

Direct probing of the adsorbate-substrate chemical bond using angle-dependent x-ray-emission spectroscopy

A. Nilsson, P. Bennich, T. Wiell, N. Wassdahl, N. Mårtensson, and J. Nordgren
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

O. Björneholm and J. Stöhr
IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099
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Angle-dependent x-ray-emission spectroscopy is a method for studying adsorbed molecules, which makes it possible to directly probe the electronic states responsible for the surface chemical bond. This technique allows the separation of the adsorbate density of states both in terms of atomic site and orbital symmetry. This is demonstrated for CO adsorbed on Ni(100) and Cu(100). The occupied part of the 2π - $3d$ adsorbate-substrate bond, projected on the C and O atoms, is observed directly.

When a molecule is adsorbed on a metal surface by chemical bonding, new electronic states of the molecule are formed. The direct observation and identification of these states is still an experimental challenge. For noble- and transition-metal surfaces the adsorption-induced states overlap with the metal d valence band and their signature is therefore often obscured by bulk substrate states. This complication has prevented techniques such as photoemission and inverse photoemission, for example, from providing reliable information on the energy of chemisorption-induced states and has left questions unanswered regarding the validity of different theoretical models. However, it was recently shown that x-ray-emission spectroscopy (XES), in spite of its inherent bulk sensitivity, can be used to investigate adsorbed molecules.¹ Due to the core hole localization, this technique has the power of projecting out the partial density of states around each atomic site. In this way it is possible to distinguish the individual atomic contributions to the surface chemical bond and, in particular, visualize the contribution from each individual atom in the adsorbed molecule without interference from the substrate.

In this paper we show how the molecular bonds at a surface and their symmetry can be directly probed by angle-dependent XES, using CO adsorbed on Ni(100) and Cu(100) as examples. The use of high-intensity monochromatized synchrotron radiation in the excitation process and angle-dependent emission intensity measurements allow states of different symmetries to be separated and the adsorbate-substrate chemical bond to be projected out on the individual atoms in the adsorbate. The occupied part of the $2\pi^*$ state is shown to hybridize with the $3d$ band differently on the C and O ends of the adsorbate. No intensity at the Fermi level is observed on the adsorbate, in contrast to the predictions of the resonance model for molecular chemisorption on transition metals.²

The experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) using the multiple wiggler beam line 10-1, which is equipped with a spherical grating monochromator (SGM). The XES spectra were recorded

using a grazing incidence grating spectrometer³ mounted to detect emission perpendicular to the incident x rays. The energy resolution of the spectrometer was set to 0.5 eV for both the C and O K emission spectra. The energy widths of the incoming x rays were around 1 eV for C and 2 eV for O. For the angle-dependent XES measurements the sample was rotated around an axis parallel to the incoming beam such that the incident x rays maintained a fixed angle of 2° – 5° with respect to the surface in order to achieve a high surface sensitivity.¹ The valence-band photoemission spectrum was measured using a He discharge lamp and a hemispherical electron analyzer with an overall resolution of 0.2 eV.

For clarity we show in Fig. 1 the experimental geometry of the emitted x rays with respect to the molecular orientation on the surface and review the symmetry selection rules for electric dipole transitions involving the K shell.⁴ In the x-ray-absorption process the linearly polarized incident radiation leads to $1s$ - σ and $1s$ - π transitions if the E vector is parallel or perpendicular to the molecular axis, respectively.⁴ The same symmetry rules also hold for the emitted x rays. However, since we do not analyze the polarization of the emitted x rays, symmetry information only comes from the fact that the E vector is always perpendicular to the direction of the emitted x rays. In the case of normal emission from CO adsorbed perpendicular to the surface we therefore probe transitions from the two degenerate π orbitals to the $1s$ core hole, whereas in grazing emission transitions from one of the π orbitals and the σ orbital are seen. This means that in normal emission orbitals with pure π symmetry can be observed and in grazing emission both π and σ orbitals are probed.

Figure 2 shows C and O K emission spectra recorded at the two different geometries together with a He II (40.8 eV) photoemission spectrum measured close to the normal electron emission direction for CO on Ni(100) in the $c(2\times 2)$ structure. Before discussing the XES results a few statements about the technique are appropriate. In order to create a clean core hole state without any shakeup satellites, threshold ex-

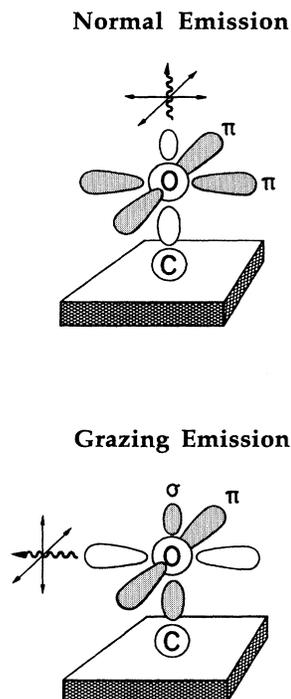


FIG. 1. Schematic of the molecular orientation of CO with respect to the E vector for the emitted light.

citation to the lowest unoccupied π orbital (287.5 and 533.5 eV) was used.^{1,5} We also note that in XES the final state of the transition does not involve a core hole but contains a valence hole similar to valence-band photoemission. For metallic systems, such as chemisorbed molecules, the Fermi-level position in the x-ray spectrum is obtained from the corresponding core-level binding energy.⁶ Thus the XES spectra in Fig. 2 have been put on a binding energy scale by subtracting the core-level photoemission binding energies for the O $1s$ (532.1 eV) and C $1s$ (285.9 eV) levels for $c(2 \times 2)$ CO/Ni(100), respectively.⁷

The ultraviolet-photoemission-spectroscopy (UPS) spectrum clearly shows the Ni $3d$ valence-band peak between 0 and 4 eV binding energy and the two peaks at higher binding energy, which are associated with the overlapping 1π and 5σ states at 7.5 and 8 eV, and the 4σ state at 10.5 eV, respectively.^{8,9} In XES the 1π , 5σ , and 4σ states are also observed as indicated in Fig. 2. The 4σ state is observed only in the O K grazing emission spectrum. This is understood from the fact that only grazing emission is sensitive to σ -orbital symmetry and that the 4σ state is mainly a mixture of O $2p$ and C $2s$ atomic orbitals. Only the O $2p$ component yields any intensity through the dipole selection rule. The 5σ and 1π states are seen in both the C and O emission spectra. The 5σ peak is only seen in grazing emission while the 1π peak is maximized at normal emission, in accordance with Fig. 1. This is clearly seen in the O K spectra where only one peak is observed for normal emission which reflects π -orbital symmetry, i.e., the 1π orbital. In the grazing O K spectrum a shoulder appears at higher binding energy. This state has σ -orbital symmetry and can be attributed to the 5σ orbital. The $1\pi/5\sigma$ ratio is different in the C and O

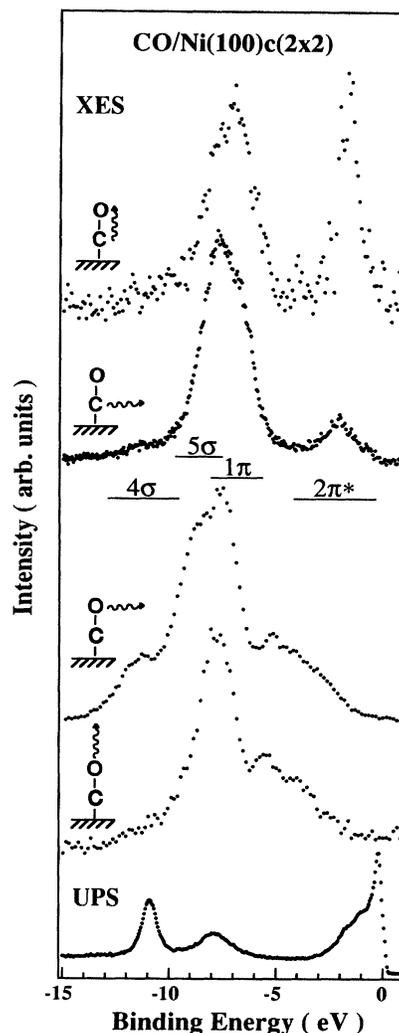


FIG. 2. Grazing and normal C and O K emission spectra and a UPS spectrum of CO on Ni(100) in the $c(2 \times 2)$ structure. The corresponding core-level photoemission binding energy has been subtracted from the x-ray-emission spectra.

grazing emission spectra, showing that the 1π state is more localized on the oxygen end of the molecule, while the 5σ state is localized mainly on the C end. In fact, the 1π state only gives rise to a slight asymmetry of the 5σ peak in the C spectrum. These results clearly show the capability of probing the individual atomic contributions in the orbitals of the adsorbate.

We now turn to the adsorbate-substrate derived states which can be seen as spectral features between the Fermi level and the 1π state. The UPS spectrum is in this region dominated by electron emission from the Ni $3d$ band. However, there are some changes in the spectrum upon adsorption around 2 eV which have also been observed in previous photoemission work.⁹⁻¹¹ We can make three important observations concerning these states in the XES spectra: (i) the spectral intensity is largest in the normal C K emission spectrum and its angular dependence follows that of the 1π state, (ii) the intensity at the Fermi level is close to zero in all

spectra, and (iii) the energy positions and spectral distributions are very different for the two atoms. Because of the π character of these states we attribute them to the occupied part of the $2\pi^*$ orbital. Since this orbital in the free molecule is strongly polarized towards the carbon end of the molecule it is expected to be most prominent in the carbon spectrum, as observed in Fig. 2.

Adsorption of CO on *d*-metal surfaces has served as the prototype system for molecular chemisorption. It has generally been assumed that the interaction with the metal surface leads to a "back-donation" of electrons into the empty molecular $2\pi^*$ antibonding orbital. There exist two different models to describe the $2\pi^*$ adsorbate-substrate chemical bond. One is the molecular-orbital approach, which suggests a splitting of the $2\pi^*$ level into occupied bonding and unoccupied antibonding 2π -*d* hybrid states.^{12,13} The occupied states are attributed mainly to *d*-metal character and the antibonding states mainly to molecular $2\pi^*$ character. Secondly, there is the resonance model, where the CO $2\pi^*$ level is suggested to be resonantly broadened by the interaction with the metal.² The tails of this broadened band would extend below the Fermi level and therefore create some degree of $2\pi^*$ occupancy. The latter model implies a high density of adsorbate states at the Fermi level, allowing for local electron-hole pair excitations.

Our results allow us to distinguish between the molecular-orbital and the resonance models. In the C *K* emission spectra the 2π states appear around 2 eV below the Fermi level. The intensity at the Fermi level is low, which does not fit into the resonance model. This rather suggests that the chemical bonding to the surface should be described in a molecular-orbital picture with the formation of an occupied bonding 2π -*3d* hybrid state far below the Fermi level. However, the different energy positions of the π band in the C and O *K* emission spectra show that this model is also oversimplified. The π band in the O *K* emission spectra has the same onset as in the C *K* emission spectra but extends all the way down to the 1π peak with maximum intensity around 5 eV binding energy. The classification in terms of original molecular 1π and 2π states is thus insufficient. The substrate-CO hybrid states will contain new π orbitals which are formed by rotations (new linear combinations) of the original 1π and 2π orbitals. These rotated orbitals may in turn be classified in terms of their bonding (1π -type) or antibonding (2π -type) character with respect to the intramolecular CO bond but they are not the same orbitals. We can envisage that the original 1π states hybridize with the bottom of the *d* band leading to bonding and antibonding states (viewed as an isolated two-level interaction this will correspond to a repulsive contribution). The bonding states can be related to the main 1π peak and the antibonding ones to the 5-eV structure as seen in the oxygen spectra. These states will also have varying amounts of original 2π character. In fact, by comparing the carbon and oxygen spectra, it is seen that the 5-eV structure corresponds to rotated π states with little C $2p$ character, i.e., an O $2p$ lone-pair state. An indication of hybridization between 1π and $3d$ states was also suggested in a previous photoemission study of the valence band for CO on Ni(100).¹¹ Viewed on the carbon site, on the other hand, we mainly see the manifestations of the 2π -*3d* interaction which leads to states closer to the Fermi level.

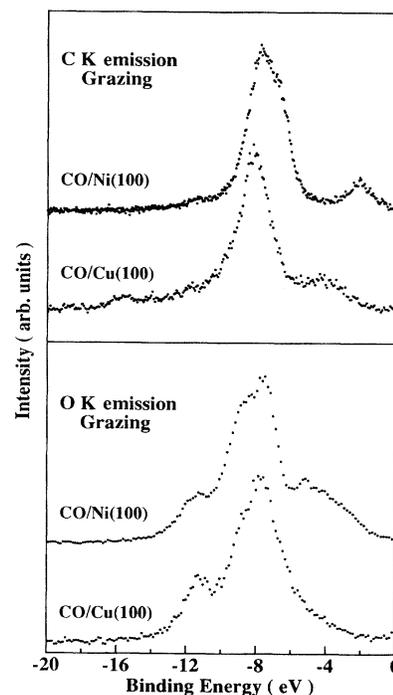


FIG. 3. Grazing C and O *K* emission spectra of CO on Ni(100) and Cu(100).

The above results show the importance of the *d*-band location in accounting for the different hybridization on the carbon and oxygen atoms. XES results for $c(2 \times 2)$ CO on Cu(100), shown in Fig. 3, give further evidence for this effect. While the on-top adsorption site for CO on Cu(100) is the same as for Ni(100), the Cu *d* band is shifted downwards in energy resulting in a much weaker chemisorption bond. The XES spectra shown in Fig. 3 exhibit energy positions for the 4σ , 5σ , and 1π CO states similar to previous UPS measurements.¹⁴ The new adsorbate-substrate π bonding states are now shifted to higher binding energies. In the case of the C *K* emission spectrum the new π state appears at 4 eV binding energy, a shift of 2 eV in comparison with Ni. For the O *K* emission the π states completely merge; only a tail is observed from the 1π state.

In conclusion, we have demonstrated using x-ray-emission spectroscopy how the adsorbate density of states in adsorbed CO on Ni(100) can be separated in terms of atomic sites and orbital symmetries. The adsorbate-substrate bonding states of π symmetry are shown to hybridize with the $3d$ band differently on the C and O ends of the molecule. No intensity at the Fermi level is observed on the adsorbate, in contrast to the predictions of the resonance model.

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