Core Hole Double-Excitation and Atomiclike Auger Decay in N_2

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Core hole decay spectra of the free N_2 molecule show evidence for hitherto unobserved molecular resonances both below and above the *K*-shell photoionization threshold. Based on earlier calculations they are assigned to doubly excited neutral states which could not be seen below threshold in recent high resolution absorption spectra because of the more intense core-to-Rydberg excitations. By calculating the Auger spectrum of core-excited nitrogen atoms, we show that the features are atomiclike.

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One of the best known inner shell absorption spectra is that of gas phase N_2, which has been extensively investigated both theoretically and experimentally. Because of the many spectral features it is widely regarded as a prototype system for inner shell absorption, in particular, for its interpretation in terms of the equivalent core model [1]. The well resolved features between the $1\sigma_u^{-1}1\pi_g$ bound state transition and the $1s$ ionization potential have all been interpreted as core-excited Rydberg transitions. The assignment of several features close to threshold, however, gives rise to some difficulties due to the many overlapping resonances. To clarify the interpretation of these features, angle-resolved ion yield spectra have been measured more recently by Shigemasa *et al.* [2] and Lee *et al.* [3]. Between 407 and 410 eV these spectra show several degenerate resonances of different symmetry which cannot be separated in the normal absorption spectrum. Because of a net negative value of the asymmetry parameter, β, a strong contribution of states of π symmetry was identified in the angular-resolved spectra and assigned by Lee *et al.* [3] to $nd\pi$ core-to-Rydberg transitions. These states were not included in the analysis of Chen, Ma, and Sette [1], who instead added four unspecified extra peaks in their fitting routine in order to account for unresolvable structure near threshold. If $nd\pi$ Rydberg states indeed have to be taken into account in the interpretation, Lee *et al.* [3] point out that it is necessary to contemplate a failure of the equivalent core model.

In contrast, we show in the present Letter that the cross section close to threshold is not only determined by Rydberg resonances, but also contains an important contribution from neutral double excitations [two-hole–two-particle (2h2p)]. These states were predicted by Arneberg *et al.* [4] several years ago for the region both above as well as below the $1s$ ionization threshold. We infer their existence from the observation of distinct transition lines in the corresponding electronic decay spectra. The latter cannot be explained by the decay of core-excited Rydberg states but rather as atomiclike features following dissociation.

The experiments have been performed using the undulator beam line X1B [5] at the National Synchrotron Light Source, Brookhaven. A cylindrical mirror analyzer (CMA) was used as the energy dispersing element [6]. Electrons enter the analyzer at an emission angle of 54.7° with respect to the propagation vector of the incident light which is coincident with the cylinder axis. This configuration allows angle-resolved and angle-integrated spectra to be measured simultaneously. The pass energy of the analyzer was set at 40 eV, which corresponds to an estimated kinetic energy resolution of 320 meV. The photon energy resolution was set to ~400 meV.

The N_2 decay spectra above 370 eV kinetic energy are shown in Figs. 1(a) to 1(g) for various photon energies between 407 and 413 eV. Spectra (a)–(c) were excited below threshold (409.9 eV), while spectra (d)–(g) were excited up to 3.4 eV above threshold. At these photon energies the valence photoelectron lines of N_2 (the triple peak structure above 390 eV and the broad structure above 370 eV) overlap between 370 and 405 eV with the decay lines. The photoelectron spectrum excited at 355 eV is shown for comparison in (h).

As the photon energy is tuned across the *K*-shell threshold a new feature with 384 eV kinetic energy (accompanied by a small feature at 376 eV) is first observed in the decay spectra at a photon energy 1.3 eV below the ionization threshold [Fig. 1(b)]. It acquires maximum intensity just at threshold before vanishing at a photon energy of 413 eV. A distinct resonance behavior is thus apparent. At excitation energies above threshold the extra decay features cannot be explained by normal or satellite Auger transitions since the chosen photon energies are too low for excitation of even the lowest shakeup satellite at 417.9 eV [7] or any known continuum resonances in N_2. Below the ionization threshold the extra peaks cannot be explained by the decay of core excited Rydberg states. As shown by Eberhardt *et al.* [8] the spectator lines of such transitions are located below 375 eV kinetic energy. This is demonstrated by the decay spectrum of the $1s^{-1}3p$ Rydberg state [Fig. 1(a)]. Apart from a 6 eV shift to higher energy the complete spectrum is almost identical to the normal Auger spectrum.

Since the extra features at 384 and 378 eV cannot be explained by any known core hole states, we conclude

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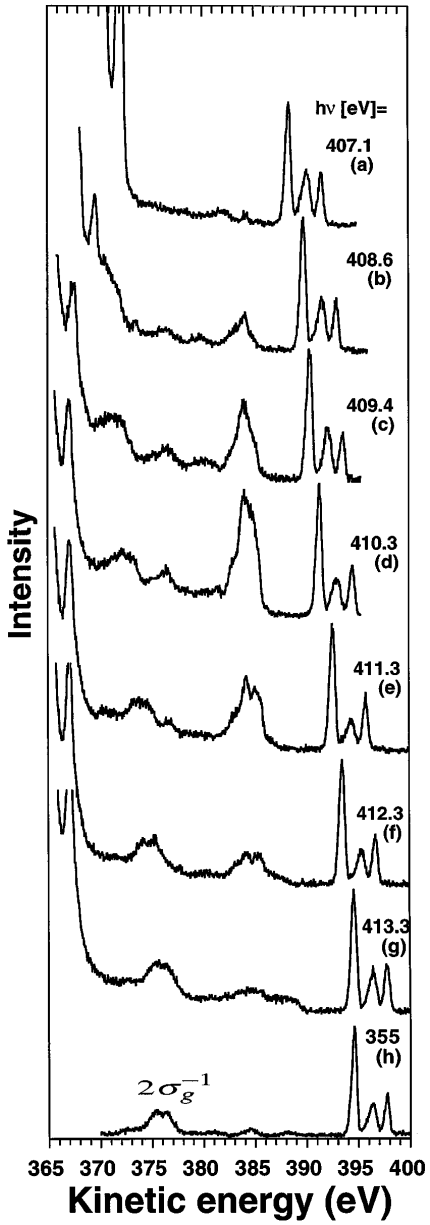

FIG. 1. The electronic decay spectra of N_2 excited from 2.8 below to 3.4 eV above threshold (a)–(g). The spectrum (a) was measured at the $1s^{-1} \rightarrow 3p$ Rydberg resonance. Note that the photon energies below threshold (409.9 eV) a distinct feature arises in the decay spectra at 384 eV kinetic energy, containing at most 4% of the total Auger intensity. The photoelectron spectrum of the valence region excited below the N 1*s* resonances is shown in (h). It has been shifted to higher kinetic energies to coincide with (g).

that there must be additional, hitherto unobserved resonances immediately below and above threshold. Obvious candidates are the 2h2p excited neutral states predicted by Arnebert *et al.* [4]. Two series of double excitations are expected from the calculation, one just around threshold and a second one 4–6 eV above. Only this second series could be identified in the high resolution absorption spectrum by Chen, Ma, and Sette [1] since they do not overlap with other features. The role of multielectron resonances around threshold, on the other hand, has been ignored in the assignment of the experimental absorption spectra of N_2 and indeed of other small molecules [9]. The first series is due to the $1\sigma_g^{-1}1\pi_u^{-1}1\pi_g^2$ and $1\sigma_u^{-1}3\sigma_g^{-1}1\pi_g^2$ electronic configurations. The second series in the continuum involves Rydberg excitations and gives rise to a complicated decay spectrum [10].

How can the relatively simple decay spectrum of the first series of the 2h2p states [Figs. 1(b)–1(f)] be explained? The double excited molecule can in general decay via participator or spectator processes. The former channel would result in 2h1p final states for which the final state energies are the same as those of valence level photoelectron final states. These are seen in the photoelectron spectrum of N_2 as weak features located between the dominant 1h lines [Fig. 1(h)]. Thus, the participator decay could in principle be responsible for the extra decay transitions at 384 and 378 eV, even though their kinetic energy remains constant in Fig. 1. This would occur if different 2h1p final states were reached as a result of varying the excitation energy. However, we would then expect the shape of the overall peak envelope to change considerably, since the Franck-Condon factors differ for transitions between different electronic states. In fact, in Fig. 1 hardly any change in the fine structure can be seen. Also, on varying the photon energy by 4 eV or more it is very unlikely that the energy difference between the excitation energy and the final state energies would always give exactly the same kinetic energy, as is observed for the extra features in Fig. 1. Moreover, the angular distribution of the Auger electrons does not show any asymmetry in the decay peak at 384 eV, as would be expected for a participator decay of an aligned intermediate state [11] to which the suggested doubly excited configurations can couple. Spectator decay would result in 3h2p states in which all three holes are located in the valence levels. The binding energy of the lowest 3h2p final states has been calculated by Langhoff *et al.* [12] to be above 34 eV relative to the neutral ground state. Depending on the photon energy the decay feature at 384 eV kinetic energy corresponds to a binding energy between 24 and 30 eV and is thus too low to be explained by spectator decay. The most common core hole decay modes, the participator and spectator processes, can therefore be ruled out.

A quite different relaxation channel of molecular core hole states is dissociation followed by atomic core hole decay. Although this process is normally far less likely than molecular decay, it was observed for the first time in the decay of the $3d^{-1}4p\sigma^*$ state in HBr by Morin and Nenner [13] and subsequently for other small molecules [14]. In the case of H_2S, Svensson *et al.* [15] have recently observed fast dissociation of neutral 2h2p states excited into the continuum. Although dissociation has not been observed in N_2, the singly excited $1\sigma_g^{-1}3\sigma_u$

shape resonance in O_2 is strongly dissociative as recently discussed by Kuiper and Dunlap [14]. We propose that this mechanism pertains in the present case and show by calculation (see below) that the feature at 384 eV is caused by the decay of a singly core-excited N atom. Clearly, the presence of the two electrons in the π_g antibonding orbital gives these core-excited 2h2p molecular states a strongly dissociative character.

A comparison with the valence excited states of the equivalent-core molecule NO [16,17] predicts for the doubly excited N_2 molecule with two excited electrons in the π_g orbital a drastic increase of 0.3–0.4 Å in the internuclear equilibrium distance relative to the ground state value (Fig. 2). There is thus a high probability for population of continuum orbitals in the core-excited intermediate state [18]. Consequently, dissociation can be observed for which the probability decreases exponentially with the

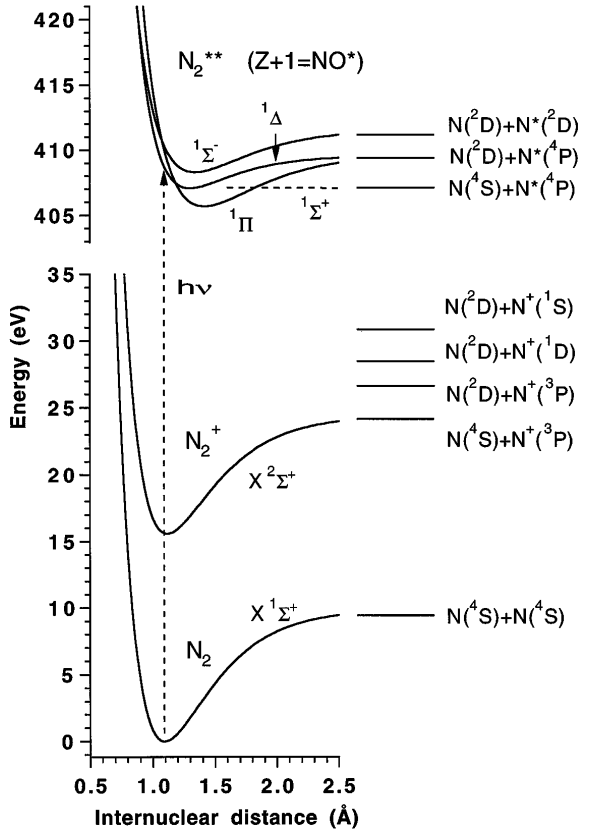

FIG. 2. The potential curves and energy levels of the initial, intermediate, and final states. Those of the doubly excited molecular states of N_2 have been approximated by the valence-excited neutral NO molecule [16,17] using the equivalent core approximation. The valence-excited electron configuration $4\sigma^2 1\pi^3 2\pi^2$ of NO can couple to the $^2\Sigma^+$ and $^2\Pi$ states, while the configuration $4\sigma 1\pi^4 2\pi^2$ gives $^2\Delta$ and $^2\Sigma^-$. Two different states of the excited oxygen atom are formed by dissociation, of which ^3P is the energetically lowest and ^1D the second lowest. Within the $Z + 1$ approximation the electronically excited oxygen atom is equal to a core-excited nitrogen atom except for the spin multiplicity being quartet instead of triplet and doublet instead of singlet for the nitrogen states.

lifetime of the core-excited state. If such a doubly excited N_2 molecule dissociates, one atom ends up in the electronic ground state configuration ($1s^2 2s^2 2p^3$) while the other one remains as a singly core-excited neutral atom with an extra electron in the $2p$ shell ($1s^1 2s^2 2p^4$). The maximum kinetic energy for the decay of the core-excited atom is given directly by the excitation energy minus the energy difference between the molecular ground state and the ionic ground state of the nitrogen atom. The dissociation of the ground state nitrogen molecule into the ground state atoms requires an energy of 9.76 eV [19]. The minimum energy for ionization of the nitrogen atom is 14.54 eV [20]. Hence, at the minimum excitation energy of 408.6 eV the transitions from the ground state N_2 into atomic final states must occur at kinetic energies below 384.3 ± 0.4 eV. In the experimental spectrum excited at 408.6 eV in Fig. 1(b) the highest energy decay features are indeed found below 384.5 eV. This result also agrees quantitatively with the calculations performed. We have computed the total energies of all the jj-coupled $1s^1 2s^2 2p^4$ initial states and $1s^2(2s^2 2p^4)^{-2}$ final states using the multiconfiguration Dirac-Fock code of Grant *et al.* [21]. Transition probabilities between the states, denoted here with LS symbols, were then obtained with the method described in Ref. [22]. The final state energies have additionally been adjusted with respect to the lowest value by using the energy differences from Moore [20]; the corrections are in the order of 1 eV.

As given by the $Z + 1$ approximation the three lowest potential curves of the doubly excited N_2 molecule are shown in Fig. 2 to converge to the dissociation limit in which a core-excited N atom in the ground state $1s^1 2s^2 2p^4(^4P)$ is formed. At about 2 eV higher excitation energy, a dissociation limit corresponding to the core-excited atomic state $1s^1 2s^2 2p^4(^2D)$ is reached. In Fig. 3 the calculated atomic decay spectrum from these two states is shown as a bar diagram and compared with the experimental spectrum of Fig. 1(d). The transition from the ground state $1s^1 2s^2 sp^4(^4P)$ of the core-excited atom to the ground state $1s^2 2s^2 2p^2(^3P)$ of the N^+ ion is calculated at 384 eV kinetic energy; it accounts for the maximum of the decay feature. The calculated decay of the $1s^1 2s^2 2p^4(^2D)$ state, on the other hand, yields two transitions on each side of the peak. The experimental spectra in Figs. 1(d)–1(f) indeed reveal two shoulders, which at higher excitation energies become proportionally more intense. They are due to transitions from the ^2D state to the $1s^2 2s^2 2p^2(^1D, ^1S)$ final states; while in agreement with the experiment theory predicts negligible intensity for the $^2D \rightarrow {}^3P$ transition at 388 eV. At kinetic energies less than 380 eV the ionic $1s^2 2s 2p^3$ final states are reached. Only little intensity is predicted for these transitions between 375 and 380 eV kinetic energy, which is in qualitative agreement with the experiment. In contrast, the intensity of the transitions below 373 eV seems to be strongly overestimated by theory even

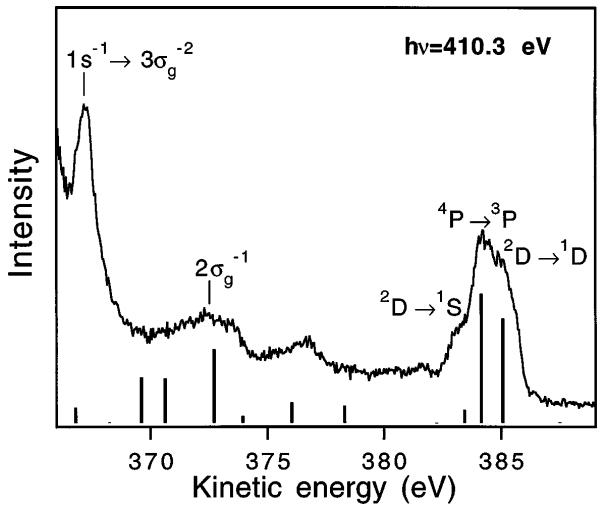

FIG. 3. The calculated Auger spectrum (bar diagram) from the $1s^1 2s^2 2p^4 (^4P, ^2D)$ core-excited N atoms in comparison with the experimental decay spectrum of Fig. 1(d). The electronic configuration of the assigned final states is $1s^2 2s^2 2p^2$.

through a quantitative comparison within this region is uncertain due to an accidental overlap with the broad $2\sigma_g^{-1}$ photoelectron peak of N_2. However, small discrepancies between the experiment and pure atomic calculation can be understood in the sense that the decay still proceeds under a certain molecular influence.

In conclusion, electronic decay spectra of N_2 excited near the K-shell ionization threshold reveal doubly excited neutral states. The transitions are due to the $1\sigma_g^{-1} 1\pi_u^{-1} 1\pi_g^2$ and $1\sigma_u^{-1} 3\sigma_g^{-1} 1\pi_g^2$ configurations and extend over a region from 1.5 below to 2 eV above the threshold. Such states have so far not been observed in the absorption spectrum below threshold since they are obscured by the core-to-Rydberg transitions. The observation may explain the recently measured net negative asymmetry parameter close to the K-shell threshold, since these double excitations can also give states of total Π symmetry. The decay lines of highest kinetic energy are in quantitative agreement with calculations of the resonant Auger decay from core-excited nitrogen atoms which result from rapid dissociation of the core-excited N_2 molecule. The present results show that the core-level absorption spectra of small molecules should be interpreted with care even if fitted spectra are in excellent agreement with experimental data.

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