Double and triple excitations near the *K*-shell ionization threshold of N₂ revealed by symmetry-resolved spectroscopy

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High-resolution photoion yield spectra of N_2 are measured near the *K*-shell ionization threshold. Previously unresolved multiple excitations are distinguished in the Σ- and Π-symmetry-resolved spectra, which were obtained from the ion yield spectra recorded at 0° and 90° relative to the polarization direction. The three $^1\Pi_u$ and two $^1\Sigma_u^+$ doubly excited states are clearly identified. Furthermore, a weak Π-symmetry feature just at the σ^*-shape resonance position ($\sim$419 eV) is definitely resolved and assigned to the lowest $^1\Pi_u$ triple excitation with the help of quantum chemical calculations.

Soft x rays can excite the deep core electron. Molecular *K*-shell excitations have been important subjects since the high-resolution soft-x-ray absorption spectrum of N_2 was first measured using synchrotron radiation [1], resulting in numerous experimental and theoretical studies of free, condensed, and chemisorbed molecules [2,3]. The molecular *K*-shell excitation spectra have been interpreted primarily in terms of single electron excitations: (i) strong bound-state resonances to low-lying vacant valence orbitals in the photon energy region of $E < E_{th}$ (inner-shell ionization threshold), (ii) weak bound-state excitations to Rydberg orbitals converging to E_{th}, and (iii) σ^*-shape resonances in the continuum ($E > E_{th}$). In addition, however, multiple excitations are significant features of these spectra. It is of fundamental importance to reveal what types of multielectron excitations are accessible through the single photon excitation and what dynamics follows the multielectron excitation in free, condensed, and chemisorbed molecules. An important aspect of the multiply excited states in adsorbed molecules is the localization of positive charges after the subsequent Auger-type decay, which may lead to particularly efficient ion desorption from the solid surface [4]. The doubly or triply excited state is more repulsive than the ionized state and singly excited state, since the excited electrons in antibonding orbitals can increase dissociative character. However, it is generally hard to identify the multiple excitations embedded in the ionization continuum. In the present work, we focus on the observation of previously unknown double and triple excitations involving the N 1*s* electron of N_2 and their experimental and theoretical characterization. Although a similar experiment has already been performed [5], poor statistics and energy resolution have prevented us from observing the multiply excited states in detail.

The present experiments were carried out at the 750-MeV electron storage ring of the UVSOR facility in IMS. A newly constructed bending magnet beamline BL4B, employing a varied-line spacing plane grating monochromator with an 800 l/mm laminar grating, was used [6]. Asymmetric slit widths of 25 and 15 μm for the entrance and exit slits, respectively, provide an energy resolution of $\sim$60 meV over the photon energy region of interest. The symmetry-resolved spectra were measured with the same method as previously reported [7,8]. Fragment ions emitted following the photoexcitation and Auger decay were detected using two identical ion detectors. The ion detectors on a plane perpendicular to the incident radiation were set at 0° and 90° relative to the electric vector of the light. The retarding voltage of +2 V was applied to eliminate parent ions and slow fragment ions, which slightly degrade the degree of symmetry decomposition. The acceptance angle of each ion detector was ±10°. The calibration for the detection efficiencies of the two ion detectors and the correction for the imperfection in the angular resolution were dealt with using the same procedure as the previous work [7,8]. The Σ- and Π-symmetry-resolved spectra correspond to the 0° and 90° ion yields after these corrections, respectively.

Figure 1 shows our high-resolution *K*-shell photoabsorption spectrum of N_2 which is very similar to that published by Chen and co-workers [9]. The 415-eV features are already assigned to some double excitations with the Π symmetry [5]. The symmetry assignment can be easily obtained from angle-resolved photoion-yield spectroscopy (ARPIS), where
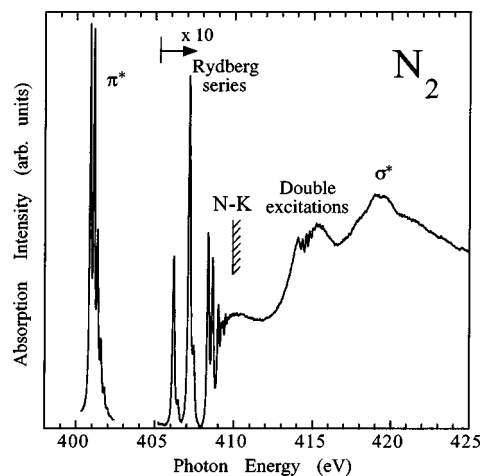

FIG. 1. High-resolution *K*-shell photoabsorption spectrum of N_2.

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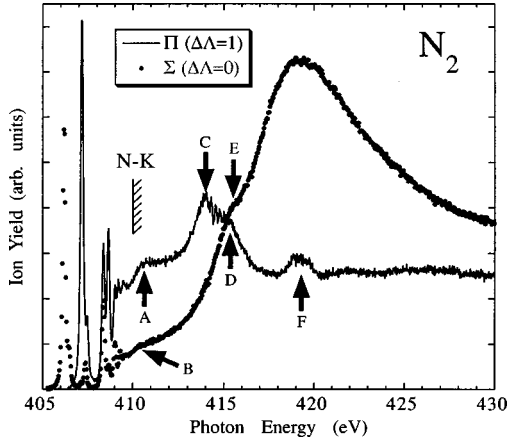
FIG. 2. Symmetry-resolved photoion yield spectra near the K-shell ionization threshold of N_2. Solid line and dots represent the partial cross section for the $^1\Sigma_u \leftarrow X\,^1\Sigma_g^+$ ($\Delta\Lambda = 0$) and $^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ ($\Delta\Lambda = +1$) transitions, respectively.

the $\Delta\Lambda = 0$ (parallel) and $\Delta\Lambda = \pm 1$ (perpendicular) transitions are clearly distinguishable in the case of the diatomic molecule [5,10–15]. Furthermore, Neeb *et al.* noticed that the photoabsorption cross section close to E_{th} (N $1s$) contains a significant contribution from double excitations [16]. The double excitation is essential from the viewpoint of electron correlation in molecules [17]. Recently, Neeb *et al.* distinctly found a double-excitation feature at only 0.6 eV above E_{th} (N $1s$) = 409.9 eV in addition to the well-known double excitations at ~415 eV as shown in Fig. 1. They initiated the constant-final-state (CFS) spectroscopy applied to repulsive states not easily accessible in conventional photoabsorption; that is, they have measured the partial electron yield spectra for the electron kinetic energy of around 384 eV to identify the doubly excited state in N_2 [18]. However, in the CFS spectroscopy the excited states with different symmetries cannot be distinguished, the spectral resolution depends on the electron energy resolution in addition to the incident photon-energy resolution, and the Auger-like peak is sometimes disturbed by the photoelectron peak.

The 384-eV band, which was assigned to the atomiclike Auger decay after ultrafast fragmentation in a dissociative doubly excited state by Neeb *et al.* [16], has been very recently assigned to the molecular Auger decay during the vibration around a long equilibrium bond length of a weakly bound, doubly excited state by Naves de Brito *et al.* [19]. The atomic or molecular decay is dependent on the relative energy position between the vertical excitation energy and the dissociation limit as well as on the dissociation speed; that is, the atomic and molecular Auger decays take place in the case of the excitation energy that is higher and lower than the dissociation limit, respectively. In either case, it is obvious that the CFS spectrum of the 384-eV band provides information on the doubly excited states.

Figure 2 shows the Σ- and Π-symmetry-resolved spectra near the K-shell ionization threshold of N_2 ($E > 405$ eV), excluding the $1s$-π^* energy region ($E = 401$ eV) in the photoabsorption spectrum shown in Fig. 1. Features labeled from A to F near and above E_{th} which may arise from mul-

tiple excitations, are clearly seen in the Σ- and Π-symmetry spectra. Further statistics are required to identify some features above F and it remains undiscussed here. A very strong and broad enhancement is found at about 419 eV only in the Σ-symmetry spectrum, and is definitely assigned to the σ^*-shape resonance. Furthermore, in the Σ-symmetry spectrum, a very weak feature B just above E_{th} and a low-energy shoulder structure E of the shape resonance are distinctly observed. On the other hand, the Π-symmetry spectrum shows feature A just above E_{th} and clear enhancement F just at the σ^*-shape resonance position, in addition to the well-known double-excitation features C and D at ~415 eV [20,21]. It should be noticed that the ~415-eV feature in the photoabsorption spectrum of Fig. 1 is composed of not only the Π-symmetry components C and D but also the Σ-symmetry component E. In the 384-eV electron yield spectrum [18], the three broad peaks assigned to the doubly excited states show intensity maxima at ~410.5, 414, and 416 eV. The energy positions of the Π-symmetry features A, C, and D are in good agreement with them. In addition, we have distinguished two weak and broad features with the Σ symmetry, B and E, which have been predicted theoretically [18] but not experimentally found before.

The excited states using the outer valence molecular orbitals ($2\sigma_u$, $3\sigma_g$, and $1\pi_u$) into the lowest unoccupied $1\pi_g$ (π^*) orbital consist of one single, three double, and seven triple excitations for the $^1\Pi_u$ states, and no single, two double, and four triple excitations for the $^1\Sigma_u$ states. The $X\,^1\Sigma_g^+$ ground state and the one single, three double, and lowest triple excitations for the $^1\Pi_{ux}$ states are described as follows:

$$\Phi(X\,^1\Sigma_g^+) = (1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2$$
$$\times (x)^2(y)^2(x^*)^0(y^*)^0,$$

$$\Phi(1\,^1\Pi_{ux}) = {}^S(1\sigma_u, x^*),$$

$$\Phi(2\,^1\Pi_{ux}) = {}^S(1\sigma_g, y^*)\,{}^S(y, x^*) - {}^S(1\sigma_g, x^*)\,{}^S(x, x^*),$$

$$\Phi(3\,^1\Pi_{ux}) = {}^S(1\sigma_g, y^*)\,{}^S(x, y^*),$$

$$\Phi(4\,^1\Pi_{ux})\,{}^S(1\sigma_g, x^*)\{{}^S(y, y^*) - {}^S(x, x^*)\},$$

$$\Phi(5\,^1\Pi_{ux}) = {}^S(\sigma_u, x^*)$$
$$\times (y^*)^2(3\sigma_g)^0 \quad \text{for the shorter distance,}$$

$$= {}^S(\sigma_u, x^*)\,{}^S(y, x^*)\,{}^S(x, y^*) \quad \text{for the longer distance,}$$

where x, y, x^*, and y^* denote the $1\pi_{ux}$, $1\pi_{uy}$, $1\pi_{gx}$, and $1\pi_{gy}$ orbitals, respectively, and the $^1\Pi_{ux}$ states are degenerate with the $^1\Pi_{uy}$ states. Note that

$$^S(a,b) = ab[\alpha\beta - \beta\alpha] = |(a_\uparrow)(b_\downarrow)| - |(a_\downarrow)(b_\uparrow)|$$
$$= |(a_\uparrow)(b_\downarrow)| + |(b_\uparrow)(a_\downarrow)|,$$

$$^T(a,b) = ab[\alpha\beta - \beta\alpha] = |(a_\uparrow)(b_\downarrow)| + |(a_\downarrow)(b_\uparrow)|$$
$$= |(a_\uparrow)(b_\downarrow)| - |(b_\uparrow)(a_\downarrow)|,$$

TABLE I. Energy of observed features in the symmetry-resolved K-shell photoabsorption spectra of N_2 along with calculated energy and proposed assignments for them. An asterisk denotes relative energy to the $1s$ electron ionization potential of 409.9 eV.

Peaks	Photon energy (eV), expt.	Relative energy (eV), theory	Proposed assignments
A	410.6(0.7)*	0.7*	$1\sigma_g^{-1}1\pi_u^{-1}-1\pi_g^2$ ($^1\Pi_u$)
B	410.6(0.7)	0.7	$1\sigma_g^{-1}3\sigma_g^{-1}-1\pi_g^2$ ($^1\Sigma_u$)
C	414.0(4.1)	3.2	$1\sigma_g^{-1}1\pi_u^{-1}-1\pi_g^2$ ($^1\Pi_u$)
D	415.2(5.3)	6.3	$1\sigma_g^{-1}1\pi_u^{-1}-1\pi_g^2$ ($^1\Pi_u$)
E	415.6(5.7)	7.2	$1\sigma_g^{-1}2\sigma_u^{-1}-1\pi_g^2$ ($^1\Sigma_u$)
F	419.2(9.3)	9.3	$1\sigma_u^{-1}3\sigma_g^{-2}-1\pi_g^3$
			$1\sigma_u^{-1}1\pi_u^{-2}-1\pi_g^3$ ($^1\Pi_u$)

$$^S(a,c)^S(b,c)=-^T(a,c)^T(b,c)=-^S(a,b)(c)^2,$$

where the superscripts T and S denote triplet and singlet spin couplings, respectively, and the normalization has not yet been carried out. The two double excitations for the $^1\Sigma_u^+$ states are described as follows:

$$\Phi(1\ ^1\Sigma_u^+)=\ ^S(\sigma_u,3\sigma_g)[(x^*)^2+(y^*)^2],$$

$$\Phi(2\ ^1\Sigma_u^+)=\ ^S(\sigma_g,2\sigma_u)[(x^*)^2+(y^*)^2],$$

where these configurations are strongly mixed with each other. Thus, the three $(1s\rightarrow\pi^*)(\pi\rightarrow\pi^*)$ doubly excited states $\Phi(2\ ^1\Pi_u)$, $\Phi(3\ ^1\Pi_u)$, and $\Phi(4\ ^1\Pi_u)$ are assigned to A, C, and D, and the two $(1s\sigma)(3\sigma_g/2\sigma_u)\rightarrow(\pi^*)^2$ doubly excited states $\Phi(1\ ^1\Sigma_u^+)$ and $\Phi(2\ ^1\Sigma_u^+)$ are assigned to B and E. There is no other doubly excited state involving the $2\sigma_u$, $3\sigma_g$, and $1\pi_u$ electrons, and the doubly excited state involving the $2\sigma_g$ electron is very high in energy. Then what is the feature F? The lowest $1\pi_u$-$1\pi_g$ shake-up state with the threshold around 420 eV might get some intensity through the conjugate shake-up mechanism and be contributive to band F. However, the intensity of F seems to be too strong to come only from the conjugate process. The lowest triply excited state $\Phi(5\ ^1\Pi_u)$, $\{1s\rightarrow\pi^*\}\{(\pi)^2\rightarrow(\pi^*)^2\}$, or $\{1s\rightarrow\pi^*\}\{(3\sigma_g)^2\rightarrow(\pi^*)^2\}$ is a more probable candidate.

In order to identify the triple excitation theoretically, we have carried out *ab initio* configuration-interaction (CI) calculations, where most single and double substitutions are allowed from the full valence reference space involving all the valence orbitals $2\sigma_g$, $2\sigma_u$, $3\sigma_g$, $1\pi_u$, $1\pi_g$, and $3\sigma_u$. We used the symmetry-adapted, i.e., delocalized, orbitals, and obtained almost the same results in the potential-energy curves (not shown in the present work) even when starting from the localized core-hole orbitals. This indicates that the present configuration space is reasonably stable for the orbital choice. In the previous CI calculations [18], the triply excited states showed a small dependence on the orbital choice, since the reference space was not fully constructed. The basis functions used and other computational details are the same as in the previous work [18]. The vertical transition energies calculated are summarized in Table I. The feature F is definitely assigned to the lowest triply excited state.

The present calculations have shown that all the double and the lowest triple excitations involving the $2\sigma_u$, $3\sigma_g$, and $1\pi_u$ electrons are converging to the same dissociation limit, ^2D and ^2D ($1s$ hole), and have the minimum potential energies below the dissociation limit. The dissociation limit is located at 1.8 eV above the vertical ionization threshold from the ground state; therefore, the lowest Π and Σ doubly excited states A and B, which have vertical transition energies of 0.7 eV and minimum potential energies at $R\sim1.4$ and ~1.3, respectively, are not dissociative. On the other hand, the other doubly and triply excited states have much shallower potential-energy curves and are dissociative after the vertical excitation. The uppermost state F gives the most efficient repulsive force to the N–N bond.

The existence of the triple excitation is also discussed in recent photon-stimulated ion desorption (PSID) of atomic and molecular ions from diatomic molecules chemisorbed on metal surfaces [22]. PSID is a very sensitive tool to identify dissociative states, that is, multiply excited states, with small photoabsorption cross sections. Feulner *et al.* [22] reported that the N^+ and N^{2+} PSID signals from chemisorbed N_2 molecules on Ru(001) rise up at about 20 eV above the π^* resonance, where there is no corresponding feature in the total electron yield spectrum which is thought to be equivalent to the photoabsorption spectrum. The rise in the atomic PSID signals is interpreted as the onset of the formation of a three-hole state, on the basis of the previous results for CO/Ru(001) and CO/Cu(111) in the O $1s$ ionization region obtained by the same research group [23]. Considering a possible core-level energy shift in the chemisorbed system, it is plausible that the enhancement of the atomic PSID yields is attributed to the triple excitations of the feature F having the $^1\Pi_u$ symmetry found in the present work, which is about 18 eV away from the π^* resonance.

It should be noted that multiple-peak structures for C and D in the Π-symmetry-resolved spectrum are observed in Fig. 2. The repulsive state cannot give fine structures such as molecular vibrations. As discussed by using the potential-energy curves [18] and by comparing with the optical data of core-equivalent molecule NO [9], the vibrational sidebands of the Rydberg shake-up states converging to the lowest shake-up ionized state at around 419 eV are the most probable candidate for the fine structures. Based on the potential-

energy curves [18], the lowest shake-up state associated with the N $1s$ ionization and simultaneous $\pi \to \pi^*$ excitation has an equilibrium bond length of ~1.3, and the Rydberg shake-up states involving the N $1s \to$ Rydberg and simultaneous $\pi \to \pi^*$ excitation can be mixed with the double excitations involving the N $1s \to \pi^*$ and simultaneous $\pi \to \pi^*$ excitation to gain their intensities.

In conclusion, high-resolution angle-resolved ion-yield spectra of N_2 have been measured near the K-shell ionization threshold. The Σ- and Π-symmetry spectra have realized complete symmetry decomposition of the excited states of interest and revealed previously unresolved multiple excitations in the continuum. Based on the theoretical consideration, it can be concluded that the feature F in the Π spectrum just at the shape resonance position is attributable to the lowest triple excitation, which involves the simultaneous excitation of two valence electrons, $3\sigma_g$ or $1\pi_u$, into the $1\pi_g^*$ orbital accompanying the N $1s\sigma_u \to 1\pi_g^*$ transition. The present result supports the interpretation that the rise of atomic PSID signals from chemisorbed N_2 molecules is related to the onset of a triple excitation with heavily repulsive character.

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