Femtosecond Nuclear Dynamics at Core-valence Doubly Excited States

Excitation of a core-electron in molecules can be accompanied by promotion of one or more valence electrons, due to electron relaxation (valence polarization) and the correlation effect. Such core-valence doubly excited states lie above the corresponding core ionization thresholds. They are accordingly embedded in the electronic continua, and relax via resonant Auger decay as well as autoionization. The time scale for their electronic decays is comparable to low-frequency vibrational periods; thus the decay processes can be subject to competition with nuclear motion in the femtosecond regime. A novel mechanism of femtosecond nuclear dynamics is unveiled here for the first time using advanced photoelectron spectroscopy. The experiment was performed using a high-resolution electron energy analyzer (Gammadata-Scienta SES-2002) at the soft X-ray photochemistry beamline **BL27SU**.

More than one hundred photoelectron spectra have been measured for molecular nitrogen in the photon energy region of 412.5-417.3 eV at small photon energy intervals of 50 meV [1] to investigate all the autoionization features of doubly excited states. For effective presentation of the photoelectron spectra obtained, they were assembled in a two-dimensional (2D) map as shown in Fig. 1. The 2D map shows remarkable vibrational features of $N_2^+(1\sigma_{g/u}^{-1})$, particularly in the photon energy range of 415-416.5 eV. Such vibrational excitations result from the autoionization of doubly excited states, because the direct inner-shell ionization brings few vibrational excitations to the formed $N_2^+(1\sigma_{g/u}^{-1})$ states.

Our *ab initio* configuration-interaction calculation yields three doubly excited states in the corresponding photon energy range, and their theoretical potential energy curves are plotted in Fig. 2(a). The potential energy curves imply that photoexcitation in the Franck-Condon region populates the doubly excited states above their dissociation asymptote. The doubly excited states, therefore, start dissociating immediately after photoexcitation. The vibrational excitation feature of $N_2^+(1\sigma_{g/u}^{-1})$, observed on the 2D map, manifests the relative rates for nuclear motion and autoionization. In the limit of very fast autoionization, the autoionizing molecule has the same geometry as the initial state of $N_2(X^1\Sigma_g)$, and few vibrational excitations determined by the Franck-Condon factor between $N_2(X^1\Sigma_g)$ and $N_2^+(1\sigma_{g/u}^{-1})$ should be given. At the other extreme (very slow autoionization), the molecule undergoes Auger decay before autoionization, and the autoionization feature should disappear in the 2D map. In the intermediate case, which is equivalent to the present situation, the average geometry of the molecule at a time corresponding to the mean lifetime for autoionization determines the vibrational structure of $N_2^+(1\sigma_{g/u}^{-1})$.

The vibrational excitations up to 3 eV for $N_2^+(1\sigma_{g/u}^{-1})$ can be seen around a photon energy of 416 eV in Fig. 1. This value of vibrational excitation corresponds

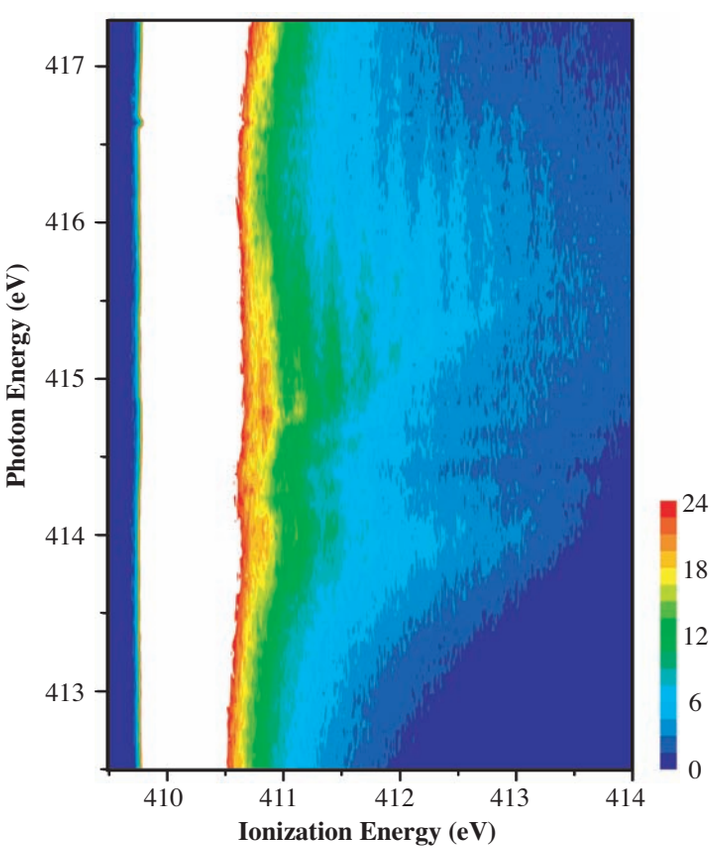

Fig. 1. Two-dimensional map of the inner-shell photoelectron yields from molecular nitrogen as a function of photon energy and ionization energy. The intensities on the 2D map are plotted on a linear scale, while the intensities of low vibrational levels of the $N_2^+(1\sigma_{g/u}^{-1})$ formed are truncated to clarify weak structures.

to autoionization around an internuclear distance of about 1.4 Å [see Fig. 2(a)]. The classical mechanical simulation indicates that it takes about 4 fs to reach an internuclear distance of 1.4 Å after the Franck-Condon transition [see Fig. 2(b)]. This time scale is comparable to that of the resonant Auger decay of the doubly excited states, which exhibits the possibility of competition between autoionization and resonant Auger decay by moving on the dissociative potential energy curve.

This work clearly demonstrates, for the first time, femtosecond nuclear dynamics of core-valence doubly excited states interacting with electronic continua. Extension of this work using short-wavelength free electron laser sources with inherently short pulses, that can be done in the near future, would provide us more details about nuclear-electronic dynamics in core-excited states.

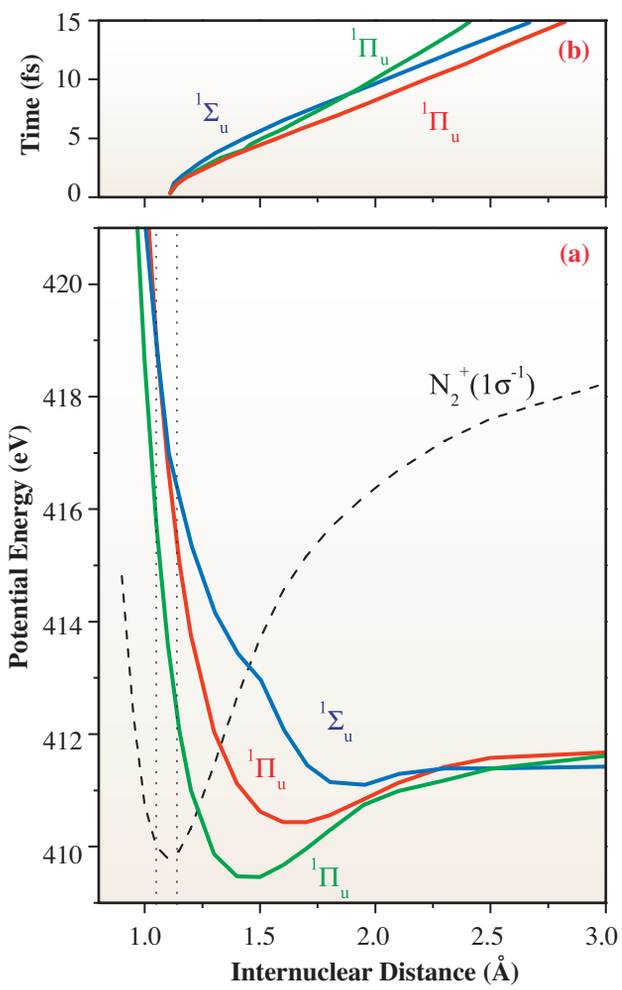

Fig. 2. **(a)** Potential energy curves calculated for the doubly excited states of N_2 lying at 413-416 eV, as well as that for $N_2^+(1\sigma^{-1})$. **(b)** Results of a classical mechanical simulation of the nuclear motion on the potential energy curves in **(a)**. Time measured from the photoexcitation at the equilibrium internuclear distance of the neutral ground state is plotted as a function of the internuclear distance elongated by the nuclear motion.

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References

[1] *Y. Hikosaka, T. Kaneyasu, E. Shigemasa, Y. Tamenori and N. Kosugi: Phys. Rev. A* ***75*** *(2007) 042708.*