Autoionization as a Tool for Interpretation of X-Ray Absorption Spectra: N_2/Ni(100)

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A new and general method to separate x-ray absorption (XA) features is presented. The XA spectrum is monitored by detailed recordings of autoionization data. The technique is applied to the N_2/Ni(100)$c(2\times2)$ system, for which the N 1s 2π resonance is separated into the two components originating from the inequivalent nitrogen atoms. The XA peaks exhibit large differences in line shape, which is successfully explained in terms of the hybridization strengths of the XA final states. The total intensities of the XA peaks provide important information regarding the ground state of the adsorbed molecule.

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X-ray absorption spectroscopy (XAS) [also denoted near edge x-ray absorption fine structure (NEXAFS)] provides a local probe of the unoccupied density of states since it selects one atomic species at a time [1]. The method has mainly been used to study the electronic structure around atoms of different elements. However, in systems with inequivalent atoms of the same element, the x-ray absorption (XA) spectrum becomes complicated due to overlapping spectral features. The energy separations between these are usually small and, furthermore, the shape and intensity of the spectral components may vary quite a lot, which precludes a straightforward separation.

In the present paper we show for the first time how an XA spectrum can be decomposed into its individual components by monitoring it through the autoionization decay. The decay process of a core excited atom mainly involves the valence electrons localized at the same atomic site [2,3]. Hence the decay spectra could exhibit significant variations depending on which atom was core ionized. The separation procedure is demonstrated for the N $1s\to2\pi^*$ spectrum for N_2/Ni(100)$c(2\times2)$. In this system the N_2 molecules are chemisorbed with their axes perpendicular to the surface plane [4,5] leading to two inequivalent nitrogen atoms. With x-ray photoelectron spectroscopy (XPS), two well-separated N 1s peaks are observed with a chemical shift of 1.3 eV [6]. This difference can be attributed solely to the atomic localization of the final state core hole in the adsorbate. The adsorption of N_2 on Ni involves hybridization of the unoccupied molecular $2\pi^*$ orbital (corresponding to the $1\pi_g$ orbital of the free molecule) with the Ni 3d band. These hybrid states are split into an occupied part below and an unoccupied part above the Fermi level [7,8]. The XA π resonance is thus formed by excitations from the N 1s level to the unoccupied parts of the $2\pi^*$ derived orbital.

The decomposition of the XA spectrum shows two π resonances with different widths and line shapes, which is explained in terms of different hybridization strength between the adsorbate and substrate in the two final states. Furthermore, the integrated intensities of the two resonances provide quantitative information on the ground state $2\pi^*$ population, which is found to be asymmetric.

The experiments were performed at the MAX synchrotron radiation facility in Lund, using a modified SX-700 monochromator [9]. The XA spectra were recorded at normal incidence in partial electron yield mode with a photon energy resolution at the N K edge of 0.15 eV. The autoionization spectra were recorded by a 200 mm radius hemispherical electron energy analyzer of Scienta type at normal incidence and 40° emission angle. The electron energy resolution was 0.4 eV. The absolute photon energy was determined using first and second order radiation [10].

Figures 1(a) and 1(b) show the N 1s XP (from Ref. [6]) and XA spectra of N_2/Ni(100)$c(2\times2)$ on a common energy scale, referring to photon energy in the XA case and binding energy relative to the Fermi level in the XP case. The XP spectrum consists of two peaks, separated by 1.3 eV. The peak with the lowest binding energy, 399.4 eV, corresponds to ionization of the outer N atom, whereas the high binding energy peak at 400.7 eV is due to ionization of the inner N atom [5,6]. No such clear splitting is observed in the XA spectrum. The 2π resonance consists of a main peak at a photon energy of 401.0 eV, with a shoulder at 400.4 eV. Comparing the two spectra, the absorption threshold is seen to coincide with the low binding energy peak in the XP spectrum as generally observed for chemisorbed systems [7,10].

Several autoionization spectra were recorded at photon energies around the π resonance, six of which are shown in Fig. 2. These show only the resonant parts, i.e., a spectrum recorded 10 eV below the N $1s\to2\pi^*$ threshold has in all cases been subtracted in order to remove the very weak spectral features in this region due to direct photoemission. Two main observations are made: The spectral features have constant kinetic energies and there is a big change in the spectrum as the photon energy is increased from 400.8 to 401.0 eV. This is best seen at a kinetic energy around 379 eV where the intensity increases dramatically. The observation of constant kinetic energies agrees with what has been previously found for

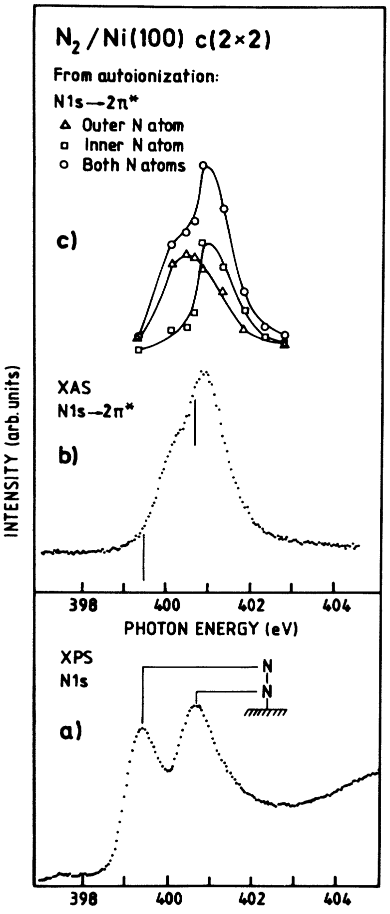

FIG. 1. (a) N 1*s* photoemission (XPS) spectrum and (b) x-ray absorption (XAS) spectrum of N_2/Ni(100)*c*(2×2), where the XPS binding energies are marked with lines. (c) Separation of the N 1*s* XAS 2π resonance for N_2/Ni(100)*c*(2×2) into absorption peaks from the inner and outer atoms, respectively, by using autoionization data. The estimated relative error in each point is ± 10%.

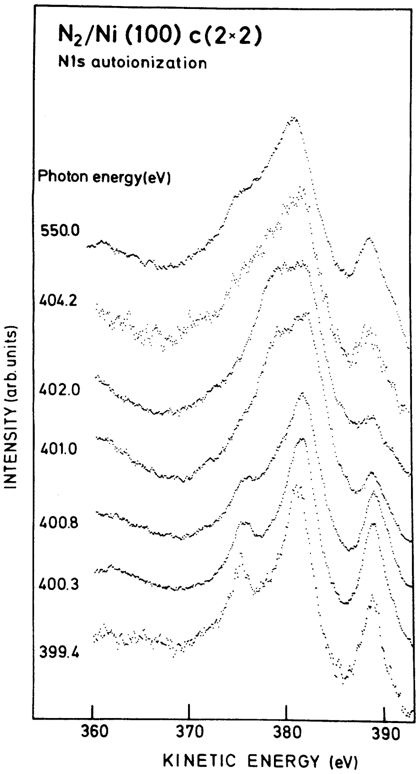

FIG. 2. N 1*s* autoionization spectra of N_2/Ni(100)*c*(2×2) recorded for photon energies around the 2π resonance and high above threshold.

CO chemisorption systems [11–13]. This is due to the delocalized nature of the excited electron for strongly chemisorbed systems, which leads to similar core excited states prior to the decay. This state can be regarded as locally almost identical to the XPS final state [11–13]. Previous investigations have also shown that the complete spectral shapes are the same for different excitation energies. At first sight this is in disagreement with the observations in Fig. 2. However, we note that the change occurs at a photon energy corresponding to the N 1*s* binding energy of the inner N atom. The binding energy corresponds to the absorption threshold, i.e., the lowest possible core excitation energy for that core hole site [7]. Based on these observations, it is evident that the change from the 400.8 to the 401.0 eV spectrum is due to excitation of the inner N atom.

Only the outer atom can be excited at a photon energy of 399.4 eV. The corresponding autoionization spectrum thus represents the autoionization spectrum of this atom. The photon energy of 404.2 eV is well above the π resonance and the corresponding autoionization spectrum can be assumed to consist of equal contributions from both N atoms. This is supported by the similar appearance of the spectrum recorded at 550 eV. At this energy, the intensity is definitely set by the atomic cross sections for core ionization, which is the same for the two N atoms. However, this spectrum may be slightly affected by multielectron excitations [13] which is why it is more appropriate to use the 404.2 eV spectrum for the decomposition. By a subtraction procedure, it is possible to obtain a model autoionization spectrum for the inner N atom from the 399.4 eV spectrum and the 404.2 eV spectrum. A similar procedure has previously been used in order to separate the NOO Auger spectrum for Au into two different Auger contributions [14]. It is then found that all the other N 1*s* autoionization spectra can be described as weighted sums of these model spectra.

After normalizing the spectra to the Ni 3*d* band, the total intensity of the autoionization parts can be plotted, as shown in Fig. 1(c). Since the total intensity of the autoionization spectrum follows the XA absorption cross section, a plot of these monitors the XA spectrum. The sum of the two contributions agrees well with the XA spectrum measured by partial electron yield shown in Fig. 1(b). We have thus used the autoionization technique as a tool to separate the two XA features and are now able to discuss the individual XA spectra for the two inequivalent N atoms in more detail. Since the shapes and intensities of these subspectra are not *a priori* known this could not have been done by a direct analysis of the absorption spectra.

It is observed in Fig. 1(c) that the XA peak at 400.6 eV representing the N 1*s* excitation of the outer atom has a larger width, 1.6 eV, than the XA peak of the inner N atom at 401.0 eV, which has a width of 0.9 eV. The splitting of the XA peaks originating from the inner and outer atoms is furthermore found to be 0.4 eV, compared to 1.3 eV in the case of XPS.

In a one-electron picture the XA spectrum reflects the unoccupied density of states where the position of the Fermi level is provided by the XPS core level binding energy. The total intensity of the XA spectrum is given by the number of unoccupied states in the initial state on the core ionized site. The XA spectral shape on the other hand reflects the density of states for the core hole state. This is referred to as the final state rule which has mostly been applied to metallic systems [15], but has recently been shown to also apply for chemisorption systems [7]. In the case of N_2/Ni(100)$c(2\times2)$, the two nitrogen atoms are inequivalent. This leads to different XA final states which explains the large difference in line shape for the two components. Concerning the splitting of the two components, the onset of the XA peaks is expected to coincide with the corresponding XPS peaks. The fact that the XA peak positions are separated less than the XPS peaks is a result of the differences in the final state density of states of the two atoms.

A useful analogy in order to describe the influence of a core hole is the $Z+1$ approximation [16,17]. This means that a core excited atom is replaced by the $Z+1$ atom. Within the $Z+1$ approximation, the N 1*s* excited final state for the outer and inner N atoms can be described as NO bonded through the N and O atoms, respectively. NO normally adsorbs with the N atom closest to the surface [4,18]. This orientation has thus the highest chemisorption energy, which is reflected by a lower XPS binding energy of the outer N atom for N_2/Ni(100) [5]. In contrast to this, the reverse orientation obtained with the core hole on the inner atom leads to a very small substrate-adsorbate interaction. This is also reflected by the higher XPS binding energy for the inner atom. The core excited final states can thus be described as two states with completely different hybridization strength between the substrate and the adsorbate. In the case of strong adsorbate-substrate hybridization, there is substantial broadening and splitting of the $2\pi^*$-$3d$ levels. The unoccupied $2\pi^*$-$3d$ states therefore extend far above the Fermi level. In the case of small substrate-adsorbate interaction, there is only little splitting of the $2\pi^*$-$3d$ levels, and the unoccupied $2\pi^*$-$3d$ states will be located very close to the Fermi level.

The relation between the XP and XA spectra is thus governed by the final state hybridization. The XPS binding energy determines the Fermi level for the unoccupied states in the presence of a core hole, as probed by XAS. A weak hybridization will give a high XPS binding energy, with the 2π resonance situated close above this. Relative to this situation, a stronger final state hybridization lowers the XPS binding energy, and increases the separation between this and the 2π resonance. The different final state hybridizations are thus seen to consistently explain the smaller splitting of the spectral features corresponding to the inner and outer atoms in XAS and XPS.

This model also provides an interpretation of the different widths of the two XA peaks. The widths are largely determined by adsorbate-substrate hybridization and vibrational excitations [10]. The width of the contribution to the 2π resonance originating from the core excited Ni-NN* XA final state is 1.6 eV, while the contribution from the Ni-N*N final state has a width of 0.9 eV. Since the vibrational contributions are similar, the extra broadening of the contribution from excitation of the outer atom is a consequence of the stronger hybridization with the substrate for this final state. An appropriate comparison regarding the hybridization strength of the Ni-NN* XA final state is with the Ni-C*O XA final state for Co/Ni(100). Both states are Ni-NO-like, and the width of the C 1*s* XA peak is found to be 1.7 eV [7,10] which is close to the value obtained for the XA peak representing the outer nitrogen atom.

Furthermore, the shape of the Ni-N*N 2π resonance is similar to the 0.7 eV wide vibrational envelope of the corresponding excitation in the free molecule. This is illustrated in Fig. 3, where a comparison is made with N_2 physisorbed on graphite. The π resonance for this physisorbed system is nearly identical to the free molecule. The width of the Ni-N*N 2π resonance is thus dominated by the same intramolecular vibrations, and the hybridization with the substrate gives only a minor contribution which broadens the vibrational fine structure. It may also be added that no splitting of the XA resonance occurs when N_2 is physisorbed with the axis normal to the surface due to the weak interaction with the substrate [19].

Another important property of an XA spectrum is that the transition intensity provides information about the ground state, i.e., the integrated intensity of the XA peak is proportional to the number of unoccupied states in the initial state. Integration of the two components in the N 1*s* XA spectrum shows that the area under the feature representing core excitation of the outer N atom is about 1.4 times larger (± 0.2). Because of the strong localization of the XA process to a certain atomic site, this indicates that the $2\pi^*$ orbital is asymmetric around the molecule in the initial state, i.e., there are more empty states around the outer N atom. The asymmetric population of the $2\pi^*$ orbital has also been predicted theoretically [20,21].

In order to make a quantitative comparison between the number of empty states in the gas phase molecule and

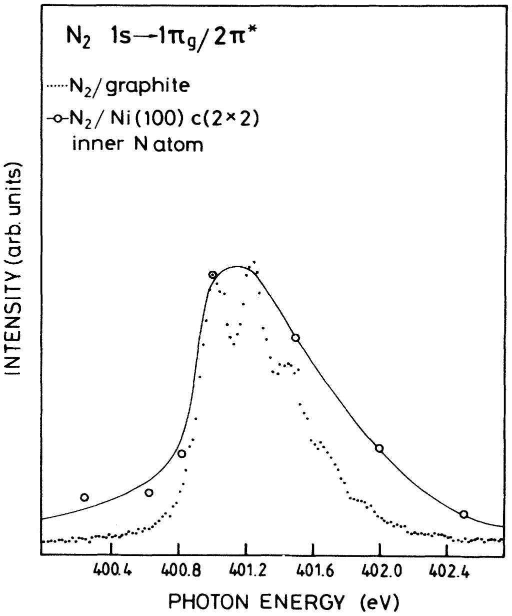

FIG. 3. XA 2π resonance for the inner N atom of N_2/Ni(100)$c(2\times2)$ compared to the π resonance for N_2/graphite.

for the adsorbate, the areas of the XA π resonances were calculated after a normalization to the step height at a high photon energy [22]. The π resonance for the adsorbate was found to have a total area that was smaller than for the free molecule. Numerically this yields that the total number of empty states for the adsorbate is 3.5 compared to 4.0 in the case of N_2 in the gas phase. Since the empty $2\pi^*$ states are asymmetrically distributed on the adsorbed molecule with a factor of 1.4, this gives 1.5 and 2.0 empty $2\pi^*$ states on the inner and outer N atoms, respectively. The most straightforward conclusion is then that upon adsorption the $2\pi^*$ population on the inner N atom increases with 0.5, whereas the $2\pi^*$ population around the outer N atom remains zero, as for the free molecule. We have thus shown how the decomposition and integration of the XA π resonance provides important quantitative information of the ground state of the adsorbed N_2 molecule.

To summarize, we present for the first time a decomposition of an XA spectrum with the use of autoionization. This method can be used for a wide variety of systems and will become increasingly feasible with the development of new synchrotron radiation facilities which will allow rapid recordings of highly resolved decay spectra. The method was applied to the N_2/Ni(100)$c(2\times2)$ system, where the 2π resonance was separated into contributions originating from the two inequivalent nitrogen atoms. The energy splitting of the two XA resonances was found to differ from the corresponding separation of the XPS peaks. Furthermore, the width for the 2π resonance representing excitation of the outer atom was shown to be much larger than for the 2π resonance of the inner atom. Both these effects were successfully explained in terms of the different adsorbate-substrate hybridization of the two inequivalent final states. Finally, it was observed that the integrated area of the component representing core excitation on the outer N atom was 1.4 times larger than the component representing core excitation of the inner N atom. This was interpreted as an asymmetry of the $2\pi^*$ orbital in the ground state. After a comparison with the XA spectrum for free N_2, it was found that the number of empty $2\pi^*$ states around the outer and inner N atoms was 2.0 and 1.5, respectively. This shows how important quantitative information regarding the ground state of an adsorbed molecule can be obtained in this way.

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[22] This comparison becomes possible since at high photon energies the step height is set by the atomic cross section, which can be assumed to be the same regardless of the state of the N_2 molecule. Furthermore, since the molecules are randomly distributed in the gas phase, an XA spectrum recorded at 45° incidence had to be used for the adsorbate. The π resonance of this spectrum was identical to the spectrum recorded at normal incidence.