Conjugate shake-up-enhanced Auger transitions in N_2

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A substantial enhancement of intensity in the high-energy part of the N_2 *KLL* Auger spectrum has been observed at photon energies a few tens of eV above the N 1*s* threshold. By monitoring the corresponding 1*s* photoelectron spectrum, we show that the effect is due to the emergence of strong conjugate shake-up satellites. As shown in previous *e*-2*e* studies for CO, such Auger spectra are useful in determining the intensity behavior of shake-up satellites in the immediate threshold regions.

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I. INTRODUCTION

Photoelectron spectra of core levels in molecules typically show a rich satellite structure on the low-kinetic-energy side of the dominant single hole photoelectron line. These satellite lines stem from complicated multielectron transitions; much has been learned about their origin by varying the photon energy. It has been shown in the *K*-shell photoelectron spectra of N_2, CO, and CO_2, for example, that the intensities of different satellite features do not display a uniform behavior as a function of excitation energy [1–8]. They may even increase in relative intensity as their thresholds are approached; indeed, certain satellites are only visible at excitation energies close to threshold. Far above threshold, the satellite intensity is dominated by the direct part of the transition moment. These normal, or direct, shake-up transitions are explained by dipole ionization of a core electron which is accompanied by a monopole excitation of a valence electron to an unoccupied orbital. The so-called conjugate part of the transition moment, on the other hand, can become significant at excitation energies close to threshold. In these latter transitions, a core electron is dipole excited to an unfilled valence orbital while a valence electron is monopole ejected into the continuum. The appearance of the extra lines at low excitation energies can be accounted for by the different selection rules for conjugated shake-up transitions. Thus, the satellites dominated by the different parts of the transition moment show an almost opposite behavior in their energy-dependent intensities. The larger the conjugate contribution, the larger is the satellite intensity at the threshold. If the direct part is more important, the satellites are observed to lose intensity at the threshold.

Since highly excited core hole states in first-row molecules decay essentially via Auger-electron emission, additional lines at higher kinetic energy should be observed in the Auger spectra [9–11]. Moreover, we would expect that the different intensity behavior of the shake-up satellites near threshold should be also reflected in Auger transition rates from the corresponding initial states. We have therefore measured a series of *KLL* Auger spectra of N_2 at excitation energies starting from the onset of the 1*s* satellite threshold to far above threshold. Indeed, we find a striking variation in the intensity of the different Auger structures above kinetic energies of 370 eV which correlates directly with the relative intensity changes of the two most prominent shake-up satellites. We show that the one-to-one correspondence between satellite Auger lines and the shake-up satellites themselves can be used to extract the intensity behavior of the shake-up satellites very close to their thresholds. The information yielded by the N_2 Auger spectra measured here thus complements the zero-kinetic-energy (ZEKE) measurements at threshold [4].

II. EXPERIMENT

The photoelectron and Auger spectra of N_2 were measured on the X1B beamline at the 2.5 GeV electron storage ring of the National Synchrotron Light Source (NSLS), Brookhaven, using a cylindrical-mirror-analyzer (CMA) -type electron spectrometer. Both the beamline [12] and the electron spectrometer [13] have been described in detail before. Briefly, synchrotron radiation from a 35-pole undulator is monochromatized with a spherical grating monochromator, in which the spherical grating is the only element between the fixed entrance and movable exit slit [14]. The inherent photon energy resolution of the monochromator is very high, as has been shown by the 1*s* absorption spectra of CO, N_2, and O_2 measured on the beamline [12]. In the present measurements on N_2, for which it was necessary to work at high intensity and thus lower resolution, the photon bandwidth was estimated to be 0.4–0.5 eV.

After leaving the monochromator the radiation passes

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through the spectrometer along the symmetry axis of the analyzer before it intersects the gas target in the excitation region. To conserve the complete cylindrical geometry, sample gases are introduced into the gas cell through a conical slit along the light beam. Combined with the 54.7° emission angle into the analyzer and an eight-segment microchannel plane detector system, the spectrometer allows angle-resolved measurements to be performed without moving any components. The energy resolution of the analyzer is 0.8% of the pass energy. Pass energies of 40 and 80 eV were used for the Auger-electron spectra, while the photoelectron spectra containing the N 1*s* main line and its satellites were taken with a 15 eV pass energy. The kinetic-energy scale of the electron analyzer was calibrated using the reported energy of 366.9 eV for the sharp diagram Auger transition to the $3\sigma_g^{-2}(^1\Sigma_g^+)$ final state [15]. Photon energies were then calibrated using the corrected kinetic energies and binding energies of either the N $1s^{-1}$ line at 409.0 eV [15] in second order or the single hole valence states $X\,^2\Sigma_g^+$ at 15.580 eV and $B\,^2\Sigma_u^+$ at 18.751 eV [16].

III. RESULTS AND DISCUSSION

Figure 1 shows the complete *KLL* Auger spectrum of N_2 recorded at photon energies of 428.3 and 538.5 eV. The higher-energy measurement resembles closely the Al $K\alpha$ spectrum ($h\nu = 1487$ eV) [11], and can be thus taken as the sudden-limit result. Inspection of the Auger spectrum at lower photon energy, measured only about 18 eV above the N 1*s* ionization threshold, reveals some interesting differences. In particular, there is much less spectral weight on the low-kinetic-energy sides of the two dominating Auger groups located at around 340 and 363 eV. These changes can be attributed to double (and to lesser extent multiple) hole initial states, which become possible with increasing excitation energy. When these shake-off states decay via Auger processes, the emitted electrons acquire a lower kinetic energy than in the case of the corresponding diagram Auger transitions.

What causes the intensity increase in the features around 375 eV kinetic energy in the lower-energy measurement of Fig. 1(b)? Since the photon energy of 428.3 eV is above the inner-shell continuum resonances such as double excitations and shape resonances [17], all processes deriving strength from resonantly excited states can be excluded. Further, at 428.3 eV photon energy, the valence photoelectron lines appear at kinetic energies above 390 eV and do not, therefore, influence the Auger spectrum. In order to examine the behavior of the features in this kinetic-energy region as the N 1*s* threshold is approached, we have measured a series of Auger-electron spectra at different photon energies (Fig. 2). They have been normalized to photon flux and gas pressure. It should be noted that the structure which shifts linearly with photon energy at the few lowest photon energies in Fig. 2 is not caused by Auger decay but is due to valence photoemission from the $2\sigma_g$ orbital.

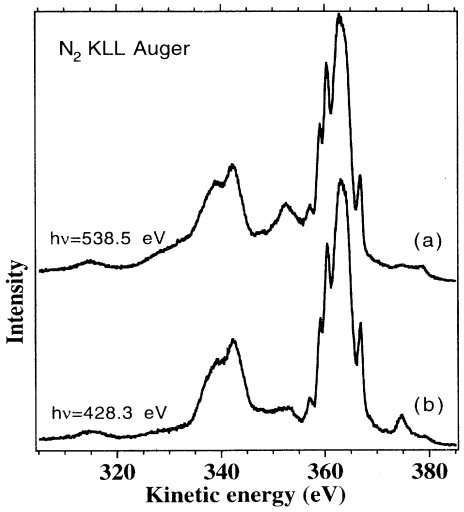

FIG. 1. The *KLL* Auger spectra of N_2 measured at photon energies of (a) 538.5 eV and (b) 428.3 eV.

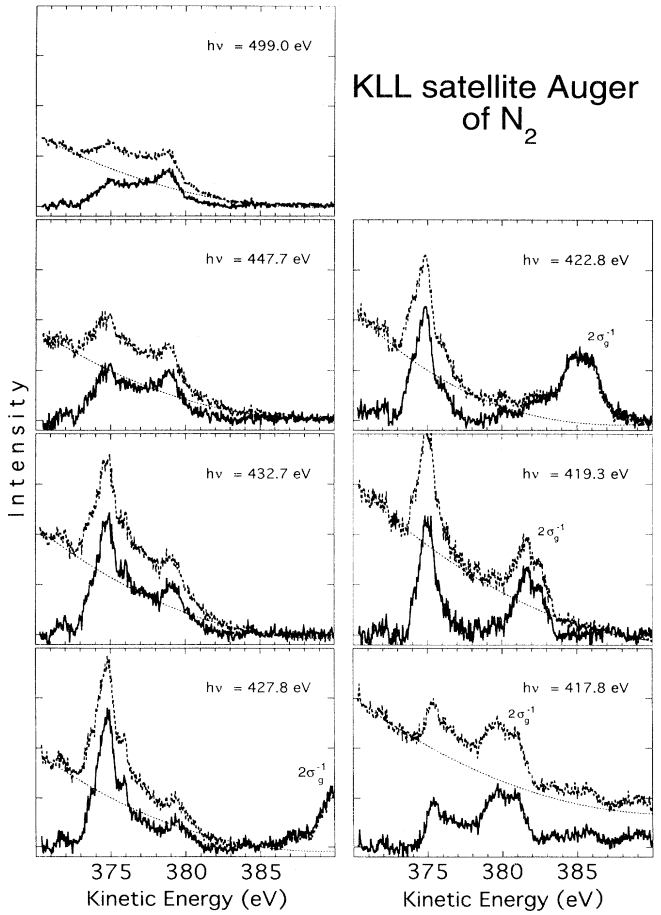

FIG. 2. The Auger spectra of N_2 in the kinetic-energy region 370–390 eV measured at different photon energies. Dashed lines represent the experimental data and dotted lines give the estimated polynomial background. Background subtracted spectra are displayed with solid lines.

Each of the Auger spectra in Fig. 2 can be roughly described by a double peak structure with the maxima at 375 and 379 eV. The spectrum recorded with 499 eV photons looks very similar to the higher photon-energy measurement of Fig. 1. On going to lower photon energies, the intensities of both Auger structures increase and their relative heights clearly change. The higher kinetic-energy component acquires about 1.5-fold the intensity at 447.7 and 432.7 eV photon energy compared to 499 eV. At lower excitation energies this peak decreases in intensity until it disappears at 422.8 eV. In contrast to the feature at 379 eV, the intensity of the Auger peak around 375 eV kinetic energy increases by a factor of 5 on going from 499 to 432.7 eV photon energy and then stays nearly constant down to a photon energy of 419.3 eV. However, at 417.8 eV it has already almost vanished. The intensity behavior of these two Auger features is depicted in Fig. 3, where the peak heights are plotted at different photon energies (open squares and triangles). From this it is quite clear that they show completely different photon-energy dependences. While the higher-energy Auger peak has only low intensity near threshold, the lower-energy feature retains nearly its maximum value down to threshold. Hence, the behavior of the lower-energy Auger component resembles qualitatively the expected energy dependence of a conjugate shake-up transition whereas the intensity of the high-energy Auger peak follows that of a direct shake-up transition.

Since these high-energy Auger structures are assumed to originate from Auger decay of the satellite shake-up states, we have also measured a series of the photoelectron shake-up spectra excited in the same photon-energy range as that used for the Auger spectra. These are shown in Fig. 4; as well as being normalized, these photoelectron spectra have also been corrected for the transmission of the electron analyzer because of the variation in kinetic energy. The uppermost spectrum measured at the photon energy of 538.5 eV shows two intense

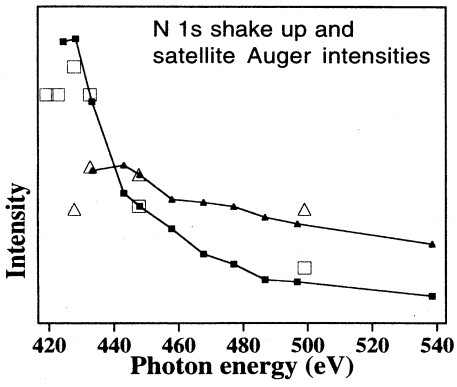

FIG. 3. The peak heights of the Auger structures located at kinetic energies of 375 eV (open squares) and 379 eV (open triangles) measured at different photon energies. The lines connecting solid squares and triangles show the intensities of the $1\pi_u^{-1}1\pi_g^2(^3\Sigma_u)1s^{-1}$ and $1\pi_u^{-1}1\pi_g^1(^1\Sigma_u)1s^{-1}$ shake-up satellites, respectively, as a function of photon energy.

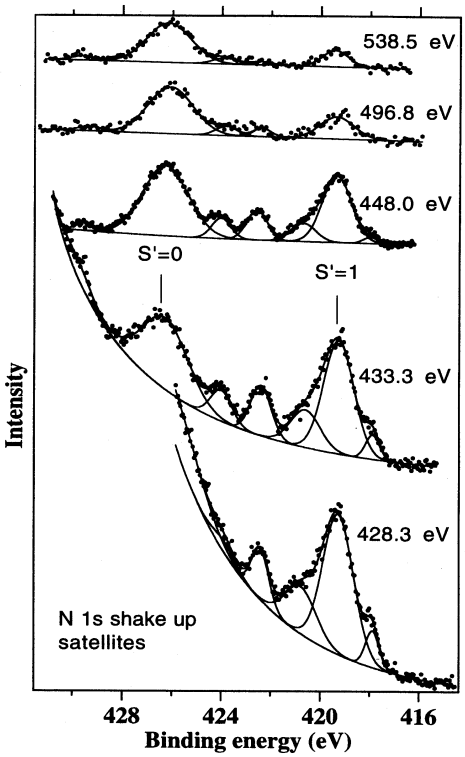

FIG. 4. The shake-up photoelectron spectra of the N 1s measured at different photon energies. Original experimental data are shown with dots and the solid lines give the least-squares fitted peaks and background. The positions of the two most intense shake-up transitions, to the final states $1\pi_u^{-1}1\pi_g^1(^3\Sigma_u)1s^{-1}$ and $1\pi_u^{-1}1\pi_g^1(^1\Sigma_u)1s^{-1}$, are indicated by their intermediately coupled spins as $S'=1$ and $S'=0$.

shake-up peaks at binding energies 419.3 and 426.2 eV. Both of them originate from the electron configuration $1\sigma_u^{-1}1\pi_u^{-1}1\pi_g^1$. The only difference is that in the lower binding energy state, the spins of the π electrons are coupled to give an intermediate triplet state ($S'=1$) while for the higher binding energy state they give a singlet ($S'=0$) [18]. The final symmetry is in both cases $^2\Sigma_g^+$, the same as for the N_2 $1s^{-1}$ single hole ionization. The 538.5 eV spectrum is quite similar to the sudden limit N 1s shake-up spectrum measured at $h\nu=1487$ eV [11]. The intensity ratio of the higher binding energy satellite to the lower one is about 4 which is, within statistical uncertainty, the same as at $h\nu=1487$ eV. At lower excitation energies the intensity ratio between the two main satellite peaks clearly decreases. At 433.3 eV, the ratio is already four times smaller than the sudden-limit value. While the intensity ratio decreases monotonically, the intensity of the singlet $\pi\pi^*$ satellite rises gradually down to a photon energy of 448.0 eV. It is, however, very difficult to tell from the photoelectron spectra what happens exactly at still lower photon energies near the singlet satellite threshold, e.g., in the spectrum excited at a photon energy of 428.3 eV.

In contrast to the singlet peak, the intensity of the triplet $\pi\pi^*$ satellite at 419.3 eV binding energy is relatively

low at high photon energies but increases strongly at excitation energies close to threshold. Below $h\nu=450$ eV, we observe additional structure emerging on both sides. Thus the increase of intensity in this energy region is caused not only by the conjugate-enhanced triplet satellite, but also partly by the excitation of these additional shake-up satellites, which are only present at lower excitation energies. The intensities of the singlet and triplet $\pi\pi^*$ satellite are also shown as a function of photon energy in Fig. 3 (the curve for the triplet satellite includes also the intensity of the additional shake-up satellites). Angonoa, Walter, and Schirmer [19] have calculated the shake-up energies for the pure conjugate shake-up satellites having symmetries other than $^2\Sigma_g^+$. These transitions are clearly resolved in our photoelectron spectra, giving further confirmation for the validity of the conjugate shake-up concept. The computed value of 8.46 eV for the lowest conjugate shake-up state $1\sigma_g^{-1}3\sigma_g^{-1}1\pi_g^1(^2\Pi_g)$ agrees well with the 8.0 eV observed for the peak on the low binding energy side of the triplet $\pi\pi^*$ satellite. The calculated shake-up energies for the next five pure conjugate satellites range from 10.01 to 11.57 eV. Some of them are covered in the spectrum by the conjugate-enhanced triplet peak while the others generated the structure at the binding energy of 420.8 eV, giving a shake-up energy of 10.9 eV. The existence of these pure conjugate shake-up satellites at threshold was inferred from the ZEKE spectrum but none of them could actually be resolved [4,5]. They have recently been studied in detail for CD, however, using conventional photoelectron spectroscopy [6–8].

A comparison of the intensities of the shake-up and Auger features in Fig. 3 shows that the higher Auger component at 379 eV follows almost quantitatively the intensity behavior of the singlet shake-up line. In a recent publication Svensson *et al.* [11] proposed that the high-kinetic-energy part of the N_2 satellite Auger spectrum is due to Auger transitions from the singlet $\pi\pi^*$ shake-up initial states to the lowest two-hole and three-hole one-particle states. These Auger transitions are shifted to higher kinetic energies by an amount equal to the shake-up energy compared to the transitions from single hole N $1s^{-1}$ states to the same final states. Thus, our experimental study on the photon energy-dependent intensities and the theoretical analysis of Svensson *et al.* [11] are complementary in proving the origin of the high-energy satellite Auger structure. By analogy, the Auger peak at 375 eV kinetic energy can be assigned to satellite Auger decay from the conjugate shake-up initial states, particularly from the conjugate-enhanced triplet $\pi\pi^*$ shake-up state. The related data points for the Auger peaks and photoelectron shake-up satellites in Fig. 3 are scaled to coincide at $h\nu=448$ eV, where the analysis of both the spectra is relatively straightforward. The present data show that the Auger spectra can be used to extract information on satellite intensities close to threshold, where photoelectron spectra suffer from background problems. This procedure has been used before by Ungier and Thomas in their *e*-2*e* coincidence measurements on CO [1]. Analyzing the Auger spectra excited at 427.8 eV, which is 1.6 eV above the singlet satellite threshold, the related Auger peak at 379 eV shows a clearly reduced amplitude compared to the Auger spectrum recorded at 432.7 eV. It is concluded from this Auger spectrum that the intensity of the singlet satellite decreases in intensity when the excitation energy approaches threshold. Exactly at threshold, the ZEKE measurement yields for the singlet satellite peak an intensity of only $2.3(\pm1.0)\%$ of the main line [4]; our Auger spectra suggest a value of $3.8(\pm1.0)\%$ at $h\nu=427.8$ eV, compared to the sudden-limit value of 8.7% [11].

The Auger spectra excited at the photon energies of 419.3 and 422.8 eV reveal that the 375 eV Auger peak from the conjugate shake-up states maintains almost its maximum intensity even in the immediate vicinity of the triplet satellite threshold at 419.3 eV. We therefore conclude that the triplet shake-up line in the photoelectron spectrum is comparatively intense at the satellite threshold. The ZEKE spectrum gives a value of 11% for the conjugate shake-up structures at threshold [4]. We cannot report an equivalent intensity ratio for these conjugate structures because of the lack of N 1*s* single hole data. However, a fit of the lowest excited photoelectron spectrum shown at the bottom of Fig. 4 yields for all the conjugate shake-up lines about 12% of the main line intensity. This spectrum is excited 9 eV above the triplet shake-up threshold. At threshold the ratio is expected to decrease somewhat, since the cross section of the N 1*s* single hole state increases rapidly as the σ^* resonance is approached [20].

In this paper, we have dealt with only one type of decay channel that is possible after shake-up satellite transitions, namely, the participator Auger process. Such excited states can, of course, also decay via spectator transitions where the excited electron does not participate in Auger decay. These are expected to cause structures below and at the same energies as the diagram Auger lines, and their extraction would require photoelectron–Auger-electron coincidence measurements. However, we can simply estimate the proportion of the satellite Auger transitions occurring at kinetic energies lower than those studied here. The intensity ratio observed between the main line and satellites in the photoelectron spectrum should be preserved in the Auger spectrum when all possible Auger decay channels are taken into account (and when x-ray emission is negligible). We observe that at $h\nu=428.3$ eV, for example, which is below the shake-off threshold, the integrated intensity of the shake-up satellites is approximately $17(\pm3)\%$ of the main line intensity. By measuring the integrated intensities of the participator structure (A_{part}) and of the rest of the Auger spectrum (A_{Auger}), cf. Fig. 1(b), the part X of the latter due to Auger transitions from shake-up states can be estimated from the relation $(A_{\text{part}}+X)/(A_{\text{Auger}}-X)=0.17$. This rough estimate shows that at least 75% of the intensity of all satellite Auger transitions would be below 370 eV kinetic energies. Some other participator Auger transitions, e.g., to the final states $2\sigma_g^{-1}1\pi_u^{-1}1\pi_g^1$, fulfill this energy condition but presumably spectator Auger decay is by far the dominant decay channel.

IV. CONCLUSIONS

The high-resolution Auger spectrum of N_2 above 370 eV kinetic energy has been measured near the core hole satellite thresholds at different photon energies. The cross sections of the two main Auger features at 375 and 379 eV show a strong dependence on the excitation energy. While the Auger structure at 375 eV remains intense down to threshold, the 379 eV feature almost vanishes at near-threshold photon energies. By also measuring the shake-up spectra in the same photon-energy range, Auger structures can be attributed to the decay of the conjugate-enhanced $1\pi_u^{-1}1\pi_g^1(^3\Sigma_u)1s^{-1}$ and of the direct $1\pi_u^{-1}1\pi_g^1(^1\Sigma_u)1s^{-1}$ shake-up states, respectively. As already shown by Ungier and Thomas in e-$2e$ studies of CO [1], satellite Auger spectra are useful in determining the intensity behavior of shake-up satellites in the immediate threshold regions. Close to threshold, the photoelectron spectra of N_2 reveal pure conjugate shake-up satellite structures on both sides of the triplet coupled $\pi\pi^*$ shake-up peak. The relative intensities of the satellites in the photoelectron spectrum only remain constant above a photon energy of 500 eV, thus putting the sudden-limit energy quite far above the N 1s threshold.

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