Transition from Adiabatic to Sudden Core-Electron Excitation: N_2 on Ni(100)

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The first systematic study of the energy dependence of a core-level shake-up feature is presented. In contrast to expectations the shake-up peak remains nearly unchanged in intensity down to ~ 15 eV above threshold. The early and abrupt turn-on of the multielectron satellite found experimentally is well explained by a theory which describes the transition from adiabatic to sudden core-level excitation by a simple exchange-interaction picture.

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One of the fundamental assumptions commonly used in the interpretation of photoemission spectra is the validity of the sudden approximation.[1,2] In the sudden-excitation limit the ionization process is so rapid that the other electrons on or near the excited atom do not have time to rearrange themselves to the new hole potential. The ion may thus be left in excited states which, relative to the lowest-energy final state, may be envisioned as multielectron excitation states where other electrons are "shaken" into the continuum (shake-off) or unoccupied bound states (shake-up). Through energy conservation these multielectron excitations manifest themselves in the photoemission spectrum as satellites or asymmetric line-shape[3] contributions.

It has long been thought that the sudden approximation should break down in the limit where the photoelectron leaves the atom slowly.[1,2] In this *adiabatic* excitation limit the electrons on or near the excited atom lower their energy by slowly adjusting to the effective atomic potential in an instantaneous, self-consistent way. Hence the multielectron shake processes do not exist and the photoemission satellites[4] and asymmetric line-shape effects[3,5] should be absent.

Despite these longstanding *qualitative* time-dependent ideas about the adiabatic and sudden excitation pictures, very few *quantitative* experimental and theoretical investigations have addressed the issue of the transition between the two excitation limits. The common view, based on the pioneering work by Carlson and Krause (CK),[1] is that of a smooth transition, with the sudden limit being reached about 200 eV above threshold.

Here we present the first systematic experimental study of a well-defined, pronounced core-level shake-up peak in the expected transition region between adiabatic and sudden excitation. We show that contrary to expectations the transition from adiabatic to sudden excitation is abrupt and essentially completed less than 15 eV above the core-level excitation threshold. We also present an interpretation of these results by a simple exchange model which is based on a simplified version of the Hartree-Fock approximation. As emphasized by Stern,[6] this model offers a contrasting alternative to the prevailing view that the energy dependence of the shake-up amplitude can be interpreted as a time-dependent crossover from the adiabatic to the sudden approximation.[1,4,5] The model also leads to predictions which can be tested experimentally.

We have investigated the 1*s* core-level photoemission and absorption spectra of molecular N_2 on Ni(110). This system and the similar N_2/Ni(100) system had previously been extensively studied by x-ray photoemission spectroscopy (XPS),[7,8] ultraviolet photoelectron spectroscopy (UPS),[9] and near-edge x-ray absorption fine-structure (NEXAFS)[10] measurements. N_2 stands up on the surface[10] and its weak chemisorption bond is found to be responsible for giant satellite features in both valence[9] and core-level[7,8] photoemission spectra. In particular, the N 1*s* XPS spectrum is composed of two peaks of approximately equal intensity, separated by $\Delta E = 5$ eV,[7] which have been associated with a screened and unscreened final state, respectively.[11-15] The low-binding-energy (E_B) peak ("main line") corresponds to a final state screened by charge transfer from the metal to the adsorbate via the 2π orbit. The higher-E_B satellite has been sug-

gested[12,14,15] to originate from a shake-up transition from a bonding to an antibonding orbital both of which are formed by hybridization of molecular 2π and metal $3d$ and $4sp$ states.[13] It is the unusually large intensity of the shake-up satellite which renders the N_2/Ni(110) system ideally suited for a detailed energy-dependent study.

The experiments were performed under experimental conditions which have been described in detail before.[10] The N 1s photoemission spectra at saturation coverage and 90 K were recorded in the constant-final-state (CFS) mode in order to minimize problems due to the steep secondary-electron background near threshold. By scanning the photon energy the N 1s core line is swept through the electron energy analyzer (cylindrical mirror analyzer, CMA) window, which is set at a kinetic energy E^* above the vacuum level. A photoemission spectrum results where increasing photon energy corresponds to increasing E_B. Spectra recorded at final-state energies $E^* = 150$, 7.5, and 2.5 eV are shown in Fig. 1. The two observed N 1s peaks are denoted as screened (S, main line) and unscreened (U, satellite). In order to obtain the relative intensities of peaks U and S at a given *excitation* (photon) energy two CFS spectra need to be compared which are recorded at final-state energies E^* that differ by the energy separation ΔE between the two peaks. This is illustrated in Fig. 1 where the intensities of corresponding peaks S and U for $h\nu \approx 414$ eV are shown as dashed lines. After background subtraction the CFS spectra were curve fitted by a Doniach-Šunjić[3] line-shape function which was convoluted with a Gaussian curve to account for the analyzer and monochromator resolution functions.

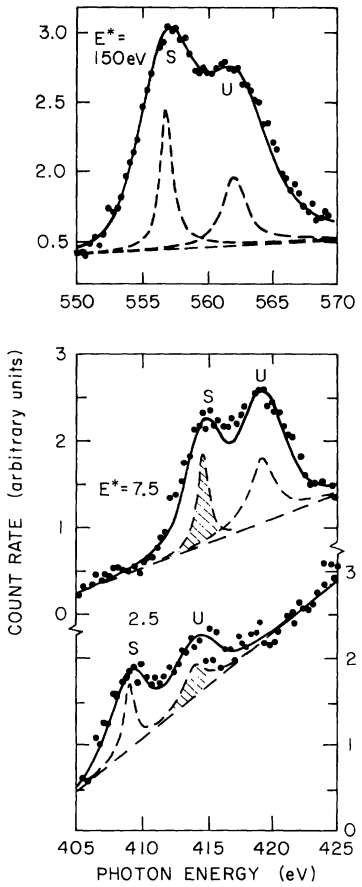

FIG. 1. N 1s photoemission spectra for N_2 on Ni(110) at 90 K recorded in the constant-final-state mode. The analyzer window (1.6 eV resolution) was set at different energies E^* above the vacuum level. Increasing photon energy corresponds to increasing binding energy. Peak S is the main line, peak U a shake-up satellite. The Doniach-Šunjić line-shape functions used for the fit are shown as dashed lines.

The obtained satellite-to-total intensity ratio $U/(U+S)$ is plotted as solid circles in Fig. 2 as a function of excitation energy E_{ex} above the N 1s threshold (400.5 eV). Surprisingly, the intensity ratio changes little (<20%) between the highest (150 eV) and lowest (~15 eV) E_{ex} values. Since the separation between peaks S and U is ~5 eV the satellite U will be absent for $E_{ex} < 5$ eV. This is confirmed by NEXAFS spectra[10] of the N K edge for N_2 on both Ni(100) and Ni(110). The NEXAFS spectra for N_2 on Ni(110) are identical to those for N_2 on Ni(100) which have been published previously.[10] In both cases the strong absorption resonance at threshold (400.5 eV) has no visible satellite at 5 eV higher excitation energy. Hence the satellite U is found to turn on abruptly in the interval $5 \text{ eV} \lesssim E_{ex} \lesssim 15$ eV. This experimental finding is well explained by the following simple exchange model for the energy dependence of the shake-up intensity. While a more detailed and complete calculation could be made,[16] one would expect the correct energy dependence to be roughly similar.

The shake-up intensity μ^s as given by Fermi's "golden rule" within the Hartree-Fock approximation is

$$\mu^s \sim |\langle \Psi_i | D | \Psi_f' \rangle|^2, \quad (1)$$

where $D = \sum_i d_i$ is the dipole operator. The Slater determinant wave function Ψ_i is constructed from one-particle eigenfunctions of the effective one-electron Hamiltonian H for the ground state;

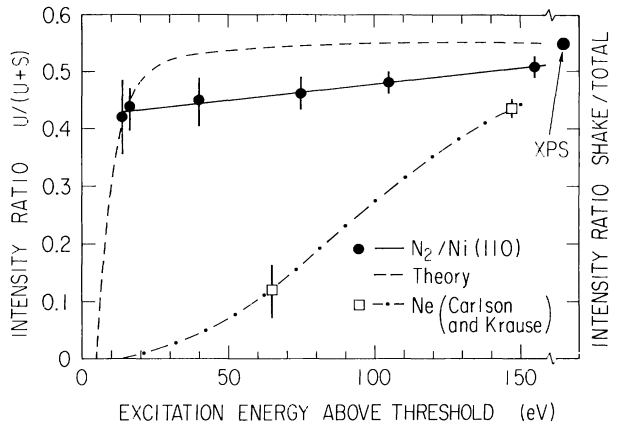

FIG. 2. Intensity ratio of the measured satellite to the total photoemission intensity for N_2 on Ni(110) (filled circles) as a function of excitation energy above the N 1s threshold (400.5 eV). Dashed line is the calculated intensity ratio from Eq. (4). The open-square data points are taken from Ref. 1 with the vertical scale adjusted to the N_2/Ni(110) scale in the sudden limit.

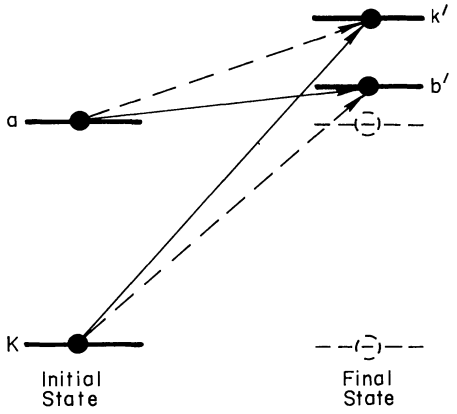

FIG. 3. Processes contributing to the shake-up intensity: direct (solid line) and exchange (dashed line).

Ψ_f', from eigenfunctions of the final-state Hamiltonian H' for the configuration with holes in a deep core level $|K\rangle$ and a valence level $|a\rangle$, and particles in a photoelectron state $|k'\rangle$ and a shake-up level $|b'\rangle$. The nonorthogonality of the initial and final one-particle states leads to a large number of terms in the expansion of Eq. (1). The most important contributions for deep core-level absorption are illustrated in Fig. 3 and are, respectively, a direct term and an exchange term. Since these virtual processes are indistinguishable their amplitudes must be added. If we keep only these dominant terms the cross section for the shake-up from $|a\rangle$ to $|b'\rangle$ can be written as

$$\mu^s = \mu_\infty^s \left| 1 - \frac{\langle K|d|b'\rangle\langle a|k'\rangle}{\langle K|d|k'\rangle\langle a|b'\rangle} \right|^2 , \qquad (2)$$

where the remaining overlap integrals have been lumped into μ_∞^s. At high energies the exchange term becomes negligible, and one recovers the sudden-approximation result. Note that the exchange term vanishes unless the photoelectron state and the shake-up states have the same parity with respect to the origin of the core orbital. Thus the energy dependence of shake-up states of opposite parity will differ strongly, whereas a conventional time-dependent treatment[1] would predict no difference.

For deep core-level absorption, the energy dependence of the matrix element $\langle K|d|k'\rangle$ is weak compared to the other terms and we neglect it. The remaining matrix element may be estimated with use of the identity

$$\langle a|k'\rangle = \langle a|H'-H|k'\rangle/(\epsilon_{k'}-\epsilon_a) . \qquad (3)$$

For a crude estimate we neglect the angular momentum dependence and replace the state $|a\rangle$ with a hydrogenic orbital, the state k' with a plane wave, and the hole potential $V=H'-H$ with that of a point charge. This gives $\langle a|k'\rangle \sim (\epsilon_{k'}-\epsilon_a)^{-2} \sim (E_{ex})^{-2}$. Similarly we put $\langle a|b'\rangle \sim (E_{b'}-E_a)^{-2} \sim (\Delta E)^{-2}$ since Eq. (2) must vanish at the shake-up energy ($E_{ex}=\Delta E$). This is simply a result of the exclusion principle preventing double occupancy of the shake-up level $|b'\rangle$. Thus the energy dependence of the shake-up cross section is predicted to behave as

$$\mu^s = \mu_\infty^s \left| 1 - (\Delta E/E_{ex})^2 \right|^2 . \qquad (4)$$

Our results imply that the sudden limit ($E_{ex} \gg \Delta E$) is reached faster if the main multielectron excitations are of low energy. Terms neglected in our treatment corresponding to rearrangement processes in lower-lying orbitals would result in a more gradual turn-on of the shake-up intensity. Also, the replacement of the core-hole potential by a point charge neglects the perturbation introduced by the shake-up particle-hole pair which for shake-off processes becomes weakly energy dependent.

For N_2 on Ni(110) the shake-up levels $|a\rangle$ and $|b'\rangle$ discussed above are bonding and antibonding π states of mostly p character and thus have the same parity as that of the photoelectron originating from an s core orbital. Comparison of the energy dependence of the shake-up intensity ac-

cording to Eq. (4) indeed shows good agreement with that measured for the shake-up peak U for N_2 on Ni(110). Especially the fast turn-on is satisfactorily accounted for as shown in Fig. 3. In making the comparison we have used the fact that the total transition probability to the main line and shake-up state is constant. The observed behavior for N_2 on Ni(110) is in marked contrast to that reported for the shake-off intensity in Ne (Ref. 1) which has long been considered characteristic for the transition from adiabatic to sudden excitation. The gradual increase of the shake-off intensity for Ne shown in Fig. 3 is, however, not in conflict with the present results but can be understood from the fact that the centroid of the shake-off energy is quite large (ΔE ~100 eV).[4] Thus the sudden limit is not reached until the excitation energy exceeds this value.

The present study establishes concepts which govern the transition from adiabatic to sudden core-level excitation. Besides contributing to the understanding of fundamental questions in photoemission theory it has direct implications for the interpretation of the near-edge structure in x-ray absorption which is of high current interest. In good accord with a recent study by Stern[17] our results indicate that shake-up features should in fact have nonnegligible intensity close to threshold.

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