Soft X-Ray Emission Studies of Adsorbates

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Soft x-ray emission spectroscopy is for the first time applied to surfaces and adsorbates. Surface sensitivity is achieved by employing synchrotron radiation in grazing incidence for the excitation. We present O K emission from adsorbed atomic oxygen on Ni(100) and Cu(100) and molecular CO on Ni(100). The observed spectral features correspond to the occupied $2p$ partial density of states of the adsorbates.

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Soft x-ray emission spectroscopy (SXES) is a well-established method for studying the electronic structure of matter [1]. Many of the advantages of this method are related to the selective properties inherent in the x-ray emission process. For example, the localized nature of the initial state of the x-ray transition makes it possible to select the emission from specific atomic sites in a system and the dipole selection rules furthermore allow separation between the various orbital symmetries in the valence region.

Because of the large escape depth of the photons SXES is normally considered a bulk sensitive technique. The method may, however, be made surface sensitive. One way of achieving this is to use low-energy electrons for the excitation [2]. Electron excitation, however, has the disadvantage that it is quite destructive to fragile systems. In the present work, which concerns adsorbate layers on metal surfaces, we therefore use a different approach, namely, excitation by synchrotron radiation at grazing incidence.

High resolution fluorescence spectroscopy in the sub-keV region is generally associated with quite low count rates. Important factors in this connection are the small solid angles involved when using high resolution grating instruments and, even more important, the very low fluorescence yields for soft x rays. Typically only 0.1% of the core hole states of low Z elements decay by x-ray emission while the large majority decays through nonradiative processes (Auger and Coster-Kronig). In the case of a monolayer on surfaces the reduced number of atoms puts even greater demands on the instrumentation. It is nevertheless quite feasible to employ the method for adsorbate studies, as is shown for the first time in this work, by using a high performance grazing incidence spectrometer properly matched to a powerful photon source.

A motivation for introducing SXES in surface science lies in the atomic selective properties of the method. An understanding of the chemisorption bond requires knowledge of the occupied electronic states. In particular, hybrid states directly related to the bonding between the adsorbate and substrate atoms are of importance. These states are, however, often dominated by the substrate-derived contributions. The electronic levels of an adsorbate can be studied using valence-band photoemission [3,4]. The adsorbate-related emission is then obtained simultaneously with the substrate emission and it is often difficult to isolate the adsorbate-derived states. By using SXES, on the other hand, it is easy to separate the adsorbate-derived partial density of states. As shown in the present work this allows the observation of very weak adsorbate states not seen by photoemission.

In this Letter we demonstrate the potential of SXES for studying the occupied density of states of adsorbates. The O K emission spectra of molecular CO adsorbed on Ni(100) and atomic O adsorbed on Ni(100) and Cu(100) are shown. Differences in hybridization between O $2p$ and metal states are clearly observed when the adsorption of oxygen on Cu and Ni is compared, reflecting the different d-band positions for the two metals. For adsorbed CO the importance of multielectron effects and the symmetry of the final hole state is discussed.

The SXES experiments were carried out at MAX-lab in Lund. White light from a bending magnet was used for excitation. A thin Al foil (≈ 130 μg/cm^2) was used to filter the exciting beam in order to reduce the background and the sample damage. The fluorescence was detected in a multigrating grazing incidence spectrometer [5,6]. A schematic drawing of the experimental setup is shown in Fig. 1.

The beam line is equipped with an ellipsoidal mirror accepting a horizontal angle of 20 mrad. The mirror demagnifies the source in order to give a focal spot (optically measured to be 0.18 mm) that matches the acceptance of the spectrometer. With this arrangement a high photon flux on the area seen by the spectrometer can be obtained. The estimated flux is around 10^{14} photons/sec and 1% bandwidth. The excitation was made at 2°-5° grazing angle and the fluorescence was detected in the polarization plane at 90° to the incident beam, i.e., near normal to the sample surface.

Details of the multigrating spectrometer have been given elsewhere [5,6]. In this experiment we used two

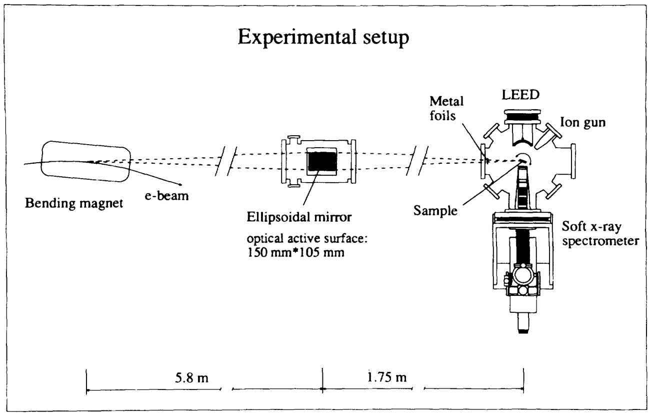

FIG. 1. Sketch of the experimental setup used for the adsorbate experiments.

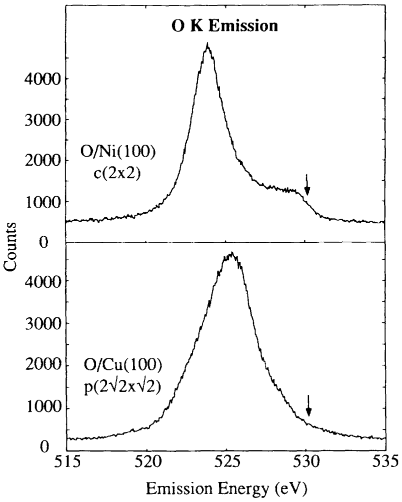

FIG. 2. O K fluorescence spectra from oxygen adsorbed on nickel and copper. The XPS binding energy positions are indicated by arrows.

spherical 5-m-radius gratings, one with 1200 lines/mm mounted at an 88.1° angle of incidence and the other with 400 lines/mm operating at an 87.4° angle of incidence. The former was used for the atomic adsorbates and, for these, spectra were taken in first order of diffraction with an instrumental resolution of 0.3 eV. The latter grating was used for CO and in this case spectra were recorded in second order of diffraction with the resolution set to 0.6 eV. The emission energy scales were checked by making separate recordings where reference lines, with known transition energies, were superimposed on the adsorbate spectra. With this procedure we estimate the uncertainties in the energy scales to be less than ± 0.5 eV. The adsorbate overlayers were prepared using standard procedures and were carefully monitored by LEED [7-9].

Figure 2 shows the O K emission spectra from adsorbed atomic oxygen on Ni(100) and Cu(100) in a $c(2\times2)$ and a $p(2\sqrt{2}\times\sqrt{2})R45°$ structure, respectively. The total recording times were about 120 min for the upper and 40 min for the lower spectrum.

The observed spectral features are related to the occupied $2p$ partial density of states of the adsorbed oxygen and are seen to be very different for the two substrates. The spectrum from oxygen on Ni(100) exhibits a broad peak (≈ 2.6 eV FWHM) at 524 eV with a prominent high-energy feature which ends with a sharp edge at 530 eV emission energy. As indicated in the figure, the edge coincides with the O $1s$ binding energy, 530.2 eV, as obtained by x-ray photoemission spectroscopy (XPS) [8]. The observed edge thus reflects the emission from states at the Fermi level [10]. The difference in energy between the edge and the main peak (6 eV) matches very well with a spectral feature observed at 6 eV binding energy in photoemission measurements [11].

The intensity ranging from the main feature to the sharp edge at 530 eV reveals that there is strong hybridization of the O $2p$ states with the Ni $3d$ band. This has not been observed previously in photoemission. Slab calculations using local density approximation [12] and the linearized augmented plane wave method [13] have been performed for O on Ni(100). These calculations predict bonding states with a large O $2p$ population 5.5 eV below the Fermi level which are mainly hybridized with Ni $4s$-p states and antibonding states with O $2p$-Ni $3d$ character centered at the Fermi level. The existence of the latter is supported by inverse photoemission measurements where unoccupied states near the Fermi level have been observed [14]. Our measurements now show that a fraction of these predicted antibonding states are occupied. Note, however, that the measurements do not provide a direct mapping of the density of occupied states since the intensities, especially close to the x-ray edge, may be somewhat affected by dynamical effects [15,16]. The presence of nondiagram transitions, which will be discussed below for adsorbed CO, could also in principle modify the spectrum to some extent although we expect the contribution in this case to be minor [17].

For O on Cu(100) all intensity falls in a broad peak (≈ 4.2 eV FWHM) centered at 525.4 eV indicating a wide distribution of O $2p$ states. The Fermi level is positioned at 530.1 eV, obtained from the O $1s$ binding energy [9]. Neither a high-energy plateau nor a distinct Fermi edge is seen. We relate this difference between the two cases to the fact that the Cu d band is found deeper below the Fermi level (≈ 2 eV) than the Ni d band. There will be a larger filling of the O $2p$ states and the antibonding resonance will (at least partly) be pulled down below the Fermi level. Photoemission measurements have indicated the presence of states above the Cu $3d$ band at around 1 eV and a broad distribution of states below the d band centered around 5.5 eV [18,19]. The onset in the x-ray emission 1 eV below the Fermi level could indicate the presence of antibonding states and the strong intensity in the peak maximum of the bonding states. However, the observation of only an asymmetric broad peak without any dip between these states clearly shows that a large degree of the occupied O $2p$ states appears at energies overlapping the Cu $3d$ band, indicating $2p$-$3d$ hybridization. This is consistent with the fact that photoemission spectra show that the Cu $3d$ states undergo some changes upon adsorption of oxygen [18,19]. Recently the oxygen-induced reconstruction of Cu has been discussed based on effective-medium theory [20]. An important parameter in these calculations is the adsorbate p level position. The parameter used gives rise to a local density of states which strongly deviates from the present result. This will be discussed in a forthcoming publication.

Figure 3 shows O K fluorescence spectra from carbon monoxide on Ni(100) in a $c(2\times2)$ structure. When recording spectra from this system considerable care has to be taken to avoid sample damage. The three spectra, labeled A, B, and C, in the top right corner of the figure, were recorded under different conditions. Spectrum A is a sum of spectra for which the adsorbate overlayer was renewed after about 30 min. Spectrum B is a sum of several recordings during which the sample was continuously moved, thereby exposing a fresh spot every 10 sec. After scanning over the whole sample the overlayer was renewed. A clear difference is seen between spectra A and B which indicates that the sample in the former case has been affected by the exciting beam. This was also confirmed by LEED. No pattern was seen after the individual recordings of A while in case B a diffuse, $c(2\times2)$ pattern appeared. Scanning the sample with higher speed, as was done for spectrum C, the LEED pattern became somewhat less diffuse although no changes in the spectral features as compared to B were seen. Spectrum C is shown enlarged in the main figure. A speed giving a fresh spot every 4 sec was used for this spectrum and the total recording time was about 50 min which required many overlayer preparations.

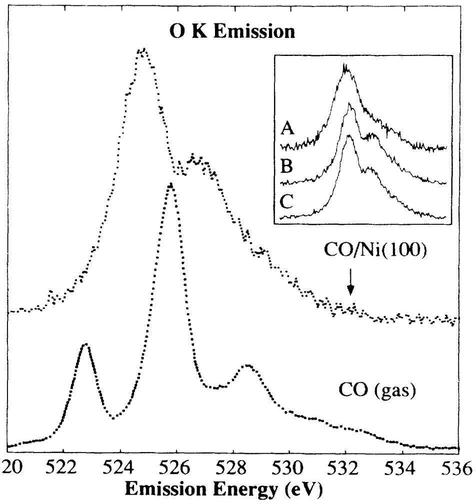

FIG. 3. O K fluorescence spectrum from CO adsorbed on Ni and the corresponding electron excited spectrum from gaseous CO. Inset: The effect of irradiation damage for the adsorbed system (see text).

For comparison, Fig. 3 also shows the corresponding electron excited gas-phase spectrum recorded with the same instrumental resolution (≈ 0.6 eV). For gaseous CO the three outermost molecular orbitals all have significant O $2p$ character and are all expected to contribute intensity to the O K emission spectrum consistent with the observation of three prominent peaks. The peaks, associated with the 5σ, 1π, and 4σ orbitals, appear at 528.4, 525.7, and 522.7 eV emission energy, respectively [21], the one due to transitions to 1π hole states being the more intense. The spectrum exhibits, in addition to the three main peaks, some extra intensity above 530 eV which has been attributed to emission from shakeup states created in the core ionization process (denoted nondiagram transitions) [21].

Going from free CO to CO adsorbed on Ni(100) the spectrum is completely changed. Only two, quite broad, overlapping peaks are seen and the spectrum has a marked high-energy tail stretching out to about 532 eV emission energy. The two peaks are separated by 1.8 eV and the one appearing at the lowest energy (524.8 eV) is the dominant one. We attribute this peak to transitions from the 1π orbital. As in the case of gaseous CO, this orbital is expected to give the main contribution to the spectrum since it involves the largest amount of O $2p$ character. Moreover, for these particular measurements on adsorbed CO, the spectral contributions from the σ orbitals are expected to be suppressed since the emission is detected in a direction near normal to the sample surface, i.e., almost along the molecular axis. Transitions to σ-type hole states should, in this geometry, give little or no intensity to the spectrum. The second peak in the spectrum, with maximum at 526.6 eV, and the high-energy tail must therefore be attributed to nondiagram transitions and $2p$-Ni $3d$ hybrid states.

Our interpretation of the spectral features for the adsorbate gains support from electron spectroscopic results. The binding energy for the O $1s$ level, as measured by XPS [7], is 532.2 eV and from ultraviolet photoemission spectroscopy spectra the 1π, 5σ, and 4σ binding energies have been determined to 7.5, 8.0, and 10.6 eV, respectively [22]. Thus, the energy difference between the O $1s$ and 1π hole states, 524.7 eV, matches very well the x-ray emission energy, 524.8 eV, obtained in the present work. In the free CO molecule the $2\pi^*$ orbital is empty, but upon adsorption it becomes slightly populated by the formation of d-π hybrid states. The occupied part of these hybrid states has mainly Ni $3d$ character and has been observed in photoemission close to the Fermi level [7,23]. These states should be very weak in the SXE spectrum and could be related to the weak onset at the Fermi level. However, there are features due to nondiagram transitions in the gas-phase spectrum at the same energy which could make a similar contribution in the adsorbate spectrum. We tentatively interpret the main intensity in the second peak and the high-energy tail due to transitions from shakeup states.

The assignment of the high-energy features to nondiagram lines may seem questionable in view of the relatively low satellite contribution to the gas-phase spectrum. However, XPS studies have shown that the intensity due to multielectron excitations has much larger spectral weight in spectra from CO on Ni(100) than in spectra from gaseous CO (e.g., [7,24]) due to the appearance of new shakeup features. It may be reasonable to expect the relative intensity of x-ray satellites to follow the same trend since the XPS process provides initial states for the x-ray emission process. The present results are consistent with recent resonant Auger studies of CO on Ni(100) which show a difference in the decay spectrum for O 1*s* states created at threshold and at high energies indicating the presence of nondiagram transitions [25,26]. It would be very interesting in the future to study the x-ray emission process of adsorbates with variable photon energy and compare the present results with x-ray spectra obtained at threshold. Furthermore, by changing the emission angle to the surface, different orbital symmetries could be probed.

In conclusion, we have recorded O *K* fluorescence spectra from the systems O/Ni(100), O/Cu(100), and CO/Ni(100), demonstrating for the first time the possibility of applying soft x-ray emission spectroscopy to adsorbate studies. The spectra show that the oxygen 2*p* states for adsorption on Cu and Ni are very different. In particular, it has for the first time been possible to identify the weak adsorbate states overlapping the *d* bands. The x-ray emission spectrum from adsorbed CO gives the possibility to identify the symmetry of molecular valence states as the measurements are angular resolved. Furthermore, the spectra are shown to be considerably affected by the emission from shakeup and shakeoff states.

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