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Rydberg and multiple-electron excitations in x-ray photoabsorption spectra of N_2 adsorbed on Fe(111)

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Near-edge x-ray-absorption fine-structure spectra from *K*-shell excitation of N_2 molecules adsorbed on an Fe(111) surface (γ state) exhibit structures which, by comparison with corresponding gas-phase data, are identified as Rydberg and π^* multiple-electron excitations. These may obviously survive in the adsorbed state because of very weak valence-orbital interactions and large internuclear separations (approximately 2.5 Å) between the adsorbate and the substrate. Due to the oriented character of the molecules on the surface, the full angular dependence of these excitations is measured for the first time.

K-shell excitation spectra of free molecules such as N_2 are usually characterized by complex structures in the threshold region, arising from resonances due to transitions into highly localized antibonding orbitals (π^* and σ^* resonances) as well as by transitions into Rydberg or multiple-electron excited states.[1] The corresponding spectra for chemisorbed molecules are generally simpler, since coupling to the substrate suppresses most of the spectral features so that only the π^* and σ^* resonances survive.[2] Here we will present evidence that excitation into Rydberg and multiple-electron states may be identified. Based on the dipolar selection rules and the oriented character of the molecules their angular dependence is investigated.

Several adsorption states of nitrogen on Fe(111) were found,[3] among which the weakly held γ state was the subject of the present investigation. These molecules are bound to the surface with an adsorption energy of about 24 kJ/mol and desorb around 85 K.[4] Their molecular axis is believed to be oriented normal to the surface plane,[5-8] and the frequency of the N—N stretch vibration is only slightly displaced from its gas-phase value,[8] indicating only weak perturbation of the molecule by the adsorption bond formation.

Near-edge x-ray-absorption fine-structure (NEXAFS) spectra were performed at the BESSY storage ring using the SX-700 monochromator. The NEXAFS spectra were recorded in the partial electron yield mode ($U_{\text{ret}} = 215$ eV) using a detector mounted below the sample. Surface-extended x-ray-absorption fine-structure (SEXAFS) data were recorded at 20° and 90° photon incidence angles, with $U_{\text{ret}} = 300$ eV in order to provide a larger energy range above the edge. Normalization to the photon flux was performed by measuring the partial electron yield of the adsorbate free surface.

The sample was kept at a base pressure of 2×10^{-10} Torr; its surface was cleaned by cycles of sputtering, annealing, and oxygen treatment and checked by low-energy-electron diffraction and Auger spectroscopy. The residual impurity concentration was below 0.03 monolayer (ML). Exposure to N_2 at 60 K caused practically exclusive population of the γ state, as probed by the N 1*s* x-ray photoemission spectroscopy (XPS) data which may serve as a sensitive fingerprint.[5] Evaluation of the integral XPS intensity by normalization to the cross section and correction for the probing depths permits determination of the absolute coverage[4] which was found to be 0.2 monolayers for 2 L N_2 exposure, used for the data to be presented (1 L $\equiv$ 1 langmuir $= 10^{-6}$ Torr sec).

Figure 1 reproduces NEXAFS spectra recorded for (b) $\theta = 10°$, (c) 50°, and (d) 90°, where θ is the angle between the surface normal and the *E* vector of the incident radiation, together with (a) the corresponding absorption spectrum of gaseous N_2 as reported by Wright *et al.*[9] Additional data recorded for $\theta = 20°$, 35°, and 70° are not shown here. The spectra are shown for the sake of comparison with the preedge region substracted and normalized at 460 eV to 100 arbitrary units.

Since N_2 in the γ state is weakly bonded, the NEXAFS spectra of the adsorbate system were analyzed by comparison with the gas-phase data leading to a fit consisting of four Gaussian peaks, a step function, and a scattering resonance profile as will be outlined in detail below. The effective symmetry[10] remains essentially that of the free molecule. The adsorbate-substrate interaction leads mainly to an orientation of the molecules. Therefore we use the $C_{\infty v}$ symmetry group assignments. The most prominent features are peaks at 401 and 419 eV whose nature and properties will serve for characterization of the adsorbed species. For gaseous N_2 the peak at 401 eV has been identified with an excitation from the N 1s to the 2p π_g level,[11] the lowest unfilled (and antibonding) molecular orbital.[9] For the adsorbate system it has to be attributed again according to a π^* resonance.[2(a)] Its intensity increases continuously with θ.

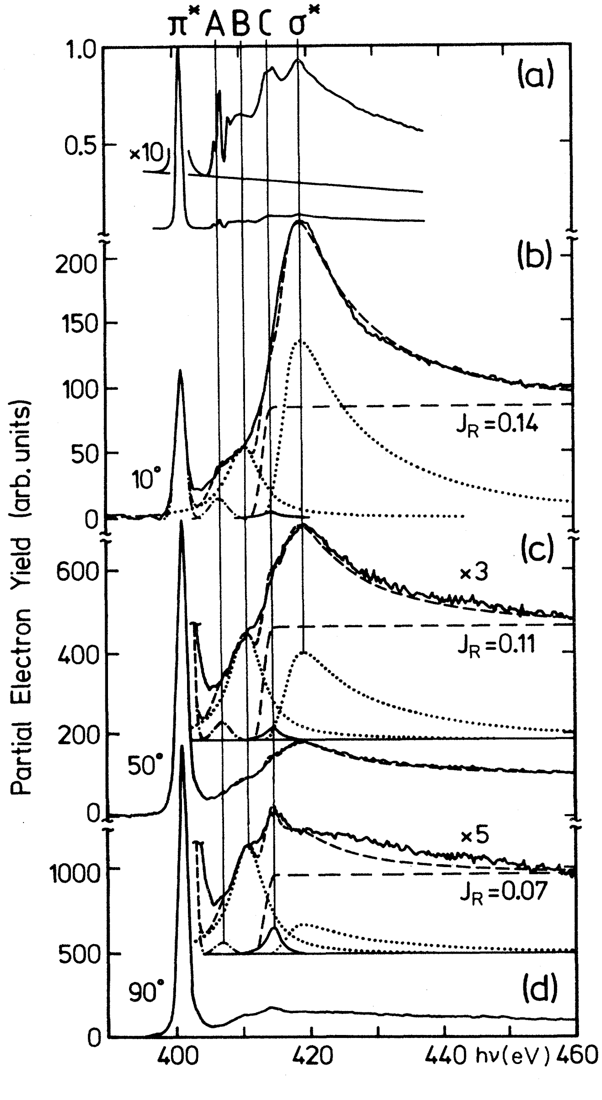

FIG. 1. (a) Absorption spectrum of gas-phase N_2 recorded by electron-energy-loss spectroscopy (Ref. 10). In (b)–(d) are shown the NEXAFS spectra of 0.2 ML γ-N_2/Fe(111) at 10°, 50°, and 90° x-ray incidence, respectively. The height of the atomic-like absorption step function, once a fit has been performed, allows the precise determination of the edge-jump ratio J_R. The knowledge of $J_R(\theta)$ permits the comparison of all the spectra on a common intensity scale.

The second prominent feature shows up at 419 eV and the angular dependence of its intensity exhibits the opposite trend. It is due to excitation of the 2$s\sigma_u$ molecular orbital and is hence denoted as σ^* shape resonance. Its energetic position has been found to be sensitively correlated with the internuclear separation in the N_2 molecule.[12,13] Since in the present case its energy coincides with the value of the free molecule, it supports that the N-N distance is not noticeably distorted in the adsorbed state. The σ^* resonance of N_2 may be considered as an increase in cross section due to the scattering of the outgoing photoelectron from the molecular potential.[14] Its asymmetric line shape can be reproduced by calculating the scattering cross section of a spherical-well potential using standard textbook partial-wave analysis.[15] The data for the σ^* resonance in Fig. 1 were fitted by using the scattering of an electron at such an effective potential exhibiting a radius of 1.1 Å (the bond length of free N_2), a depth of 19.3 eV, and a threshold energy $E_0=412.7$ eV as adjustable parameters. The same depth for "a mean intramolecular potential" in N_2 gas was also proposed earlier.[12] The angle α between the molecular axis of the adsorbed N_2 molecules and the surface normal can be derived from the angular dependence of the intensities of the σ^* and π^* resonances.[16]

Figure 2(a) shows the variation of I_{σ^*} and I_{π^*} versus $\sin^2\theta$. The data points were fitted by straight lines from least squares, from which in turn α may be derived. Analysis yields $\alpha=0\pm10°$ from I_{π^*}, while the value derived from I_{σ^*} can only point to an angle between 0° and 40° (arising mainly from the uncertainties in fitting the edge jump). It is therefore concluded that the N_2 molecules are essentially oriented with their axis normal to the surface, in agreement with previous angle-resolved ultraviolet photoemission spectroscopy data,[6] as well as with the conclusions from XPS[5] and vibrational spectroscopy.[8]

Now we turn to the remaining spectral features of Fig. 1. The gas-phase spectrum exhibits three additional peaks at 406.5 eV (A), 410.2 eV (B), and 414 eV (C). Peaks A and B were attributed to various transitions into Rydberg states while peak C comprises all excitations above the second ionization potential including shakeup processes.[9] The same features are seen in the NEXAFS of the adsorbed N_2. By visual inspection and virtue of the angular dependence, peaks B and C are seen in the raw data at 90°, 70°, and 50°. The excess intensity at 406.5 eV for the 10°, 20°, and 35° spectra indicates the existence of peak A. A quantitative analysis needs a deconvoluting procedure: Peak A is fitted with a Gaussian of 3 eV full width at half maximum centered at 406.5 eV. Its intensity is about 15% of the edge jump and, as can be seen from Fig. 2(b), independent of the angle of incidence of the radiation θ. The intensity below 412.7 eV is attributed to Rydberg series converging to the edge and is fitted by peak *B* centered at 410.2 eV. Its intensity is markedly dependent on θ as evident from Fig. 2(c). Finally the weak resonance above threshold is assigned to peak *C*, being mainly due to a multiple-electron excitation. From previous gas-phase measurements[9] a shakeup process related to the $1s^{-1}$ to π^* transition has been proposed. For such a process the molecule is left in a singly ionized excited state. However the contribution of a double excitation (neutral final state) could not be excluded. The angular dependence of peak *C* is plotted in Fig. 2(d) and shows the same trend as that from the π^* resonance, although the error bars are large in this case. For future theoretical calculations it is of importance that the relative intensity of peak *C* with respect to the main peak π^* turns out to be constant over the full range of angular variation. This experimental finding gives clear indications for a proper assignment of peak *C*.

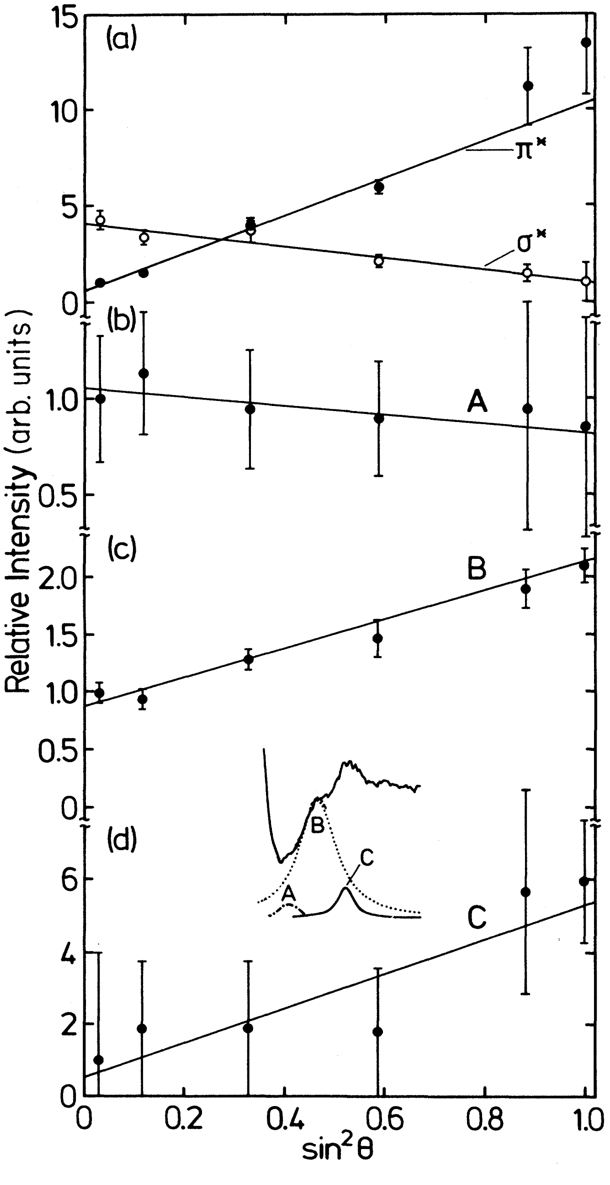

FIG. 2. Intensities relative to scale for the different resonances in the photoabsorption spectra of γ-N_2/Fe(111) vs $\sin 2\theta$. The intensities for all peaks have been normalized to J_R and its value at $\theta = 10°$ except for the σ^* resonance normalized to its value at $\theta = 90°$. Under these conditions the intensity scales for the different peaks can be directly compared. The linear functions shown are obtained using a least-squares-fitting procedure.

One might argue that the present analysis is somewhat arbitrary in character. However, there is definitely spectral structure in the energy range between the σ^* and π^* resonances—quite in contrast to reports on other systems in which the N_2 molecules are more strongly bound to the surface.[2(a)] The most obvious interpretation for this structure has to start with corresponding data for free molecules. The fact that the proposed analysis works equally well for all spectra recorded at different angles of the incident radiation is considered as the main key for the applied procedure. Higher-resolution measurements using electron excitation could resolve the Rydberg orbitals responsible for peaks *A* and *B* in the gas phase.[17] Peaks assigned to transitions to $3s\sigma$, $3p\pi$, and $3d\pi$ final states could be resolved around 406.3, 407.2, and 408.4 eV, respectively. A Rydberg series consisting of *p* states was found between 408 and 410 eV. Our peak *B* covers most of the previously cited lines with π character. In Fig. 2(c) we see that the angular dependence of peak *B* very nicely follows that of the π^* resonance of Fig. 2(a). Line *A* [Fig. 2(b)] is a superposition of the $3s\sigma$ and partly of the $3p\pi$ Rydberg states; consequently we do not detect any angular dependence out of the error bar. The existence of Rydberg-derived states for chemisorbed molecules has been considered earlier for methoxy[10,18] and carbon monoxide.[19] However an angle-dependent analysis is missing, a comparison to theory is more complicated, and the multiple-electron processes have not been considered.

Figure 3 reproduces SEXAFS data for the present system in comparison with those obtained with $c(2\times2)$-N/Cu(100).[21] No fine structure can be detected at all for N_2/Fe(111), or more precisely, its amplitudes (if any) have to be at least smaller by a factor of 3 than those of the quoted reference system. This lack of SEXAFS fine structure is most probably due to large internuclear distances *R* between N and neighboring Fe atoms which enter the SEXAFS formula through the factor $R^{-2}\exp(-2R/\lambda)$.[20] Other possible sources (lifetime effects, lateral disorder) can easily be ruled out. Model calculations show that increasing *R* from 1.8 Å (the value for the N/Cu reference system) to 2.5 Å would suppress the SEXAFS amplitude below the noise level, so that the experimental observation indicates indeed that $R \geq 2.5$ Å.

The value of 1.83 Å, as derived for the bond length between N and Fe in the *strongly chemisorbed* N/Fe(100) system,[22] can certainly be regarded as a lower limit for this quantity, while the upper limit is estimated to be 2.75 Å given by the sum of the van der Waals radius of N and the crystal radius of Fe. Apart from the just-mentioned estimate based on the SEXAFS data, there exist several

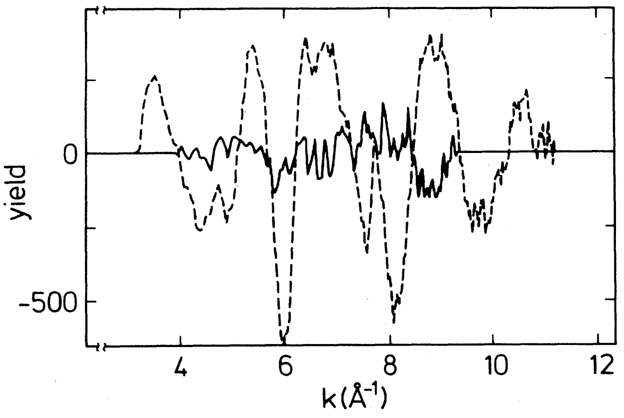

FIG. 3. The solid line shows the normal-incidence SEXAFS of γ-N_2/Fe(111). It is compared with normal-incidence SEXAFS of a $c(2\times2)$ overlayer of atomic N on Cu(100) (Ref. 21) (dashed line). The N/Cu distance is about 1.8 Å. Both yield spectra that are normalized per absorber atom. We show $\chi(k)k$ as a function of k as the most appropriate means of comparison.

other pieces of evidence pointing towards large bond lengths. (i) The bonding to the surface is very weak. (ii) The fact that the internuclear distance as well as the frequency of the N—N stretch vibration are practically not affected by the adsorption indicates that there is no substantial interaction between the valence orbitals, albeit strong enough to cause preferential orientation of the molecular axis. (iii) The XPS N 1*s* data are characterized by a double-peak structure which could be reproduced in calculations assuming a metal-N separation of 2.1 Å, while the spectrum for the more strongly held α-N_2 species (also exhibiting shorter bond length) is quite different.[5]

It is thus concluded that the relatively large distance between the N atoms and their nearest neighbors of the substrate ascertain that Rydberg excitations may "survive" in the adsorbed state. It is worth mentioning that we measure the Rydberg excitation of a N_2 molecule with a 1*s* core hole. For this case the effective principal quantum number can be calculated to be $n^*\approx2.2$ using the $3p\pi$ state, for example. In turn it follows that the $3p\pi$ Rydberg radius is not ≈5 Å but only approximately 2.5 Å, a value that falls in the same range as the separation from the surface atoms. The preferential orientation of the molecular axis enabled, on the other hand, even determination of the angular dependence of the intensities of these excitations. For free N_2 molecules, information on orientation parameters could so far only be obtained for the intense π^* and σ^* resonances.[23]

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