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Angle resolved Autoionization Spectra of Adsorbates on Metal Oxide Surfaces

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The autoionization of excited core hole states of simple adsorbates has attracted considerable attention. It provides information on the local electronic density of the valence levels. However, mainly simple adsorbates on different metal surfaces have been investigated. Here it was of considerable interest to study autoionization on oxide surfaces because effects due to the substrate are expected to be different from metals. Angle resolved autoionization spectra after resonant $C_{1s} \rightarrow 2\pi$ excitation of CO on different epitaxially grown metal oxide surfaces are presented for the first time. The spectra resemble the autoionization spectrum of CO in the gas phase. Differences between spectra on oxide surfaces and on metal surfaces are discussed.

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1. INTRODUCTION

Many of the catalysts in use in heterogeneous catalysis are metal oxides. Therefore the study of adsorption on metal oxides is of great interest. In surface science photoelectron spectroscopy is one of the most powerful tools in investigating the electronic structure of those systems. But photoionization is a complex many particle process. Especially in the inner valence region the photoelectron peaks are often accompanied by a rich satellite structure. With autoionization we can directly populate those states responsible for shake up satellites. Thus autoionization is a valuable tool for understanding the electronic structure of adsorbate systems.

2. EXPERIMENTAL DETAILS

The experiments were performed in a magnetically shielded (double metal shield) vacuum system containing facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), residual gas analysis with a quadrupole mass spectrometer, and an angle resolved hemispherical photoelectron detector (VSW HA 50). The measurements were carried out at the BESSY I storage ring on the high energy toroidal grating monochromators 1 and 2 (HE-TGM 1, HE-TGM 2). The base pressure in the system was below 4x10⁻¹⁰ mbars. The crystals were spot welded to two tungsten rods mounted on a sample manipulator. The sample could be cooled with liquid nitrogen to 80 - 85 K. Heating was achieved via electron bombardment from a filament on the reverse







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K. The oxide films were prepared by oxidation of Ni(100), Ni(111), Cr(110) and NiAl(110) single crystals in an oxygen atmosphere [1]. The surface of the crystal was cleaned by argon or neon ion bombardment, followed by annealing. CO was adsorbed by cooling the sample to T = 80 - 85 K with a background pressure of 1x10⁸ mbars CO. The Al₂O₃ was cooled down to 35 K and heated up to a temperature with a suitable coverage which was monitored by the NEXAFS peak height. To determine the angular dependence, we used a fitting procedure to obtain the areas under each peak. As the number of states is too large to fit one curve for every state, groups of states were added up to form distributions to be fitted. The energy position of those peaks was determined from the experiment. A peak was fitted whenever a structure in one polar angle spectrum was observed. Each of the spectra was fitted by a set of student-t-distributions, using identical peak positions, full widths at half maximum (FWHM) and peak shapes for all spectra. We developed a two-dimensional simplex algorithm that allows to fit the whole angle dependent set of spectra at once. In this way it was possible to optimize the positions and shapes of the distributions.

3. RESULTS AND DISCUSSION

3.1 Autoionization of adsorbates on oxide surfaces

Fig 1. shows the autoionization spectra of CO on various metal oxide surfaces and a gas phase spectrum [2-4]. The features in the gas phase autoionization spectrum are marked according to ref. [4]. At binding energies higher than 17eV 2h1p-satellites are responsible for the spectra. Two large structures at 17.5 and 22 eV dominate the gas phase spectrum. The region of lower binding energy than 17eV is dominated by three peaks in the gas phase spectrum. With CNDO Greensfunctions methods Freund and Liegener [4] determined the states being responsible for the structures. The three structures at low binding energy result from a decay mechanism which involves the 2π electron. The result are single hole states which are assigned as $5\sigma^{-1}$, $1\pi^{-1}$ and $4\sigma^{-1}$ with increasing binding energy as marked in the figure. The two large peaks in the satellite region are due to $4\sigma^{-1}5\sigma^{-1}\pi^{*}$ and $5\sigma^{-2}\pi^{*}$ states. The peak at 17.5 eV is assigned to states with only a little admixture of $5\sigma^{-1}1\pi^{-1}\pi^{*}$ configuration additionally.

The spectra for CO on Al_2O_3 are shown for three different coverages in Fig. 1. This system is characterized by a much lower binding energy compared to the systems CO/NiO(100,111) and CO/Cr₂O₃(111). The spectrum of a multilayer condensed on an Al₂O₃(111) surface is nearly identical to the gas phase spectrum. When the CO thickness of the adsorbate layer is decreased (from the bottom to the top) the spectrum alters significantly. The peaks broaden and the $5\sigma^{-1}$ state gets less intensity and nearly vanishes in the lowest coverage spectrum. Whether this indicates that the 5σ orbital is involved in the binding to the substrate is not clear at present.

The spectrum above the spectra of CO on Al₂O₃ in Fig. 1 is the autoionization spectrum of CO on Cr₂O₃(111). The CO is much stronger bound to that surface than to the Al₂O₃(111) surface. This spectrum is quite different from the spectra of gaseous CO and of CO adsorbed on Al₂O₃(111). It reveals two peaks in the single hole region and two main peaks in the satellite region at 20 and 24 eV. The peak at the lowest binding energy is at about the same location as the $1\pi^{-1}$ peak in the gas phase spectrum. The second peak which has about 2/3 of the height of the first one is located at about the same binding energy as the $4\sigma^{-1}$ peak of the gas phase. Two large features follow at higher binding energy comparable to the spectrum of gaseous CO or to the multilayer of CO, but are much broader and are significantly shifted to higher binding energy.

The two spectra at the top of Fig. 1 are the autoionization spectra of CO on NiO(111) and on NiO(100). They look very similar to the spectrum of CO on $Cr_2O_3(111)$. Only the intensity ratio of the two low binding energy features in the participator decay region has changed. The peak at higher binding energy gains intensity compared to that one at lower binding energies. A possible reason for this would be an increasing intensity of charge transfer from the substrate with an increasing binding strength.

3.2. Autoionization of adsorbates on metal surfaces

Many studies have dealt with autoionization of CO on various transition metal surfaces (e.g. [5-9]). Also the isoelectronic systems N₂/Ni(100,110) have been widely investigated [10,11]. Fig. 2 shows the results of a CNDO Greensfunction calculation for CO/Ni(110) [6] in comparison with the experiment. The calculated intensity of the states (line spectrum) was convoluted with a lorentzian of 2 eV FWHM. The dominant peak of the spectrum is located at 20 eV and is due to a mixture of $1\pi^{-1}1\pi^{-1}\pi^{*}$ and $1\pi^{2}\pi^{*}$ states. The large structure at lower binding energy is due to charge transfer states with a metal electron taking part in the decay process (e.g. $1\pi^{-1}Md^{-1}\pi^{*} = 1\pi^{-1}CT$). The single hole states do not gain any intensity in the autoionization spectrum on the metal surface. In contrast to the gas phase spectrum of CO the spectrum of the





Fig. 2: Comparison between the calculated (bottom) and measured (top) autoionization spectra of CO/Ni(110). The calculated line spectrum has been convoluted with a Lorentzian of 2 eV FWHM.

adsorbate on the metal surface is dominated by states with at least one hole in the 1π orbital. The $4\sigma^{-1}5\sigma^{-1}\pi^*$ and $5\sigma^2\pi^*$ states do not play a role in the spectrum of the adsorbate on the metal surface. Fig. 3 shows the autoionization spectra of CO on various transition metal surfaces [9] ordered by decreasing binding energy. The spectrum at the top is the spectrum of CO on a Ni surface. It is quite different from the spectra of CO on the NiO surfaces shown in Fig. 1. But the autoionization spectra of CO on the metal surfaces change significantly with the substrate. The spectrum of CO on the silver surface (a very weak chemisorbate [9]) is very similar to the autoionization spectra of CO on the transition metal oxide surfaces shown in Fig. 1. It can be stated now that the autoionization of CO on the transition metal oxides is not of the type of the strongly bound metal adsorbates.

In an attempt to answer the question if the two low binding energy peaks in the transition metal oxide spectra are of single hole character we have looked at the UPspectra. They are plotted below the autoionization spectra in Fig 4. The photoemission peaks are located at the same energies as the peaks in the autoionization spectra. In contrast to that there is no such similarity between the autoionization spectra of CO on Ni and the corresponding UP-spectra (however see Fig. 11 in ref. 5 for N₂/Ni). The reason for this is that the charge transfer states play a



Fig. 3: Autoionization spectra of CO on various transition metals [9].

dominant role in the case of the metal substrate.

However, there are significant differences between autoionization of CO in the gas phase (or the multilayer on $Al_2O_3(111)$) and CO on the oxide surface. The energy location of the two peaks in the satellite region is different as can be seen in Fig. 1. The transition metal oxides are mostly insulators. Consequently there are no free electrons. Localization plays a dominant role in the electronic structure of the oxide surfaces. Thus in the case of adsorbates on an oxide surface a charge transfer, if there is any, will mainly occur from the oxygen atoms in the surface



Fig. 4: Autoionization spectra of CO on NiO(111) and $Cr_2O_3(111)$ in comparison with UP spectra of the adsorbates. Peaks below 10 eV are due to the substrate.



Fig. 5: Fit of the autoionization spectrum of CO on a NiO surface.

towards the core hole in the adsorbate. The localized core hole on the other hand is a probe for the density of electrons in the different valence orbitals. A charge transfer from the oxygen in the surface is possible and will happen if the adsorbate binds sufficiently strong. This effect may be the reason for the differences in the low energy region of the spectra of CO on the transition metal oxides compared to the gas phase.

Furthermore there are substantial differences in the satellite region of the spectra depending on whether the molecule is adsorbed on metal or on oxide surfaces. Here a different binding mechanism plays a dominant role. While in the case of bonding on a metal surface the electronic structure of the molecule is widely rearranged it is not as strongly affected by the oxide surface. From calculations it is known that the relative orbital energies do not differ very much between gas phase CO and CO adsorbed on an oxide surface [12] while they get totally



Fig. 6: Angular dependence of the marked peaks (Fig. 5) in the CO/NiO(100) autoionization spectrum.



Fig. 7: Calculated angular dependencies of oriented gas phase molecules. The calculations were done on CNDO level.

changed on a metal surface [13,14]. Especially the energy of the 1π orbital is changed to a lower value with respect to the 5σ orbital by adsorption on a transition metal surface. The bonding mechanism on the oxide surface is mainly electrostatic. Theoretical results indicate that the π^* orbital is not filled [12]. There is no backbonding in this system. Therefore we expect major differences between the molecule on the oxide surface as compared with a metal surface.

3.3 Angular dependence

For CO/NiO(100) we have measured the angular dependence of the autoionization spectra. CO stands nearly perpendicular on the NiO(100) surface, as NEXAFS measurements reveal [15]. In order to plot the angular dependence of the autoionization intensities the spectra were fitted with the algorithm described above. Fig. 5 shows the result of such a fit. The peaks marked will be discussed in the following. Fig. 6 shows the measured angular dependencies of the system CO/NiO(100). First it has to be stated that the angular dependence is weak. The spectra were measured in steps of 5° up to a polar angle of 75° with respect to the surface normal. Peaks 1 and 2 reveal a continuously growing intensity with low intensities at small polar angles and higher intensities at higher angles. The behavior of Peak 3 is just vice versa. Maybe there is a maximum at 15° but the overall shape is going down. Peak 4 has a broad minimum around 30°. Its angular dependence is the weakest of all peaks

For the similarity with the gas phase spectra a theoretical angular dependence for oriented gas phase CO molecules has been calculated on CNDO level. The angular dependence of the decay is directly correlated to the orbitals taking part [8,11,16-18]. If the decay mechanism for the adsorbates on the oxide surfaces and in the gas phase is as similar as stated before there should be a similar angular dependence of both. The angular dependencies are shown in Fig. 7. Measurements of the anisotropy parameters of CO in the gas phase by Hemmers et al. [19,20] reveal the same shapes of the angular dependence of the autoionization spectra as the calculations for the pure configurations.

As can be seen the single hole states (Fig. 7B) reveal the same angular behavior as the first two peaks of the autoionization spectra on the oxide surface. The assumption of mostly single hole character of the low binding energy part of the spectrum is corroborated by the calculated intensities. For peak 3 of the experimental angular dependencies the calculated dependencies of the $4\sigma^{-1}5\sigma^{-1}\pi^{*}$ state and the $5\sigma^2\pi^*$ state (Fig. 7A) fit well but the slight maximum at 15° in the experimental data is not possible to explain. The fourth peak in the experiment has a totally different angular dependence than expected from the similarity with the gas phase. Here other effects must be of importance. Its angular dependence could be explained if a great amount of an $1\pi^{-2}\pi^{+}$ state (Fig. 7D) was mixed in. But also in the higher energy region higher excitations (3h2p states etc.) play a larger role.

4. CONCLUSIONS

Autoionization spectra of CO on various metal oxide surfaces change their shape with increasing heat of adsorption. While the spectrum of CO on $Al_2O_3(111)$ is very similar to the gas phase spectrum the spectra of CO on the transition metal oxides show significant differences. The low binding energy features seem to have mostly single hole character and a little amount of charge transfer especially in the second peak. The angular dependence which proofs to be a valuable tool in assigning the spectra corroborate the result that the autoionization of CO on NiO(100) exhibits some similarities with the gas phase for some bands but the angular dependence of at least one intense feature cannot be correlated with the gas phase. To finally explain the spectra perfectly some more sophisticated calculations are necessary.

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