

## Probing doubly excited ionic states of $N_2^+$ via a triple excitation above the N $1s$ threshold in the $N_2$ molecule

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Angle-resolved resonant Auger-electron spectroscopy has been carried out on the nitrogen molecule at selected photon energies around 419 eV, where a  $1s$  core electron and two valence electrons are promoted into the lowest unoccupied molecular orbital  $1\pi_g$ . Significant enhancement of a specific band, which cannot be disentangled in direct photoionization, is observed at a binding energy of 37.6 eV, with a value of the anisotropy parameter  $\beta$  much smaller than 2. We assign this new band to the transition to a doubly excited cationic state of  $N_2$ , in which two of the excited valence electrons remain in the  $1\pi_g$  orbital, proposing a “double spectator” type decay mechanism. This observation shows how to preferentially probe multiply excited configurations of cations using multiple resonant excitation.

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Doubly excited electron configurations, in which two valence electrons from one orbital are promoted to another orbital, are known to be important for proper descriptions of electron correlation in single-hole ionic states as well as in the neutral ground state of molecules. On the other hand, doubly excited ionic states in three-holes two-particles configurations, which were theoretically predicted more than 20 years ago [1], have never been experimentally identified: as such doubly-excited configurations cannot be disentangled from spectra recorded by means of conventional, nonresonant photoelectron spectroscopy.

During the last decades, a large number of spectroscopic studies, both experimental and theoretical, have focussed on states near the N  $1s$  ionization threshold in molecular nitrogen. High-resolution absorption measurements made by Chen *et al.* identified Rydberg states and broad resonances in  $N_2$  [2], and shortly afterwards symmetry resolved measurements by Shigemasa *et al.* [3] made a more precise identification of the features in this spectrum. More recently, studies of electronic decay of resonant states at excitation energies around 410 eV above the N  $1s$  ionization threshold were made and a strongly resonating feature observed at 384 eV kinetic energy could be assigned to core-hole double excitations [4,5]. Neeb *et al.* [4] suggested that the observed electronic decay corresponds to the atomic Auger decay following ultrafast dissociation, whereas a very recent high-resolution electron spectroscopy study of the same region proposed that these resonant states rather decay to molecular levels [6]. Very recently, Shigemasa *et al.* [7] investigated multiply excited states of  $N_2$  using a symmetry-resolved absorption technique combined with *ab initio* calculations.

They assigned resonances close to the N  $1s$  ionization threshold at  $\sim 410$  eV and  $\sim 415$  eV to doubly excited states and the one at  $\sim 419$  eV, which appears only in the  $^1\Pi_u$ -symmetry spectrum, to a triply excited state with an  $1s \rightarrow 1\pi_g$  core-hole ground configuration and two valence electrons promoted into the  $1\pi_g$  lowest unoccupied molecular orbital. The resonance at  $\sim 419$  eV is embedded in the well-known broad N  $1s \rightarrow 3\sigma_u$  shape resonance [8–11] located between  $\sim 416$  eV and  $\sim 422$  eV and thus has not been observed earlier in any ordinary absorption measurement.

In this paper, we will show that highly correlated ionic states can be probed efficiently by resonant Auger spectroscopy via triple excitation above the core threshold. By using 419 eV photons, we excite two valence electrons simultaneously with a N  $1s$  core electron into the  $1\pi_g$  orbital borrowing intensity via initial and/or final state correlation thus reaching a triply excited neutral intermediate state. This triply excited intermediate state will predominantly decay via an Auger process to three-holes two-particles ionic state configurations in the broad  $2\sigma_g^{-1}$  inner valence band.

The experimental spectra were recorded at the undulator beamline 27SU [12,13] at SPring-8, an 8-GeV-synchrotron-radiation facility in Japan. The polarization vector  $\mathcal{E}$  of the undulator light may be set to horizontal (first harmonic) or vertical (0.5 th harmonic) [14]. The electron spectra were measured using a hemispherical electron-energy analyzer (Gammadata Scienta SES-2002) fitted with a gas cell. The lens axis is in the horizontal direction, at right angles to the photon beam direction [15]. In this arrangement, the electron spectra recorded with horizontal and vertical polarization correspond to the photoemission parallel and vertical to the  $\mathcal{E}$  vector, respectively. Thus the photoelectron asymmetry parameter  $\beta$  can be extracted from the normalized intensities  $I(0^\circ)$  and  $I(90^\circ)$  measured for horizontal and vertical polarizations, respectively. The monochromator bandpass was set

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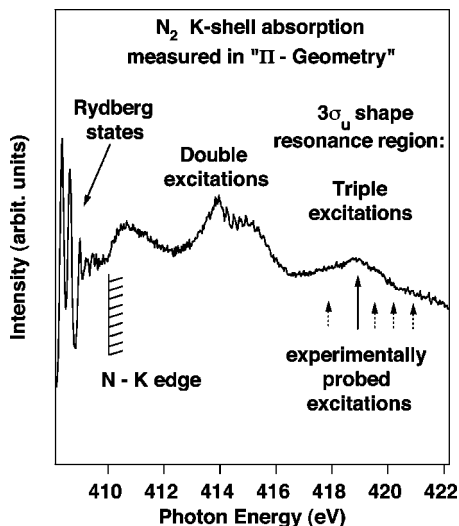


FIG. 1. N<sub>2</sub> K-shell photoabsorption spectrum recorded with an ion yield detector positioned perpendicular to the electric-field vector  $\mathcal{E}$  of the incident light.

to  $\sim 90$  meV full width at half maximum (FWHM), the electron spectrometer bandpass to  $\sim 70$  meV and the inhomogeneous Doppler broadening due to thermal motion of the sample molecules is estimated to be  $\sim 50$  meV, resulting in a total experimental linewidth for the electron spectra of  $\sim 140$  meV. The absorption measurements were performed by measuring the ion yield with a long time-of-flight (TOF) spectrometer [16] placed between the monochromator and the electron spectrometer. The TOF spectrometer is equipped with a microsphere-plate detector at the end of a 690-mm-long drift tube mounted perpendicular to the  $\mathcal{E}$  vector, in order to efficiently detect fragment ions arising from states of  $^1\Pi_u$  symmetry. The absorption spectrum is energy calibrated to the values given in Ref. [2]. The energy scale of the electron spectra is calibrated relative to valence state energies in Ref. [17]. In order to absolutely calibrate the photon energies used for the Auger experiments, absorption measurements were performed before recording the electron spectra. The nominal value of the photon energy was controlled during the measurements by recording the X, A, and B valence bands of N<sub>2</sub><sup>+</sup>. N<sub>2</sub> gas was commercially obtained with a stated purity of  $>99.99\%$ .

In Fig. 1 we present, for the purpose of orientation, the ion yield spectrum measured as described above. In this spectrum the resonance regions discussed above are clearly visible. A similar spectrum was measured recently by Shigemasa *et al.* [7] in the photon energy region around 419 eV, where the  $3\sigma_u$  shape resonance is located. They found a weak band, which is assigned to a triply excited state of  $^1\Pi_u$  symmetry. We focus on this photon energy region.

Figure 2 contains a series of electron spectra from the decay of core-excited states with energies close to 419 eV. The measurements were made at five different photon energies indicated by arrows in Fig. 1, at angles both parallel and perpendicular to the  $\mathcal{E}$  vector. The spectral features in the 34–42 eV binding energy region have been studied theoretically [1,18,19] and experimentally with somewhat lower en-

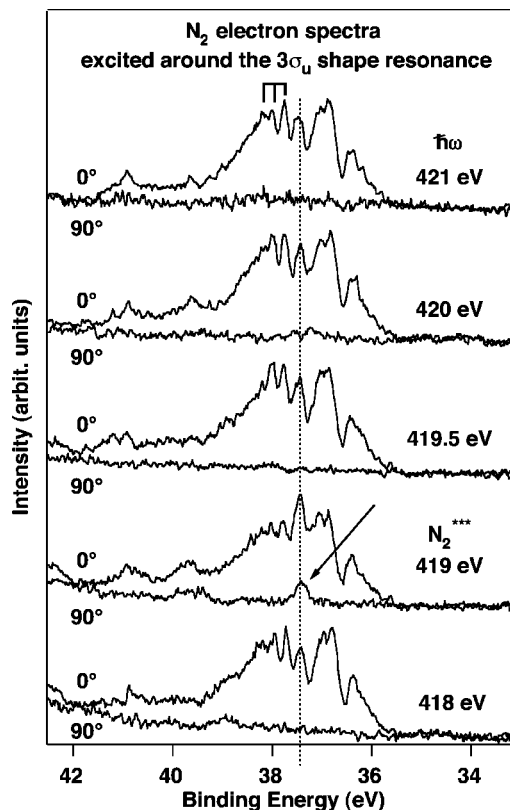


FIG. 2. Angle-resolved electron spectra recorded across the N  $1s \rightarrow 3\sigma_u$  shape resonance for five different photon energies indicated by arrows in Fig. 1. A vibrational progression in the 38 eV range is marked by bars.

ergy resolution [20–22] in a series of earlier papers. Schirmer *et al.* [18] first investigated strong correlation effects for this band, which lead to a splitting of the  $2\sigma_g$  ionization band into various subbands and Krummacher *et al.* [20] confirmed experimentally the breakdown of the independent particle model for the  $2\sigma_g^{-1}$  band in N<sub>2</sub>. Neeb *et al.* [21] and Kivimäki *et al.* [22] investigated electron emission in the vicinity of the N  $1s\sigma \rightarrow 3\sigma_u$  shape resonance as well as at some discrete resonances. In all these previous works, the band in the 34–42 eV binding energy region is identified as the direct  $2\sigma_g^{-1}$  photoionization band, where the photoelectron intensity reflects directly the  $2\sigma_g^{-1}$  single-hole pole strength. The so-called polarization configuration interaction calculations (cf. Ref. [1]) predict the presence of several three-holes two-particles states in this binding energy region. These highly correlated configurations have, however, never been experimentally disentangled.

Looking more closely at Fig. 2, we see fine structures covering the entire binding energy region between 35.5 and 39.5 eV in the 0° measurements (i.e.,  $\mathcal{E}$  vector parallel to the axis of the electron lens of the electron spectrometer). The binding energy of these peaks is constant for all photon energies. The peaks show a  $\sim 200$  meV separation indicating that these structures arise from vibrational excitations of the molecular cation. The vibrational intensity distribution, which is reminiscent of the intensity distribution of the valence-band spectrum recorded at  $\hbar\omega = 60$  eV (see Ref.

[23]), remains nearly constant throughout the  $3\sigma_u$  shape resonance region. In contrast, the spectra measured with the  $\mathcal{E}$  vector perpendicular to the electron spectrometer lens ( $90^\circ$ ), are nearly featureless with very little signal with the exception of the 419 eV excited spectrum. Thus, all of the states in this particular binding energy region are characterized by a  $\beta$  value close to 2, which is the case for photoemission from a pure atomic  $s$  orbital. The  $2\sigma_g$  molecular orbital is mainly composed of N  $2s$  orbitals and, therefore, a high  $\beta$  value is expected. However, at the isolated photon energy of 419 eV a band marked by the dashed line at the binding energy of 37.6 eV appears in the  $90^\circ$  spectrum, showing  $\beta < 2$  for this band. Correspondingly, the vibrational feature at 37.6 eV is strongly enhanced in the  $0^\circ$  spectrum. This band has a width of  $\sim 300$  meV (FWHM). No significant resonant enhancement is observed for any other photoelectron bands in the entire binding energy region between 15 eV and 35 eV for all photon energies used in the present study. How can such a peculiar behavior of the band at 37.6 eV be understood?

For the sake of argument, we first assume that in the photon energy region of interest only the  $3\sigma_u$  shape resonance is present. Molecular shape resonances are conventionally described as one-electron phenomena associated either with temporary trapping of the photoelectron by the molecular potential [8,9,24,25] or with the promotion of a core electron to an unoccupied molecular orbital [26]. These resonant structures are quite broad in energy (typically 5–10 eV) due to a short lifetime of such states of the order of  $\sim 10^{-16}$  sec. It has been shown previously that multielectron excitations play an important role in the shape resonance region, thus putting the general validity of an one-electron description into question [27–31]. The shape resonance enhances the photocurrent but may also influence the angular distribution of the outgoing electrons. In previous studies of N  $1s$  photoelectrons from  $N_2$ , a continuous change in the asymmetry parameter  $\beta$  has been found over the entire shape resonance region for electrons with kinetic energies between 5 and 30 eV (cf. Ref. [8]).

However, as was pointed out above, the  $2\sigma_g^{-1}$  band neither resonates nor exhibits successive intensity changes through the  $3\sigma_u$  shape resonance. Rather, both the relative intensity and the  $\beta$  value remain essentially constant for all photon energies used in the present experiment except for the structure at 37.6 eV in the 419 eV spectrum. The deviating response of the 37.6 eV peak at 419 eV photon energy with respect to both relative intensity and angular distribution is indicative of the presence of a much narrower intermediate state than the  $3\sigma_u$  shape resonance. Indeed, the present dataset shows that the resonance linewidth must be smaller than 1.5 eV (see Fig. 2), which corresponds to a long lifetime compared to the shape resonance. The sharp resonant enhancement of this photoelectron band agrees with the resonant  $^1\Pi_u$  state associated with a triply excited configuration assigned by Shigemasa *et al.* [7]. The key question is why only the narrow band at 37.6 eV binding energy is markedly influenced at  $\hbar\omega = 419$  eV photon energy, and not the entire  $2\sigma_g^{-1}$  photoelectron band?

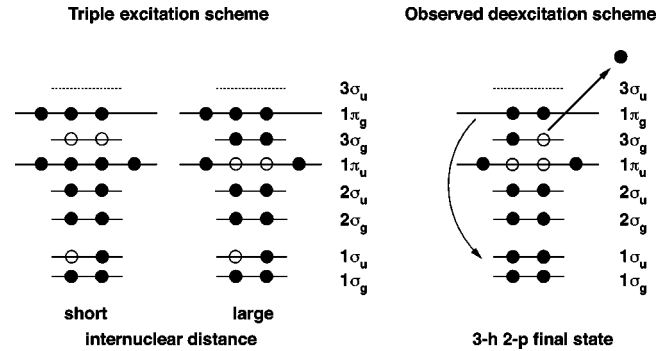


FIG. 3. The triple excitation schemes as proposed in Ref. [7] and one of the possible deexcitation channels leading to a three-holes two-particles final state of the cation (“double spectator” decay).

This question can be answered by taking into account the photoabsorption process as well as possible deexcitation channels. Two triply excited configurations of  $^1\Pi_u$  symmetry are proposed by Shigemasa *et al.* [7],  $1\sigma_u^{-1}3\sigma_g^{-2}1\pi_g^3$  and  $1\sigma_u^{-1}1\pi_u^{-2}1\pi_g^3$  (cf. Fig. 3). The triple excitation is forbidden within an independent particle approximation [7]. Thus the excitation process becomes possible only via initial-state correlations, where  $3\sigma_g^{-2}1\pi_g^2$  and/or  $1\pi_u^{-2}1\pi_g^2$  configurations are mixed into the ground-state configuration, and/or final-state correlations, where the singly-excited configuration  $1\sigma_u^{-1}1\pi_g^1$  is mixed into the final-state configurations [7]. The decay from the triply excited state is expected to be governed by the main configuration. Note that the Auger decay is a two electron transition. Thus, the most favorable decay channels should be such that one electron from the outermost orbitals fills the created core hole whilst another electron from one of the outermost orbitals is released into the continuum leaving the system in a three-holes two-particles final-state configuration. Such a decay process would be referred as double spectator within the independent particle model (cf. Fig. 3). From Table III in Ref. [1], we can indeed see that such configurations exist in the binding energy range of interest. Promising candidates for our Auger final state are  $3\sigma_g^{-1}1\pi_u^{-2}1\pi_g^2$  of  $^2\Sigma_g^+$  symmetry calculated at binding energies of 36.26 eV and 37.19 eV, as well as  $2\sigma_u^{-1}1\pi_u^{-2}1\pi_g^2$  of  $^2\Sigma_u^+$  symmetry calculated at 38.08 eV and 39.42 eV binding energy. Please note from Fig. 2 that small traces of resonant enhancement can be seen as well in the photoelectron band around 38.9 eV binding energy supporting these possibilities. A further candidate for our Auger final state is the  $1\pi_u^{-1}3\sigma_g^{-2}1\pi_g^2$  configuration of  $^2\Pi_u$  symmetry, calculated at binding energies of 35.43 eV and 36.22 eV. The fact that we could not identify the latter bands in our measurements suggests that the leading configuration of the triply excited state is most likely  $1\sigma_u^{-1}1\pi_u^{-2}1\pi_g^3$ . Other decay channels may also be possible, but would involve more than two electrons, thus they are much less probable. Moreover, the fact that we cannot observe a significant enhancement of the single-hole main band or the two-hole one-electron bands strongly suggests that the triply excited state decays into three-holes two-particles configurations.

The decrease in  $\beta$  of the subband at binding energy of

37.6 eV by triple excitation may be explained either by an enhancement of a parity unfavored component [32] or by an enhancement of high  $l$  components. However, since the triply-excited state is assigned to a singlet state, the possibility of contributions from the parity unfavored component can be excluded (see, e.g., Ref. [33]), leaving the interpretation in terms of high  $l$  components as the only reasonable alternative. Contributions from  $d_g$  and  $f_u$  waves is negligible in direct photoionization from  $2\sigma_g$  N  $2s$ -like orbital but can be significant in decay processes from a triply excited state, since this decay enhances the photoemission from a valence orbital with N  $2p$  character. Then either  $d_g$  or  $f_u$  waves become allowed, depending on the symmetry,  $\Sigma_u$  or  $\Sigma_g$ .

In conclusion, the inner valence cationic states of the nitrogen molecule in the 35–42 eV binding energy range, commonly assigned to  $2\sigma_g$  band, have been studied by angle-resolved resonant Auger-electron spectroscopy, performed at selected photon energies in the  $3\sigma_u$  shape resonance region. The  $\beta$  parameter of the  $2\sigma_g$  band is found to be close to 2

for most of the shape resonance region. A strong resonance enhancement of the subband at 37.6 eV binding energy is observed at the discrete resonance state energy at 419 eV, lowering the  $\beta$  value for this subband substantially. We conclude that at 419 eV photon energy, the new pathway via a triply excited resonant state enhances strongly the population of doubly excited cationic states. This observation shows how to preferentially probe multiply excited configurations of cations by means of resonant Auger-electron spectroscopy via multiple resonant excitation.

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