relating to the formation of N_3^+.

The UV absorption spectrum of the same sample shows the single sharp band at 272.7 nm is readily assigned to the transition $A\ ^2\Sigma_u^+ \leftarrow X\ ^2\Pi_g$ of N_3 [2]. The weak progression appearing around 190 nm with an average interval 884 cm^{-1} is attributed to the transition of $D\ ^2\Pi_g \leftarrow X\ ^2\Sigma_g^+$ of N_2^+ [3]. The complex progressions distributing in the 225–192 nm region correlated well to the transition $A\ ^2\Sigma_u^+ \leftarrow X\ ^2\Pi_g$ of N_3 at 272.7 nm. Based on the isotopic (^{15}N-) experiment, the observed progressions might be classified to three groups as shown in Figure 1. We employed time-dependent density functional theory (TD-DFT) to calculate the vertical excitation energies of low-lying electronic states of N_3 with the PW91PW91/aug-cc-pV5Z. According to the TD-DFT calculations of vertical excitations of the three of the first five excited doublet states, $2\ ^2\Pi_u$, $1\ ^2\Sigma_g^+$, and $1\ ^2\Sigma_g^-$, of N_3 lying in 5.79, 5.83, and 6.43 eV above the ground state $X\ ^2\Pi_g$, respectively; are in a good agreement with our observations of three progressions in the spectral region 223–192 nm. Also considering vibronic symmetry of $D_{\infty h}$ molecules, only the transitions involving the bending modes of π_u symmetry are allowed. The observed intervals might correspond to the bending modes of the upper states with one or two quanta excitations, since the ν_2 (bending) mode of N_3 in the ground state is determined 472.0 cm^{-1} experimentally and the ν_2 mode in the state $1\ ^2\Sigma_g^+$ was predicted to be 1044 cm^{-1} by MRCI-SD. The calculations with MRCI-SD(Q) method are performed for further information of the upper states of N_3 [4].

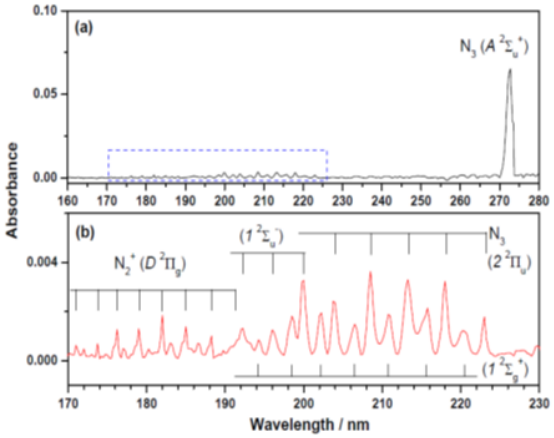

Fig. 1 UV absorption spectra of N_3 in solid N_2.

[Reference]

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