X-Ray Emission Spectroscopy of NO Molecules Adsorbed and Coadsorbed with Oxygen on Ru(001)

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INTRODUCTION

X-ray emission spectroscopy (XES) has recently proven to be a very promising tool for the investigation of trends in the chemical bond of adsorbates to surfaces [1]. For low Z-elements the final states reached after fluorescence decay of the core hole state are energetically equivalent to valence electronic states reached in photoemission. Due to the localisation of the core hole excited in the primary step of the emission process this technique is highly atom specific. The transition matrix element involved is the dipole matrix element so that angle dependent measurements on oriented adsorbates allow the use of symmetry selection rules to assign the spectral features. On the basis of comparisons with model calculations it has been suggested that the observed intensities can be interpreted in terms of the symmetry restricted local valence electronic density of the adsorbates in the ground state i.e relaxation effects in the initial core hole state appear to play a minor role.

The goal of our joint study was to test the applicability of the technique and the appropriate interpretation for more complicated coadsorption systems of NO and oxygen on a Ru(001) surface. The adsorption of NO on the bare Ru(001) surface is particularly interesting because two very distinctly different NO adsorption states (v_1- NO and v_2-NO) are populated simultanously in this case. The two states can be distinguished for example using vibrational spectroscopy or high resolution x-ray photoelectron spectroscopy (XPS). Coadsorption of NO with oxygen on the Ru(001) surface leads, depending on the preparation, to a situation where either v_1-NO or v_2-NO is present on the surface. Both NO adsorption states have been characterised very thoroughly in our lab using different techniques like vibrational spectroscopy, work function measurements, XPS and geometric structure determination with LEED [2]. On the basis of these results it has been suggested that the two states are very different in terms of electronic structure (v_1-NO being electronegative and v_2-NO being electropositive). Due to energetic differences in the positions of the respective x-ray absorption resonances the two species can even be excited separately in the case where both are present simultaneously on the surface. Hence XES with resonant excitation should be ideally suited to gain more insight on the atom specific electronic structure of these two adsorption states.

EXPERIMENTAL

The experiments have been performed at the Swedish endstation at beamline 8.0. The x-ray spectrometer, which can be rotated around an axis parallel to the incoming beam, is based on three interchangeable grazing incidence gratings in combination with a moveable multichannel detector [3]. The resolution of the spectrometer for our experiments was about 0.5 eV. The preparation of the different layers was controlled by high-resolution XPS using a SCIENTA electron analyzer which can also be rotated around the incoming beam.

RESULTS AND DISCUSSION

Figure 1 shows results for the v_1-NO species in the presence of oxygen. The top part of the figure shows the states with σ-symmetry while in the bottom part the π-states are depicted. For both symmetries the results for N-K-emission (full symbols) and O-K-emission (open symbols) are

plotted on a common binding energy scale. Before we start with the discussion it should be noted that the intensity of the features seen in the emission spectra is governed by the local 2p-character of the respective orbitals because of the dipole transitions to the 1s-core orbitals. The relative intensities of the features seen in the O and N K-emission spectra, respectively, are normalized in such a way that the areas of the two sets of spectra are equal.

First we will discuss the states with σ-symmetry. From the spectra it is quite clear that the 2p-contribution to the 4σ-orbital is localized on the nitrogen end of the molecule while the 2p-contribution of the 5σ-orbital seems to be more evenly distributed. The contribution of σ-type orbitals (marked by a horizontal line) in the region of the metal d-bands closer to the Fermi level is fairly small.

This is quite different in the case of the π-type states. Here the states close to the Fermi level (again marked by a horizontal line), are much more pronounced. For the oxygen end of the molecule the 2p-derived contributions are higher than for the nitrogen end. It is also obvious that the maxima are significantly shifted in energy. Pronounced differences between the oxygen and nitrogen ends of the molecule are also observed for the 1π-orbital. Here the 2p-character is more pronounced on the nitrogen end of the molecule. Particularly interesting is the observed splitting of the 1π-orbital (see inset). We attribute this splitting to the fact that the v_1-NO-species are adsorbed in rows of threefold hollow sites on the surface parallel to adjacent oxygen rows in a (2x1)-configuration. In this configuration the symmetry of the NO-molecule is reduced and the 1π-orbitals along the rows and perpendicular to the rows are no longer degenerate.

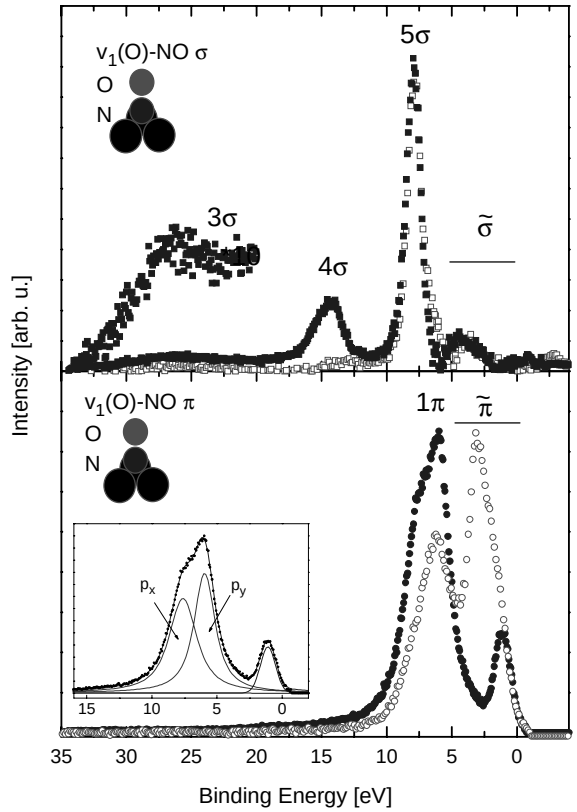

Figure 1: Symmetry resolved XE spectra for oxygen and nitrogen of v_1-NO +O /Ru(001)

In the following we will compare the results for the v_1-NO species with those obtained for the on-top v_2-NO species, again in the presence of coadsorbed oxygen. Figure 2 shows the resulting XE-spectra for the v_2-NO species in the presence of oxygen. The top part of the figure shows again the states with σ-symmetry while in the bottom part the π-states are depicted. As before we plot the results for N-K-emission (full symbols) and O-K-emission (open symbols) for both symmetries on a common binding energy scale.

Comparison of the states with σ-symmetry reveals that in the case of the v_2-species the 2p-character of the 4σ-orbital is more evenly distributed across the molecule. The states with σ-symmetry in the range of the metal d-band are even less visible than before.

While the differences between the two species are not so striking in the σ-type orbitals, they are much more pronounced in the π-system. Again there are strong π-symmetric states close to the Fermi level in the range of the metal d-band. As in the case of v_1-NO, the 2p-character of these states is more localized on the oxygen end of the molecule. In comparison to the v_1-species the intensity of these features is now significantly reduced. Even more striking is the complete

absence of a splitting of the 1π-derived states. This can be understood on the basis of the known geometry of the v_2-NO species. As mentioned above this species is adsorbed in an on-top position surrounded by oxygen atoms in a hexagonal configuration. Therefore the molecule is still in a high symmetry configuration and the 1π-orbital is degenerate.

Currently we are in the process of comparing our experimental results with density-functional cluster calculations for the two different NO-species [4]. It appears as if the ground-state calculations of the local 2p-character of the valence electronic distribution already explain most of the trends observed quite satisfactorially. Most of the features observed can be explained qualitatively in a three-center bond picture between NO and Ru. The differences in electronic structure between the two species correlate well with the expectations from the known changes in the structural parameters [2]. However, particularly in the d-band regime the differences are much less than expected from the previously assumed differences in electronegativity which may be due to influences of core hole screening.

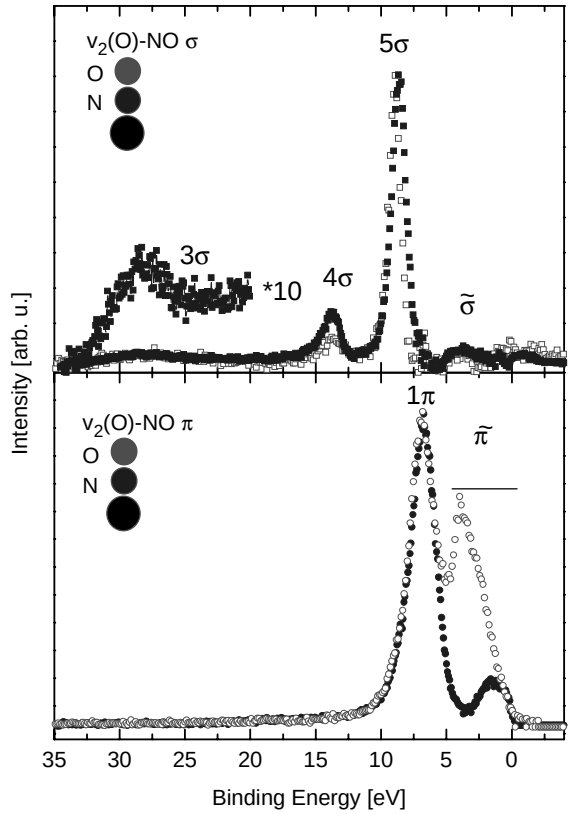

Figure 2: Symmetry resolved XE spectra for oxygen and nitrogen of v_2-NO +O /Ru(001)

In summary, even though the local charge distribution can only be derived in a symmetry restricted sense from the XES data, the information obtained is nevertheless unique and provides a very important experimental measure for the quality of theoretical descriptions of adsorbate chemical bonds.

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