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Relation between x-ray photoemission binding energies and absorption resonance energies for CO adsorbates

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We present a comparison of x-ray-photoemission-spectroscopy (XPS) binding energies and x-ray absorption resonance energies ($1s \rightarrow 2\pi$) for various CO states, in particular adsorbates. We show that the energetic position of the bound π resonance of adsorbed CO molecules is equal for weakly chemisorbed CO on Cu(100) and on Cu(110), and that it coincides with the lowest-energy peak observed in photoemission. This is at variance with earlier results and theoretical predictions for CO adsorbates, and it is different from the results obtained for strongly chemisorbed CO species, which show a 1–2 eV lower XPS threshold energy. The new results will be discussed with emphasis on the influence of charge-transfer screening on the relation between peak positions in near-edge x-ray absorption fine-structure (NEXAFS) and x-ray-photoemission spectroscopy. Important conclusions are that only for strongly chemisorbed CO, not for CO/Cu, the lowest-energy XPS peak represents the "adiabatic" final state of the core-hole system, and that XPS threshold energies should not be generally taken as reference for NEXAFS peaks.

Near-edge x-ray absorption fine-structure spectroscopy (NEXAFS) is a powerful tool for the determination of the geometric orientation and of trends in the intermolecular bond lengths[1] of adsorbed molecules. Very recently the line shape and the exact energetic position of the observed molecular absorption resonances have attracted greater interest mainly because of the availability of more intense synchrotron light sources and monochromators with higher resolution.[2] This electronic information allows a more detailed consideration of the dynamics of the photoabsorption process and the adsorbate-substrate interaction. In this respect the exact determination of the energy position of the resonances in relation to the ionization threshold of the respective core level is especially important for the understanding of fundamental processes such as screening dynamics,[3] lifetime of excited states,[4] and the use of empirical correlations to determine the intermolecular bond length from resonance positions,[5] for which the question of an appropriate reference level has to be settled.

We wish to point out that there is an important difference between core-excited states of isolated and adsorbed molecules. For isolated molecules, the lowest possible core-ionized state is determined by the position of the lowest unoccupied molecular orbital with respect to the continuum limit, i.e., the ionization potential. In contrast, for adsorbed molecules a nonzero possibility for a core-ionized (charge-transfer screened) final state with a delocalized hole at the Fermi edge exists which can be lower in energy than corresponding neutral core-excited states. This fully screened state—which need not necessarily be observable in a particular system—now takes on the role of the continuum limit, while the external continuum limit (same screened hole, but electron removed to infinity in vacuum) loses importance.

It has turned out that a crucial factor in comparing the excitation energies for different species and their ionization thresholds is the accurate calibration of the photon energy scale. To shed some light on the influence of adsorbate-substrate interaction on relaxation phenomena we have investigated a series of CO-adsorption systems representing different strengths of the adsorbate-substrate coupling [CO/Cu(100) and CO/Cu(110), CO/Ni(111), and (CO+K)/Ni(111)]. We have put special emphasis on the calibration of the photon energy scale to ensure the compatibility of the data from different runs.

The experiments were performed at the Berliner Elektronenspeicherring GmbH BESSY using the HETGM monochromator. The NEXAFS spectra were recorded in the partial-yield mode using a VG-CLAM spherical sector analyzer at a constant-energy window representing the main peak of the corresponding *KLL* Auger spectrum. Great care was taken in calibrating the photon energy scale to an accuracy of ±0.3 eV by measuring the Fermi-edge position and a substrate core level in the constant-final-state (CFS) mode. To guarantee the accuracy of the energy window in the CFS mode we also calibrated the energy analyzer (±0.1 eV) with a conventional x-ray source (Mg *Kα*, Al *Kα*) using a standard procedure,[6] prior to taking the NEXAFS spectra. In the case of CO/Cu(100) and CO/Cu(110) for which differences have been reported in the literature[7–9] we mounted both samples on the same manipulator and measured the resonance positions in the same run changing nothing but the sample position to assure absolute compatibility of the results for the two crystal faces. The samples were prepared using standard procedures, and the data were taken for saturated CO layers.

Figure 1 shows two NEXAFS spectra for CO/Cu(110) and CO/Cu(100), respectively, taken at the C *K* edge

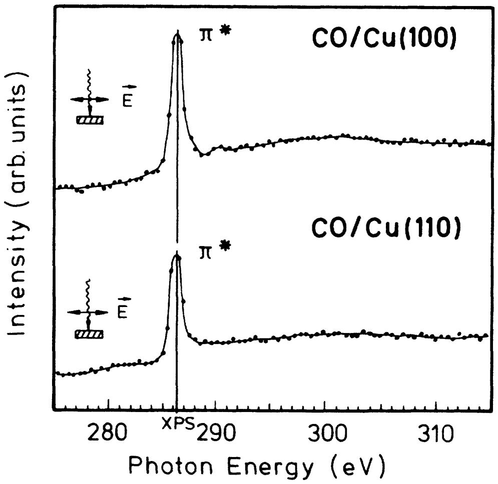

FIG. 1. C *K*-edge absorption spectra for CO/Cu(100) and CO/Cu(110) taken in the Auger yield mode (CFS energy: 267 eV) with normal incidence of the incoming light (*s* polarization). The position of the XPS peak with lowest binding energy is marked by a vertical line.

(Auger partial-yield mode; CFS energy 267 eV) with the polarization vector of the incoming light parallel to the surface, i.e., normal incidence. The position of the lowest binding energy x-ray photoemission spectroscopy (XPS) peak is marked by a vertical line. Both spectra show a very pronounced π-resonance reflecting the well-known fact that CO is adsorbed with the molecular axis oriented normal to the surface.[10] One can clearly see that the two π resonances line up almost perfectly in contrast to previously published results.[8,9] It is also obvious that their energy positions coincide with the measured XPS energies of the "well-screened peak," i.e., the peak with the lowest binding energy, within experimental accuracy.

Figure 2 shows NEXAFS spectra taken under the same conditions at the O *K* edge (Auger partial yield mode; CFS energy = 512 eV). The position of the lowest binding energy XPS peak is again marked by a vertical line. In complete agreement with the carbon edge data the spectra at the O edge show a very similar energy position of the π resonance for the two systems. The XPS energies are again close to, or slightly higher than [by 0.3 eV for CO/Cu(100)], the π-resonance energies. To summarize the experimental results for the two Cu samples we conclude that CO on both substrates shows almost identical absorption energies of the π resonances. For both edges we measure a π-resonance energy which is equal or even smaller than the photoionization energy referenced to E_F measured for the XPS peak with the lowest binding energy.

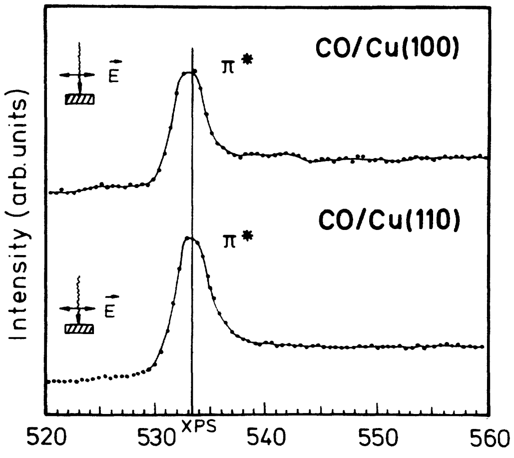

FIG. 2. O *K*-edge absorption spectra for CO/Cu(100) and CO/Cu(110) taken in the Auger yield mode (CFS energy: 512 eV); other details as in Fig. 1.

This result is in contrast to our observations for strongly bound CO adsorption systems [CO/Ni(111) or (CO+K)/Ni(111)].[7] In these cases we have shown that the photoemission process far from threshold leads to a core-ionized state which is *lower* in energy than the corresponding resonantly excited state (bound π resonance), although the latter and the final states in the adiabatic limit of the photoemission process are usually considered to be very similar (having a partially occupied 2π orbital).[11] This energy difference disappears for the weakly bound CO/Cu systems. This is in disagreement to a recently published theoretical model,[12] according to which the onset of the absorption spectrum should in all cases coincide with the XPS energy, i.e., with the centroid of the "adiabatic" XPS peak. The theoretical results are based on a resonance model for the interaction between the 2π orbital of adsorbed CO and the metal substrate which is basically derived from local-density theory considerations of chemisorption.[13] In this model the CO-2π orbital is shifted to lower energies due to the effective metal substrate potential and broadened due to the possibility of resonant tunneling of electrons between adsorbate and substrate. These hybridization effects are considered to be small so that no splitting of the 2π level occurs as one would have expected according to conventional models of CO chemisorption.[14] Consequently, the relaxation of the core-ionized state is characterized by a partly filled 2π resonance, i.e., by the filling of that part of the resonance which is pulled below the Fermi level by the Coulomb attraction of the 1*s* hole, while the resonantly excited state is characterized by electron transfer from the core level to the empty part of the resonance above E_F. Hence the core ionization threshold (i.e., the lowest-binding-energy XPS peak with respect to the Fermi level) should always be positioned at the onset of the absorption spectrum. The energy difference between the π peak in the NEXAFS spectrum and the threshold XPS energy in this model is given by the position of the maximum of the 2π-resonance level with respect to the Fermi level and should be determined by the strength of the adsorbate-substrate interaction. Consequently, one would expect that the energy difference is largest for weakly chemisorbed systems. This is clearly at variance with our results.

In the following we therefore try to give an explanation for the observed trends in the relation between XPS core-ionization threshold and resonance position with special emphasis on the weakly chemisorbed species. We propose that the different behavior observed for weakly chemisorbed CO on Cu, as opposed to the strongly bound CO systems, is in fact due to a less well-screened XPS final state whereas the photoabsorption final states appear to be fairly equivalent for all systems studied; the latter are even comparable to the bound resonance state of the isolated CO molecule.[15]

An alternative explanation for the observed trends of the differences between absorption energies and photoionization energies could be based on the fact that the absorption process is governed by the dipole matrix element thus projecting out the local *p* density of states. In this model the position of the π resonance would be determined mainly by the maximum of the *p* density of states at the site of the core hole. The lowest screened core-ionized state could, however, involve large contributions from the metal *d* states thus being sensitive to the position of the metal *d* band (which of course is different for Ni and Ru as compared to Cu). A static model like this cannot be ruled out on the basis of our data set. We favor, however, a model which includes the dynamics of the screening process and can also account for observed trends in the core hole decay spectra. In the following we will therefore concentrate on a dynamic screening model.

To further elucidate the role of screening and its influence on relative energy positions we summarize trends in the XPS spectra of CO molecules with different adsorbate-substrate coupling. Figure 3 shows O 1*s* XPS spectra for a variety of adsorption systems representing different chemisorption bond strengths. In addition to the well-known fact that the shape of the photoelectron spectrum changes drastically for the weakly chemisorbed systems CO on Cu (Ref. 16) and Ag (Ref. 17) exhibiting the so-called "giant" satellites, one observes a clear trend for the peak with the lowest binding energy ("adiabatic" peak) which is believed to correspond to a well-screened final state in all cases. This peak is shifted by more than 2 eV towards higher binding energy when comparing the two extremes CO on Ni(111) [or coadsorbed to K on Ru(001) or on Ni(111)] with CO on Ag. This shift is by far larger than the respective shift of the 2π-resonance energies which is about 0.6 eV indicating the importance of final-state screening in the photoionization compared to the resonant-excitation process. In the latter case relaxation effects should be less important as the resonant absorption process always ends up with a similar neutral, i.e., well-screened, final state. Hence it can be concluded that the π-resonance energies are less dependent on the chemical environment than the XPS energies due to the difference of screening effects.

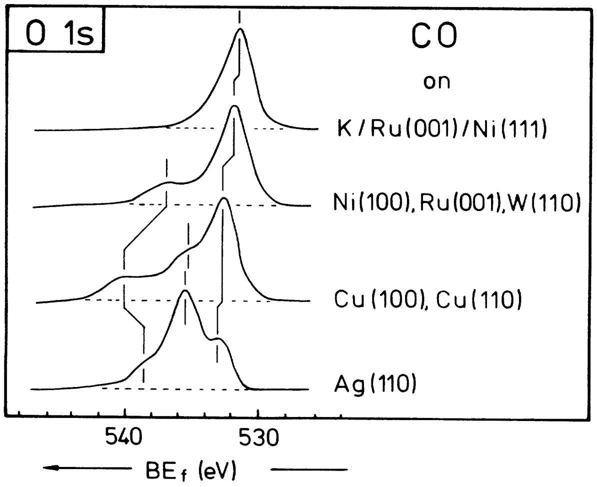

FIG. 3. O 1*s* XPS spectra for CO on different substrates representing decreasing chemisorption bond strengths from top to bottom. The CO/Ag(110) spectrum was taken from Ref. 17.

Whereas for strongly chemisorbed systems [(CO +K)/Ni,Ru, and CO/Ni] the core-hole final state with the lowest energy is reached via complete charge-transfer screening, this apparently does not apply in the same way to weakly chemisorbed CO on Cu, for which the resonantly excited final state has a comparable or even lower energy than the lowest-energy XPS peak. Auger decay spectra also indicate that in the case of weakly bound species neither the lowest-energy XPS peak nor the resonantly excited 2π-state represent the core-hole ground state of the system which is preferentially reached before the Auger decay takes place.[18,19] This and the present result imply that for CO/Cu (and probably also for CO/Ag) a core-hole ground state exists that is not observed as peak in the XPS spectrum. The reason is likely the weak coupling of CO to Cu or Ag which leads to a negligible probability of this ground state to be reached as XPS final state on the time scale of the photoionization process.

The same conclusion can be applied to the case of carbonyls. It has recently been established[20] that for carbonyls the π-resonance energy is very similar to that of the isolated CO molecule while the XPS photoemission energy is shifted by several eV to lower binding energies due to partial occupancy of the 2π-derived level of the carbonyl in the core-ionized state. Nevertheless this XPS state still has a higher energy than the resonantly excited state. This result can also be derived from the Auger decay spectra of the two different Auger initial states.[21] Finally, the trivial extension of this trend is the isolated or condensed CO molecule for which the energy difference between the (lower) resonantly excited final state and the core-ionized (XPS) state is largest due to the complete lack of charge-transfer screening.[7,15]

It is thus plausible that the resonantly excited ($1s \rightarrow 2\pi$) state which represents a neutral and hence "self-screened" final state shows very small energy variations for different CO environments whereas the XPS final state is much more sensitive due to the large influence of external screening contributions. Thus the energy difference between the resonantly excited state and the "well-screened" XPS final state mostly depends on the relaxation of the photoionized final state being of course largest for the free CO molecule with evidently no external screening. The difference becomes smaller and disappears for improved external charge-transfer screening (isolated CO $\rightarrow$ carbonyls $\rightarrow$ CO/Cu). Finally, for strongly chemisorbed systems the energy difference even changes sign because relaxation is so effective that the "well-screened" XPS final state with screening charge in the 2π-derived orbital is lower in energy than the π-resonant state. The weakly chemisorbed systems apparently have to be considered as an interesting intermediate case. Here the lowest-energy XPS peak clearly represents a partially screened final state because the coupling to the substrate is too weak to allow for an equally effective rearrangement of charge as in the case of the strongly bound systems, at least on the time scale of the XPS process, although some charge-transfer apparently occurs.

In conclusion, we emphasize the importance of considering the relaxation process as major source of the observed changes in the photoemission spectra of adsorbed CO (and probably many other) molecules whereas the neutral final state of the resonant $1s \rightarrow 2\pi$ photoabsorption process apparently shows only minor dependence on the strength of the chemisorption bond. We also note that final-state screening is most effective for photoionization of strongly chemisorbed molecules, in this case leading to a state which is lower in energy than the resonantly ($1s \rightarrow 2\pi$) excited state. As a consequence the energy of the lowest binding energy peak observed in photoemission shifts from energies below the resonantly excited state (for strong coupling) to equal or higher energies for intermediate coupling (CO/Cu, carbonyls) ending up with a much higher energy in the unscreened final state of isolated CO. For the understanding of the inter-relationship between the different final states of the photoabsorption process, and especially the evolution of these states in time, theoretical models are needed which explicitly include the dynamics of core-excited states. A static picture like the one proposed by Gumhalter *et al.*[12] is certainly not adequate to completely describe the observed phenomena.

It is stressed that for a discussion of shifts of resonance energies, like that of the σ resonance, as a function of bonding strength and bond length it is unsuitable to take the ionization threshold ("adiabatic" XPS peak) as a reference since this is largely determined by final-state relaxation, at least in the case of adsorbed CO (and probably other adsorbates). The problem is less crucial but still important if the main influence on XPS shifts is due to initial state, i.e., chemical, changes.[22]

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[1] J. Stöhr and D. A. Outka, J. Vac. Sci. Technol. A **5**, 919 (1987).

[2] See, e.g., *Proceedings of the VUV 9 Conference, Hawaii, 1989* [Phys. Scr. (to be published)].

[3] W. Eberhardt, E. W. Plummer, C. T. Chen, and W. K. Ford, Aust. J. Phys. **39**, 853 (1986).

[4] D. Menzel, P. Feulner, R. Treichler, E. Umbach, and W. Wurth, Phys. Scr. **T17**, 166 (1987).

[5] F. Sette, J. Stöhr, and A. P. Hitchcock, J. Chem. Phys. **81**, 4906 (1984).

[6] M. T. Anthony and M. P. Seah, Surf. Interface Anal. **6**, 95 (1984).

[7] W. Wurth, C. Schneider, R. Treichler, E. Umbach, and D. Menzel, Phys. Rev. B **35**, 7741 (1987).

[8] C. T. Chen, R. A. DiDio, W. K. Ford, E. W. Plummer, and W. Eberhardt, Phys. Rev. B **32**, 8434 (1985).

[9] J. Stöhr, J. L. Gland, W. Eberhardt, D. Outka, R. J. Madix, F. Sette, R. J. Koestner, and U. Doebler, Phys. Rev. Lett. **51**, 2414 (1983).

[10] C. L. Allyn, T. Gustafsson, and E. W. Plummer, Solid State Commun. **24**, 531 (1977).

[11] P. S. Bagus, A. R. Rossi, and Ph. Avouris, Phys. Rev. B **31**, 1722 (1985).

[12] B. Gumhalter, K. Wandelt, and Ph. Avouris, Phys. Rev. B **37**, 8048 (1988).

[13] N. D. Lang and A. R. Williams, Phys. Rev. B **18**, 1722 (1978).

[14] G. Blyholder, J. Phys. Chem. **68**, 2772 (1964).

[15] A. P. Hitchcock and C. E. Brion, J. Electron Spectrosc. **18**, 1 (1980).

[16] J. C. Fuggle, E. Umbach, D. Menzel, K. Wandelt, and C. R. Brundle, Solid State Commun. **27**, 65 (1978).

[17] S. Krause, C. Mariani, K. C. Prince, and K. Horn, Surf. Sci. **138**, 305 (1984).

[18] W. Wurth, C. Schneider, R. Treichler, E. Umbach, and D. Menzel, Phys. Rev. B **39**, 8725 (1988).

[19] W. Wurth and E. Umbach (unpublished).

[20] E. Rühl and A. P. Hitchcock, J. Am. Chem. Soc. **111**, 2614 (1989).

[21] W. Eberhardt, C. T. Chen, W. K. Ford, E. W. Plummer, and H. R. Moser, in *DIET II,* edited by W. Brenig and D. Menzel (Springer, Berlin, 1985).

[22] R. McLaren, S. A. C. Clark, I. Ishii, and A. P. Hitchcock, Phys. Rev. A **36**, 1683 (1987).