

Evidence against atomiclike resonant Auger decay in N_2 doubly excited core states by high-resolution experiments

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Resonant Auger spectra following the decay of doubly excited core states in N_2 in the range 409–411 eV have previously been assigned to “atomic” lines indicating ultrafast dissociation. Using high-resolution synchrotron radiation electron spectroscopy from the MAX II facility in Sweden we have remeasured the resonant Auger spectrum of N_2 in the vicinity of the N $1s$ threshold. Contrary to earlier studies, we find vibrational progressions that can be associated with the final $C\ 2^2\Sigma_u^+$ and $2\ 2^2\Pi_g$ states in N_2^+ . We conclude that the decay leads entirely to molecular final states.

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Many molecular core-excited states are dissociative or predissociative. In some cases, the nuclear dynamics are so rapid that electron emission takes place on the same time scale as dissociation. Ultrafast dissociation is a term used to describe such a fast event, placing it in the femtosecond regime [1]. Since ultrafast dissociation takes place on a comparable time scale with the Auger decay, it is possible to detect deexcitations taking place in the molecule and in the dissociated fragment on the same time scale. What has been observed [2,3] is that the decay spectra exhibit narrow atomiclike resonance lines, attributed to decay events taking place in the fragments after dissociation, and broad molecular spectral structures caused mainly by decay taking place near the equilibrium distance of the molecule. One way to separate the molecular from the fragment peaks is to study their dispersive behavior when the ionizing radiation is tuned within an energy interval including the resonance. By varying the photon energy around the value corresponding to the resonance maximum, we can selectively prepare the core-excited state both on top of the resonance and detuning from the top in small wavelength steps. Molecular and atomic peaks show different dispersive behaviors upon shifting the frequency of the ionizing light on and around the resonance. In particular, the center of gravity of the molecular broad structures follows the Raman-Stokes dispersion law [4], while the atomic narrow lines remain constant in kinetic energy. This behavior can be understood simply on the grounds of energy conservation: while for decays to molecular final states the only energy dissipation channel is the kinetic energy of the ejected electron, and therefore this energy disperses linearly with the photon energy, in fragment decay there is an additional channel, which is the nuclear coordinate, and therefore part of the energy put into the system by the primary excitation goes to the motion of the nuclei mov-

ing apart, and the kinetic energy of the outgoing electron remains constant while the photon energy is changed.

Ultrafast dissociation of core-excited molecules was first observed by Morin and Nenner [1] in 1986, and since then the phenomenon has been the subject of a large number of studies (see, e.g., [2,3]). In 1995, the first observation of ultrafast dissociation associated with the Auger decay of doubly excited core states was observed [5]. Core-hole double excitation is a relatively weak satellite processes, comparable to shake-up satellites associated with core photoionization. Because of the low cross section relative to direct photoionization, the corresponding emission lines in the Auger decay spectra are difficult to observe. In 1996, Neeb *et al.* [6] reported “atomiclike” resonant Auger decay in N_2 when exciting in the vicinity of the N $1s$ ionization threshold. Their assignment was based on the fact that the observed structures did not appear to disperse in kinetic energy when exciting to doubly excited core hole states slightly above and below the N $1s$ threshold. Also, atomic *ab initio* calculations of the Auger decay spectrum of core-excited atomic nitrogen showed a fair resemblance to the observed peaks around 385 eV kinetic energy.

In order to help the discussion, in Fig. 1 we show four spectra taken around the N $1s$ threshold. In these medium-resolution spectra, plotted on the kinetic-energy scale, we also included the results from the *ab initio* calculations presented in Ref. [6]. The spectra shown in Figs. 1(b), 1(c), and 1(d) are taken at the pseudomagic angle, while in the spectrum shown in Fig. 1(a) the analyzer is placed perpendicular to the polarization vector of the excitation beam. In it, the contribution of the direct photoemission lines is minimized while the contribution from the resonant structures is kept almost unchanged. This is due to the fact that the angular distribution is isotropic for the resonant lines. The reported “atomic” structures are relatively broad, which is surprising if the lines originate from atomiclike transitions taking place in a situation where the two nitrogen atoms are decoupled. The width of such lines is rather narrow and is independent

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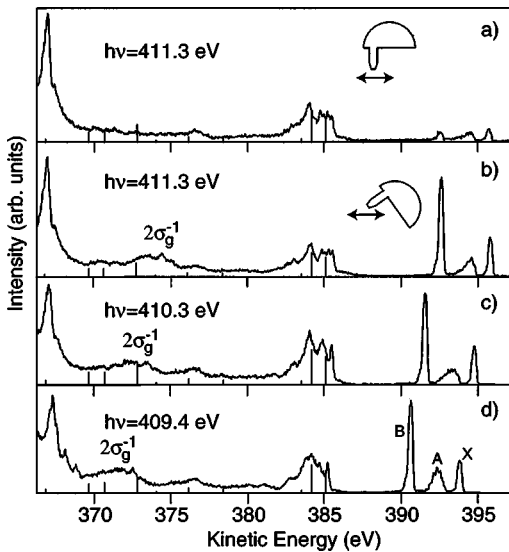


FIG. 1. The overview resonant Auger spectra of doubly excited N_2 around the $N\ 1s$ threshold. In (a), the analyzer is placed perpendicular to the polarization vector of the excitation beam. In it, the direct photoemission lines are minimized. The resonant features are nearly isotropic. In (b), (c), and (d), the pseudomagic angle was used, suppressing the angular dependency effects from the observed bands. The bars indicate where the atomic lines were predicted.

of the monochromator bandwidth [4]. Furthermore, at least four peaks around 384 eV are present, where the calculations predict only three. A possible good candidate for an atomic peak, the sharpest peak just above 385 eV, is not fixed in kinetic energy when the excitation energy is changed. The calculation also predicts fairly intense lines around 370 and 375 eV which overlap with the $2\sigma_g^{-1}$ direct photoemission band at the pseudomagic angle. The $2\sigma_g^{-1}$ band disperses with the photon energy when plotted on the kinetic-energy scale. An inspection of the spectra in Figs. 1(b), 1(c), and 1(d) does not show structures fixed in kinetic energy that match the calculated atomic peaks. This finding is even clearer in the Fig. 1(a) spectrum where the direct photoemission lines are almost suppressed, and no sharp atomic lines can be assigned to the calculated spectrum. Therefore, from all ten lines predicted by the *ab initio* calculation with measurable intensity, only three can be related to observed peaks in the experimental spectra. These facts alone are enough to rule out the atomic peak hypothesis. In order to explain the nature of the observed peaks around 384 eV a much smaller monochromator bandwidth was used while keeping the analyzer resolution unchanged (see the discussion below). One would expect no change in the “atomic peak” width due to this narrowband excitation.

Very recently, the work of Ref. [6] was followed up by partial electron-yield measurements and calculations where it was shown that one could magnify the contrast for the doubly excited core-hole states by monitoring the intensity of the atomiclike structures for excitation energies around the $N\ 1s$ threshold [7]. The partial electron-yield spectrum was obtained by setting a kinetic-energy window at 384 eV and scanning across the threshold region. Three dominant structures were observed at around 410, 414, and 416 eV photon

energy. In the calculation, potential curves were presented for the singly excited $N\ 1s \rightarrow \pi^*$ state and for the doubly excited core-hole states of interest, in particular, the two lowest curves of Σ and Π symmetry with the dominant configurations of $1s\sigma_u^{-1}3\sigma_g^{-1}1\pi_g^2$ and $1s\sigma_g^{-1}1\pi_u^{-1}1\pi_g^2$. From Fig. 3 of Ref. [7] it can be seen that the corresponding adiabatic potential curves intersect very close to the ground-state equilibrium distance of about 1.1 Å. The vertical excitation energies for these curves are 0.6 and 0.46 eV. These curves provide a theoretical basis for the interpretation of the partial electron-yield spectrum of Ref. [7]. Note that the calculated potential curves clearly correspond to bound states, even if the minimum is shifted outward by a few tenths of an Ångström. Possible final-state potential curves such as those of the final $C\ 2^2\Sigma_u^+$, $D\ 2^2\Pi_g$, and $2\ 2^2\Pi_g$ states also have a minimum shifted in the same direction. These states also have a similar leading configuration to the core-excited states. These facts were not commented on by the authors of Ref. [7].

Using third-generation storage-ring facilities and state-of-the-art electron spectroscopy it is now possible to study low-intensity phenomena like the decay of doubly excited core-hole states with vibrational resolution. We have performed such a study for the atomiclike lines of Ref. [6]. We find that the so-called atomic lines belong to vibrational progressions, which coincide with the well-known $C\ 2^2\Sigma_u^+$ and $2\ 2^2\Pi_g$ states in N_2^+ [8]. A critical analysis of the origin of the nondispersion of the peaks shows that the nondispersive behavior of the unresolved peaks is attributable to insufficient experimental resolution and/or to well-known effects in molecular resonant Auger spectra, rather than to ultrafast dissociation.

The experiment was performed at beamline I 411 [9] connected to the third-generation electron storage ring MAX II at MAXLAB in Lund, Sweden. This beamline is equipped with a modified Zeiss SX 700 plane-grating monochromator and with a rotatable hemispherical Scienta SES 200 high-resolution electron spectrometer. Except in Fig. 1 the monochromator resolution was set to 50 meV and the spectrometer resolution was 45 meV, thus giving a total spectral resolution of 63 meV. In Fig. 1 the total resolution was 300 meV while the spectrometer resolution was kept the same. The gas was obtained commercially and valence-band photoelectron spectra were measured to check for impurities. The monochromator energy was calibrated to the well-known position of the $N\ 1s \rightarrow \pi^*$ $v'=0$ transition at 400.88 eV photon energy.

In Fig. 2 we display the decay spectra associated with double core excitation near the threshold together with a reference valence-electron spectrum of N_2 taken at 95 eV photon energy. For comparison it should be mentioned that the studied region corresponds to the kinetic-energy region between 380 and 390 eV in Ref. [6]. The excitation process creates states such as $1s\sigma_u^{-1}3\sigma_g^{-1}1\pi_g^2$ and $1s\sigma_g^{-1}1\pi_u^{-1}1\pi_g^2$. These intermediate states could fragment, but also decay to molecular final states such as $1\pi_u^{-1}3s\sigma_g^{-1}1\pi_g^1$, which is the leading electronic configuration of the well-known C state observed in direct photoemission [8]. In fact, in the decay spectra we observe a peak

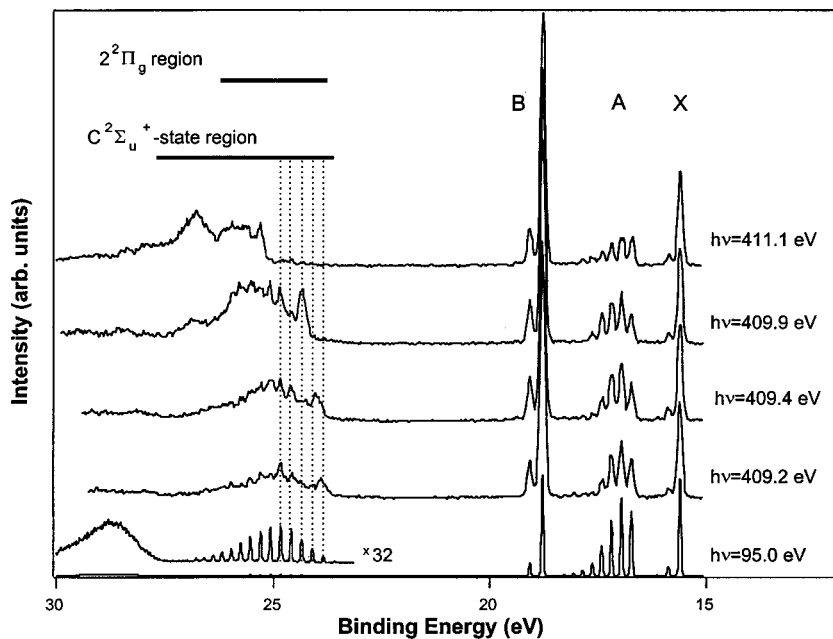


FIG. 2. The narrowband excitation resonant Auger spectra of doubly excited N_2 in the vicinity of the $N\ 1s$ threshold. As a reference we have included a direct photoionization spectrum taken at 95 eV photon energy. The investigated binding-energy region corresponds to decay to the well-known $C\ 2^2\Sigma_u^+$, D , and $2\ 2^2\Pi_g$ states of the cation.

around 25 eV binding energy with a vibrational progression whose energies coincide with those of the C state in the high-resolution photoelectron spectrum taken at 40.8 eV excitation energy [8]. As also pointed out in Ref. [8], there are two neighboring final states, the D and $2\ 2^2\Pi_g$ states, which partially overlap with the C state progression. In Fig. 3 we show a detail where the vibrational energies of the $C\ 2^2\Sigma_u^+$ and $2\ 2^2\Pi_g$ progressions are indicated. For comparison we have here used the reference resonant Auger spectrum taken at the $N\ 1s-\pi^*\ v=0$ excitation energy from Ref. [9]. The

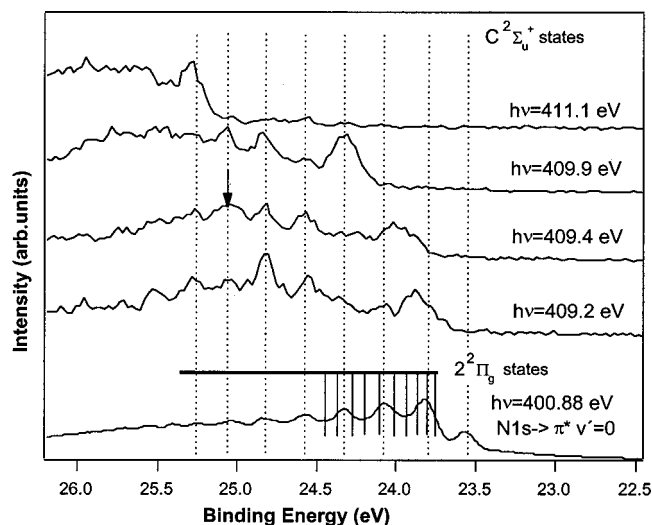


FIG. 3. A detail of Fig. 2 showing the vibrational progressions of the $C\ 2^2\Sigma_u^+$ and $2\ 2^2\Pi_g$ states. As can be seen, all essential structure can be accounted for by these progressions. Note the enhancement of the intensity at the onset of the band at lowest binding energy. This onset is due to the amplification of the intensity at a turning point of the intermediate-state potential curve (see Ref. [10]). The arrow marks a line that is broadened since it coincides with a Stokes-doubling structure [11] associated with the $N\ 1s \rightarrow \pi^*$ single excitation.

strong features in the vibrational progressions in Fig. 3 can again be explained as originating from the C state. It can also be seen that the small perturbations in the C progression—in both the singly excited reference spectrum and the doubly excited core spectra—can be accounted for by the $2\ 2^2\Pi_g$ vibrational lines. This finding of vibrational substructure is obviously incompatible with ultrafast dissociation.

The spectra were detuned below and above the $N\ 1s$ ionization threshold, including one spectrum taken exactly at the threshold energy of 409.9 eV. The resonant behavior is obvious and we conclude that the dominant decay path is to $2h-1p$ states of the singly ionized molecule. Note that the maximum of the envelope of the complex vibrational band(s) changes with the excitation and appears to exhibit a nondispersive behavior. However, such an effect is not surprising, considering the vibrational effects that can be present in resonant Auger spectra of molecules. A recent illuminating example was shown in Ref. [10], where one can clearly see a “vibrational mapping” of the potential curves. The intensities are enhanced at the classical turning points, resulting in a seemingly nondispersive character of the envelope of some structures in the spectra, as well as the observation of seemingly negative dispersion in other cases. It is clear that the present spectra show such a “false” nondispersive character of the decay lines associated with the doubly excited core-hole states. One should also mention that some lines in the progression, e.g., the line marked with an arrow in the spectrum at 409.4 eV, are spurious peaks due to an instrumental artifact. That is, the profile of the exciting radiation has a very small component (ca. 0.1%) that is due to diffuse reflection in mirrors and gratings. This stray light will cause the so-called Stokes doubling [11] of the spectral features associated with the decay of the strong $N\ 1s \rightarrow \pi^*$ excitation: this resonance is broadband excited by the stray light even if the monochromator is tuned to a different photon energy. The phenomenon is in this case rather involved, since several vibrational components of the intermediate excited

state will add at approximately the same energy giving rise to a broader Stokes-doubling peak at 384 eV kinetic energy in the middle of the progression from the doubly excited core-hole states. Since this feature remains by definition at constant kinetic energy, its presence can reinforce the apparent nondispersive behavior, especially in spectra with lower resolution. The partial yield spectrum, presented in Ref. [7] could be affected by Stokes doubling since the energy window was set at fixed kinetic energy in a region where the Stokes-doubling line should contribute.

In conclusion we have measured the resonant Auger decay spectra associated with doubly excited core-hole states near the $N\ 1s$ threshold in the nitrogen molecule. The spectra show at least one vibrational progression that energetically matches the $C\ 2\Sigma_u^+$ molecular ionic state, and transitions to the final $D\ 2\Pi_g$ and $2\ 2\Pi_g$ molecular ionic states are also observed. We conclude, at variance with previous studies,

that there is no indication of ultrafast dissociation from these doubly excited states in the energy region where earlier studies claimed evidence of atomic nitrogen peaks. The results show that the increased signal-to-background ratio, intensity, and resolution at third-generation facilities cast a different light on the dynamics of core photoionization in molecules.

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