

The vibrational structures and dissociation of N_2^+ inner valence state

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Photoionization of molecular inner valence electrons is one of interesting processes in molecular dynamics, as they are usually followed by direct or indirect dissociation producing highly excited autoionizing atoms. The aim of the present study is to investigate dissociation of the N_2^+ inner valence states by high-resolution threshold photoelectron (TPE) spectroscopy and kinetic energy measurements of fragment ions in coincidence with threshold photoelectrons, TPEPICO.

Photoelectron spectra in the energy region 28–40 eV have been measured by two groups [1,2] with He II, however, they could not give a precise assignment due to poor statistics and energy resolution. Eland and Duerr [1] have carried out PEPICO for the inner valence ionic N_2^+ , however there still remains ambiguity in their measurements.

The experimental apparatus used in the present measurements consists of two spectrometers; a TPE analyzer with a penetrating electric field and a hemispherical-type electrostatic analyzer for analyzing kinetic energy of fragment ions. These two analyzers are set at a magic angle with respect to the electric vector of incident radiation, in order to suppress the effect of angular anisotropy. The principle of the coincidence measurements adopted in the present study is described in [3].

Figure 1 shows the TPE spectrum of N_2 in the energy region 29.5–38.0 eV, in which there are three broad peaks, E, G and H, as shown in He II photoelectron spectroscopy [1,2]. It is evident that new vibrational progressions, designated by Prog1–7 in Fig. 1, are observed beside the $3^2\Sigma_g^+$ state [1,2] with the superposition of the three broad peaks. Since the energy spacing of these progressions do not correspond to that of the lower lying N_2^{2+} states, they are not associated to the N_2^{+*} Rydberg states converging to such N_2^{2+} states. In order to elucidate the origin of these progressions and broad peaks, we measured the kinetic energy distribution of fragment N^+ ions in coincidence with threshold photoelectron at the photon energies (A)–(C) shown in Fig. 1. The results of TPEPICO-KED measurements are shown in Figure 2 with the spectral resolution of ≈ 0.3 eV. It can be seen that the N_2^+ states at (A)–(C) dissociates mainly to the dissociation limits (3), (5) and (6), probably to the (7) and (8) at the higher energy. It is interesting that the dissociation to the (2) limit in connection with the recent observation by

TPEPICO study below the 32 eV [4]. The theoretical calculation of the potential energy curves and transition probabilities are needed to understand the present results.

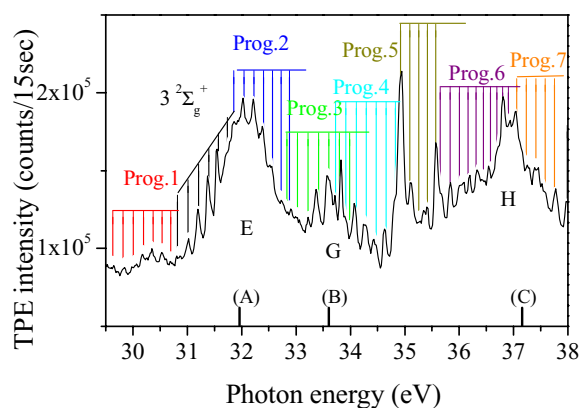


Figure 1: TPE spectrum of N_2 .

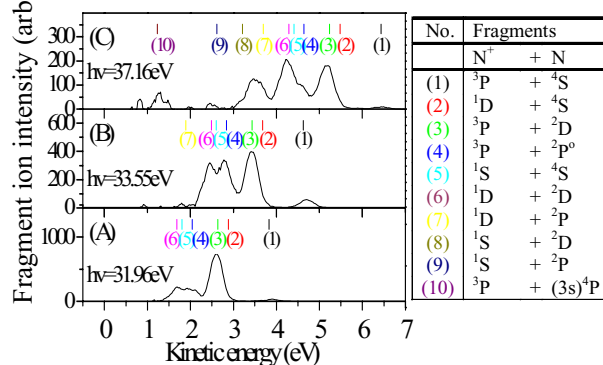


Figure 2: TPEPICO-KED spectra.

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