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Direct Experimental Measurement of Donation/Back-Donation in Unsaturated Hydrocarbon Bonding to Metals

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Abstract: Using resonant and off-resonant X-ray emission spectroscopy, in combination with ground-state density functional calculations, we examine the electronic structure of chemisorbed ethylene and benzene on the Cu(110) surface to investigate the suitability of the donation/back-donation bonding model given by Dewar[1] and Chatt and Duncanson[2] (DCD) for the interaction of unsaturated hydrocarbons with metal surfaces. We give an experimental verification of the DCD model and find donation/back-donation to be twice as large for ethylene as for benzene. In particular, the degree of $\sigma-\pi$ mixing (rehybridization) is found to correspond to the amount of donation/back-donation, which is put in relation to the aromatic and nonaromatic π characters of benzene and ethylene, respectively.

I. Introduction

A fundamental understanding of the bonding mechanism of unsaturated hydrocarbons to metal surfaces is of importance in many scientific areas such as heterogeneous catalysis, organometallic chemistry, and more applied fields such as tribology and molecular environmental science. In general, the interaction of unsaturated hydrocarbons with metal surfaces is known to induce, at a rather low heat of adsorption,[3] a weakening of the internal C−C bonds which must be due to a significant rehybridization of the molecular unit.[4−6] These characteristics are also common in transition metal complex chemistry involving unsaturated hydrocarbons coordinated to transition metal centers, like Zeises salt $K[PtCl_3(C_2H_4)]$.[7] The bonding in these organometallic metal complexes and adsorbed unsaturated hydrocarbons is commonly described in a frontier orbital approach, developed by Dewar[1] and Chatt and Duncanson[2] (DCD model).[5,8−10] In the DCD model the bonding is described as a donation of molecular π-electrons into the metal and back-donation from the metal into the molecular antibonding π^* orbital. Alternatively, the bonding mechanism has been rationalized in terms of bond preparation of the hydrocarbon molecule by an internal $\pi-\pi^*$ excitation in the formation of the surface chemical bond. This is the "spin-uncoupling mechanism",[4] which was inspired by the similarity of the geometric structure of the gas-phase $\pi-\pi^*$ triplet excited acetylene and ethylene and the adsorbed species.

To experimentally test the applicability of the DCD bonding model to hydrocarbon adsorption we need to establish the existence of occupied orbitals of π^* character and unoccupied π-orbitals. The latter would correspond to the donation and the former to the back-donation part of the interaction. Furthermore, from a chemical point of view it would be desirable to estimate the degree of donation and back-donation for different unsaturated molecules and substrates; this requires a direct measurement of the molecular orbital composition around the different atoms in the bound molecule.

Previous studies of the valence electronic structure of unsaturated hydrocarbons on metal surfaces have been based mainly on photoemission measurements[11] where the binding energy and angular-momentum composition of the valence bands are measured. These studies have been very successful in the determination of the two-dimensional band structure and symmetry of the overall adsorbate−substrate complex. However, it has been difficult to identify the specific adsorption-induced components, since the photoemission signal is strongly dominated by the emission, in particular from the d-orbitals, from the much larger number of substrate atoms.

X-ray emission spectroscopy (XES) on the other hand allows investigation of the valence electronic structure of adsorbate systems in an atom-specific and orbital symmetry -selective

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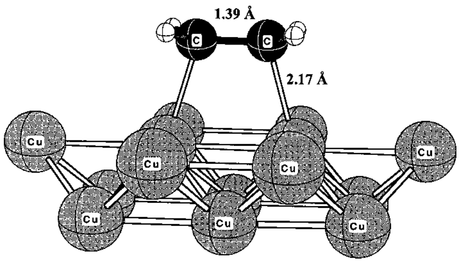
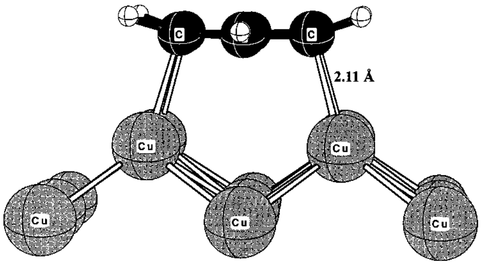
manner.[12] In this spectroscopy a core-hole is first created through an X-ray absorption process. Since the core-levels of different elements differ significantly one can selectively create the core-hole on, e.g., only the carbons in the molecules bound to the surface. The subsequent filling of the core-hole from an occupied orbital normally results in the ejection of another valence electron (Auger decay), but sometimes only a photon is emitted; the energy gives the energy difference between the occupied valence orbital and the core orbital. The intensity is proportional to the amount of 2p contribution from the core-hole atom to the valence orbital (dipole selection rule for 1s core-hole) and, since an overlap between the unfilled core-orbital and the valence orbital is required for a transition, only the *local, atom-specific* 2p character in the valence orbital is measured. Thus, this in essence corresponds to an experimental atomic decomposition or population analysis of the 2p-contributions to the occupied molecular orbitals.[12] The direction of propagation of the photon must, finally, be perpendicular to the direction of the 2p contribution that generated the emission which, for an ordered system, provides information on the spatial orientation of the molecular orbitals.

Recent experimental work in combination with ab initio ground-state calculations has been used to investigate in unprecedented detail the adsorbate electronic structure and to derive bonding models for simple molecules such as N_2[13,14] and CO[15,16] on transition metals as well as more complex molecules, such as glycine on copper.[17] The spectroscopy may be viewed as providing an experimental population analysis of the 2p-character of the molecular orbitals around a particular atom in the molecule,[12] which makes it an ideal method for investigating the orbital changes in the π-system of unsaturated hydrocarbons upon adsorption.

To address the DCD model it is essential to identify the symmetry of the adsorbate states in terms of π and π^* character or *ungerade* or *gerade* symmetry. For molecules with symmetry-related core orbitals the XES spectra show a strong variation with the excitation energy. Since, e.g., an *ungerade* core-orbital can only be filled from a *gerade* valence orbital the emission spectra will reflect the character of the intermediate core-hole state symmetry (parity selection rule[18−20]). Upon adsorption the presence of the surface may formally break the symmetry, but if the local symmetry is similar to that of the free molecule, the selection rules may still be partially retained.[10] Theoretical simulations of the resonant XES process using DFT (Density Functional Theory) have been shown to give a rather good agreement with experiments for ethylene and benzene adsorbed on Cu(110)[21] under the assumption of maintained local symmetry.



Chemisorbed ethylene on Cu(110); di-σ site



Chemisorbed benzene on Cu(110)

Figure 1. Optimal geometries for the adsorption of the nonaromatic hydrocarbon ethylene on Cu(110) (top panel) and the aromatic benzene on Cu(110) (bottom panel).

In the present paper we use the adsorption of the aromatic hydrocarbon benzene and the nonaromatic hydrocarbon ethylene on the Cu(110) surface as model systems for a direct experimental investigation of the applicability of the DCD model to the bonding of unsaturated hydrocarbons with metal surfaces (Figure 1). On the basis of resonant and off-resonant XES measurements in combination with first principles ground-state calculations, we can determine the orbital symmetry of the valence states and determine their electron occupation. Thus the degree of donation and back-donation of the molecular π and π^* orbitals with the metal can be determined and is found to be twice as large for ethylene as for benzene. The degree of donation/back-donation is mirrored by the internal $\sigma-\pi$ mixing within the adsorbed molecules. These results give an experimental verification of the DCD donation/back-donation bonding model for unsaturated hydrocarbons on metal surfaces.

II. Experiment and Computation

The experiments were performed at Beamline 8.0.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The experimental station houses in a confocal arrangement a Scienta SES-200 electron energy analyzer,[22] a partial yield detector for X-ray absorption spectroscopy (XAS), and an X-ray emission spectrometer.[23] The spectrometers and the sample can be rotated independently along the axis of the incoming beam which allows the polarization of the incoming light and the direction of detection to be varied freely. Two Cu(110) crystals were mounted at a grazing angle (5°) to the incoming beam with their "troughs" (i.e., $[1\bar{1}0]$ azimuths) parallel and perpendicular to the beam, respectively. Clean Cu(110) surfaces were prepared by repeated Ar-ion sputtering and annealing, monitored by

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photoemission spectroscopy and low-energy electron diffraction (LEED). Saturated monolayers of ethylene and benzene were prepared at 80 K.

The Cu(110) surface has 2-fold symmetry with Cu rows in the first atomic layer. For an azimuthally oriented adsorbate, the dipole selection rules governing XES discriminate different emission directions; by recording XE spectra in three different directions (normal emission and grazing emission along the [001] and [1$\bar{1}$0] directions) we can thus separate the spatial orientation of the atomic p-orbitals in the valence electronic structure.[21]

Simulated XE spectra were computed using the deMon program,[24] which implements the Kohn−Sham approach to Density Functional Theory (DFT). The gradient corrected functionals used to describe exchange and correlation were those developed by Becke[25] and Perdew,[26] respectively. The XE spectra were calculated using the resonant term of the Kramers−Heisenberg equation as implemented in the deMon program.[21] The wave functions used were those of the molecular ground state ("frozen orbital approximation"). As in earlier works the core levels were described as symmetry adapted linear combinations of the atomic C 1s orbitals.[27] The surface is represented by a cluster model consisting of 86 metal atoms, where the central Cu_{14} subunit was described at the all-electron level and the surrounding atoms were described using a one-electron effective core potential (ECP) model developed by Wahlgren and co-workers.[28] Further computational details and geometries have been given in refs 21 and 27.

III. Results and Discussion

Gas-phase ethylene belongs to the D_{2h} symmetry group and the electronic configuration is $(1a_g)^2(1b_{1u})^2(2a_g)^2(2b_{1u})^2(1b_{3u})^2(3a_g)^2(1b_{2g})^2(1b_{2u})^2$. The π-orbital is $1b_{2u}$ and the lowest unoccupied molecular orbital is $1b_{3g}$, which is of π^* character. Benzene belongs to the D_{6h} symmetry group and the electronic configuration is $(2e_{1u})^4(2e_{2g})^4(3a_{1g})^2(2b_{1u})^2(1b_{2u})^2(3e_{1u})^4(1a_{2u})^2(3e_{2g})^4(1e_{1g})^4$. The two lowest unoccupied orbitals, $1e_{2u}$ and $1b_{2g}$, are of π^* character. Upon adsorption on the Cu(110) surface the symmetry is reduced to C_{2v} for both ethylene and benzene due to the presence of the surface. To make the discussion simple, the notation of the free molecules will be used.

The Cu(110) surface has 2-fold symmetry with Cu rows in the first atomic layer. The ethylene molecule is adsorbed lying down with the molecular axis parallel with the rows in a bridge site coordinating to two Cu atoms[4,29] (Figure 1). This adsorption geometry implies that the ethylene molecule is bound in the so-called di-σ configuration. For an azimuthally oriented adsorbate the dipole selection rules governing XES discriminate different emission directions; by recording XE spectra in three different directions (normal emission, and grazing emission along the [001] and [1$\bar{1}$0] directions) we can thus project the valence electronic structure on the corresponding atomic $2p_x$, $2p_y$, and $2p_z$ orbitals.[30] Benzene is adsorbed with the molecular plane parallel to the surface with no azimuthal orientation.[10] In this case we can only resolve in- and out-of-plane states, i.e., σ and π orbitals.

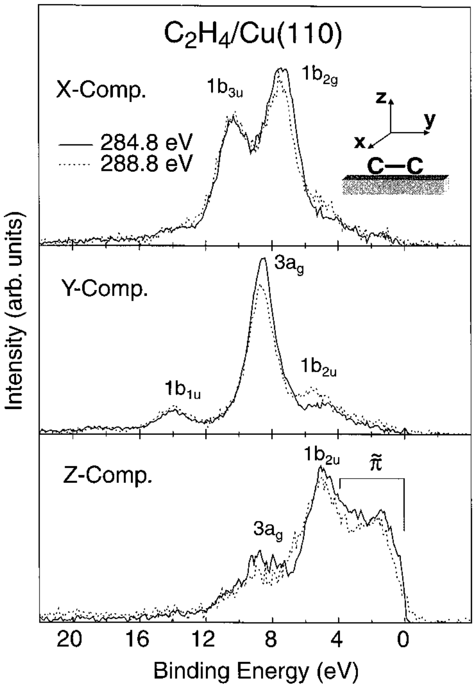

Figure 2. Resonant X-ray emission spectra of ethylene on Cu(110) excited at 284.8 and 288.8 eV excitation energies. Spectral features are labeled by the gas-phase molecular orbital notation. States arising from the surface chemical bond are denoted $\tilde{\pi}$-band.

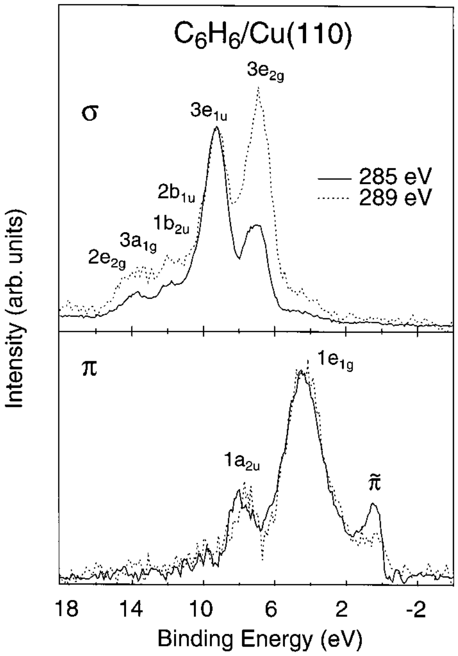

Figure 3. Resonant X-ray emission spectra of benzene on Cu(110) excited at 285 and 289 eV excitation energies. Spectral features are labeled by the gas-phase molecular orbital notation. States arising from the surface chemical bond are denoted $\tilde{\pi}$-band.

Figures 2 and 3 show XE spectra for ethylene and benzene chemisorbed on Cu(110) following excitation using two different photon energies. The polarization vector of the exciting radiation was almost perpendicular (≈85°) to the substrate surface. Hence only transitions into states derived from the π-orbitals of the adsorbate could be excited. The lower energy was chosen to coincide with the first XA resonance (*resonant excitation*) of the respective adsorbate (284.8 (ethylene) and 285 eV (benzene)). The second energy (*off-resonant excitation*) in the case

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of ethylene (288.8 eV) yields an excitation in the Rydberg region. For benzene (289 eV) it coincides with the second π^*-resonance of the surface-adsorbed species. The peak due to elastically scattered photons was removed from the XE spectra as described in earlier work.[14,31] The spectra are plotted on a binding energy scale relative to the Fermi level, obtained by subtracting the C1s core-level photoemission binding energies[32] (284.8 and 284.9 eV for ethylene and benzene, respectively).

The upper panel of Figure 2 shows the symmetry-resolved p components of the XE spectra of chemisorbed ethylene. The $2p_x$ component in the top frame is directed perpendicular to the C−C axis and parallel to the surface. Here, two strong peaks corresponding to the $1b_{3u}$ and $1b_{2g}$ orbitals are observed. These states are bonding within the local C−H unit and weakly bonding and antibonding along the C−C axis. The middle panel contains the symmetry-resolved p_y component, which is directed along the C−C axis. In this component, XE from states representing the molecular $3a_g$ and $2b_{1u}$ σ orbitals are observed. In the free molecule, these orbitals are strongly C−C bonding and antibonding, respectively, and upon adsorption these characters are retained. A third peak is observed at 5 eV, which is a component of the $1b_{2u}$ orbital along the y axis. This peak is a consequence of the internal rehybridization of the molecule. In the lower panel of Figure 2, the XE p_z component is shown. This component is orthogonal to the surface and states representing the molecular $1b_{2u}$ π orbital and the $2p_z$ component of the $3a_g$ orbital are observed. Additionally, a broad band between 0 and 4 eV is found, which we denote as the $\tilde{\pi}$ band.

Figure 3 shows the experimental XE spectra of the chemisorbed benzene on Cu(110). In the top panel, the σ states are shown, representing the $2e_{2g}$, $3a_{1g}$, $2b_{1u}$, $1b_{2u}$, $3e_{1u}$, and $3e_{2g}$ molecular orbitals. In the lower panel of Figure 2 the molecular π-states are shown, representing the $1a_{2u}$ and $1e_{1g}$ orbitals of the free molecule. Furthermore, a new peak between 2 and 0 eV is found, which we again denote as the $\tilde{\pi}$ band. This state has also been observed by two-photon photoemission spectroscopy (2PPE).[33,34]

The adsorption-related $\tilde{\pi}$-band of chemisorbed ethylene and benzene contains important information regarding the surface chemical bond. Therefore, we will center the discussion on the z component of the ethylene XE spectrum and the π component of the benzene XE spectrum.

For adsorbed ethylene a weak excitation energy dependence on the relative intensities of the two orbitals in each of the p_x and p_y component spectra can be seen. The b_{3g} and $3a_g$ orbitals are enhanced indicating that we generate more core holes of ungerade symmetry than gerade symmetry when we excite to the first resonance close to the Fermi level. This indicates that we have more contributions of $\pi^*(1b_{2g})$ than $\pi(1b_{3u})$ character on the adsorbate in the states right above the Fermi level. For the free molecule, resonant excitation into the π^*-resonance imposes strict parity selection rules on the subsequent XES.[35] If we now look in the p_z component spectra we do not see any significant change in the intensity between the two π states for the different excitation energies. We can conclude from the experiment that both the empty states close to the Fermi level and the occupied states should have both $\pi^*(1b_{2g})$ and $\pi(1b_{3u})$ character. These results are in agreement with the DCD model where a donation of π electrons into empty states and back-donation into π^* states yields a symmetry mixing in the occupied and unoccupied orbitals.

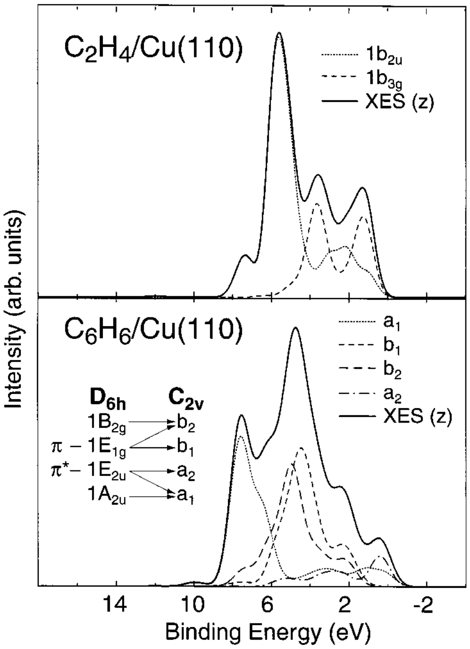

Figure 4. Calculated nonresonant X-ray emission spectra decomposed according to molecular orbital symmetry. Top panel: The X-ray emission z component of ethylene on Cu(110). Bottom panel: The X-ray emission z component of benzene on Cu(110).

In the case of benzene the dependence of the XE spectra on the excitation energy is much more pronounced indicating the preparation of core holes of more pure symmetry upon excitation to the first π^*. Upon resonant excitation the most intense σ-peak consists of three components ($3e_{1u}$, $1b_{2u}$, $2b_{1u}$), which also dominate the resonant XE spectrum of free benzene.[18] The $3e_{2g}$ peak shows significant intensity in the resonant spectrum but should be forbidden according to the parity selection rule. This behavior is known from the XE spectrum of free benzene, where the intensity has been shown to be caused by vibronic coupling to an antisymmetric C−C stretch mode.[18,36] The $\tilde{\pi}$ is clearly enhanced upon resonant excitation, which implies the same symmetry as the first π^* orbital ("LUMO-like"). There is little evidence for any π donation but, on the other hand, there is the appearance of a back-donation state of π^* symmetry close to the Fermi level. However, since the back-donation state is of relatively low intensity we cannot rule out some small symmetry-mixing also in the excited state providing only a small perturbation of the free molecule parity selection.

To investigate the hybrid states directly involved in the surface chemical bond in detail, we computed the symmetry-resolved nonresonant XE spectra of the p_z components in adsorbed ethylene and benzene[21] (Figure 4). Good agreement with experiment is found and in particular the much stronger $\tilde{\pi}$ band of ethylene compared to benzene is well reproduced. For ethylene, the $1b_{3g}$ (π^*) components and the $1b_{2u}$ (π) are shown in the gas-phase notation of the D_{2h} symmetry group, whereas in benzene the symmetry reduction from gas-phase D_{6h} to the adsorbate C_{2v} symmetry group notation does not give a one-to-one correspondence of π and π^* derived states in the

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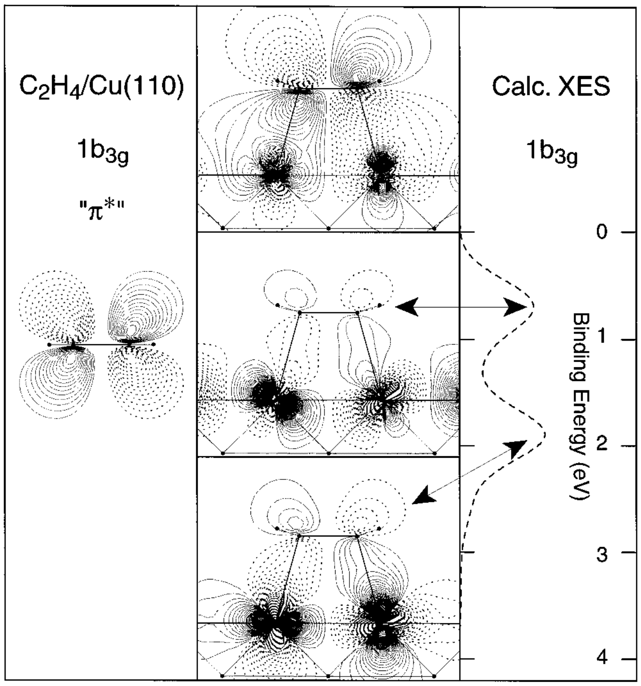

Figure 5. Molecular orbital representation of the ethylene $1b_{3g}$ (π^*) interacting with the Cu(110) surface. Left panel: The unperturbed (π^*) orbitals of free ethylene. Right panel: Calculated $1b_{3g}$ nonresonant X-ray emission component (see Figure 3). Middle panel: Corresponding molecular orbital plots of the chemisorbed ethylene.

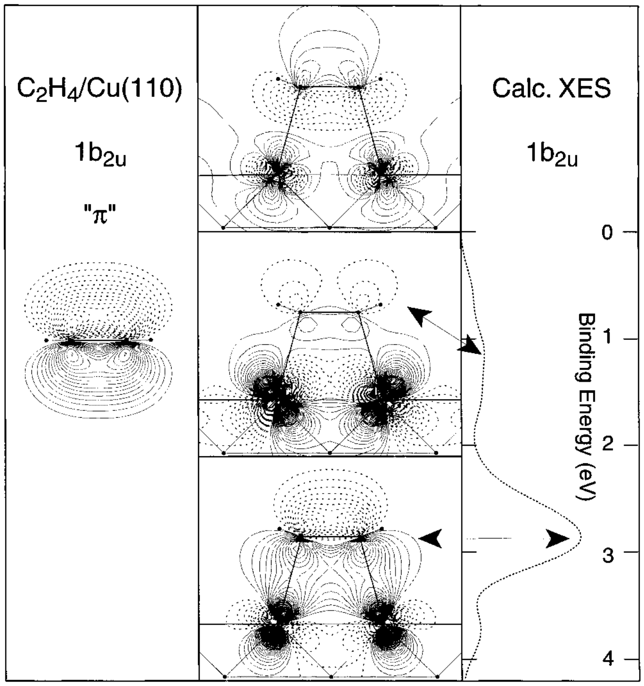

Figure 6. Molecular orbital representation of the ethylene $1b_{2u}$ (π) interacting with the Cu(110) surface. Left panel: The unperturbed (π) orbitals of free ethylene. Right panel: Calculated $1b_{2u}$ nonresonant X-ray emission component (see Figure 3). Middle panel: Corresponding molecular orbital plots of the chemisorbed ethylene.

adsorbate and we are forced to use the C_{2v} symmetry group notation. The transformation between D_{6h} and C_{2v} is shown as an inset in Figure 4.

In adsorbed ethylene an appreciable amount of $\pi^*(1b_{2g})$ occupation is observed manifested as the double peak structure between 0 and 4 eV binding energy in Figure 4. The $\pi(1b_{3u})$ orbital is observed at 5.5 eV, and additional states centered at 2 eV are found. This means that the region between the $\pi(1b_{3u})$ orbital and the Fermi level consists of a distribution of states with a mixture of π and π^* character, which is the reason for the experimentally observed weak variations of XES spectral features for resonant and off-resonant excitation. In adsorbed benzene, there is a clear separation of the same valence region between 0 and 4 eV into benzene π^* derived states of a_1 and a_2 symmetry between 0 and 1.5 eV and the benzene π derived states of b_1 and b_2 symmetry above 1.5 eV. This is the result of much weaker π and π^* mixing for benzene than for ethylene.

To illustrate these orbital interactions further, we show in Figures 5 and 6 orbital plots of the relevant hybrid states, formed in the interaction between the ethylene $\pi^*(1b_{2g})$ and $\pi(1b_{3u})$ with the Cu spd band. On the right-hand side of the figures, the symmetry-resolved spectra of the $\tilde{\pi}$ band from Figure 4 are shown again. The arrows indicate the energy position in the spectrum of the corresponding molecular orbital plots. The orbital plots in the top part of the figures correspond to empty states above the Fermi level.

The lowest orbital plot in Figure 5 shows a strongly bonding combination of the ethylene $1b_{3g}$ (π^*) with the d-orbitals of the two coordinated Cu atoms. For symmetry reasons this hybrid orbital is strongly antibonding between the two Cu atoms. Going toward the Fermi level, another strong state of $1b_{3g}$ symmetry is observed with the corresponding molecular orbital plotted in the middle panel. In comparison to the previous discussed molecular orbital, the bonding combination between the ethylene $1b_{3g}$ and the two coordinated Cu atoms is weaker. This is due to the varying contribution of the Cu d-orbitals with t_{2g} and e_g symmetry interacting with the ethylene $1b_{3g}$ at different binding energies. In a phenomenological approach, we can describe this observation as a continuous rotation of the lobes of the Cu d-orbitals, leading to maximum overlap with the ethylene $1b_{3g}$ at high binding energy and gradually diminishing overlap toward the Fermi level. The top orbital plot represents an antibonding combination between the $1b_{3g}$ (π^*) and the d-orbitals.

Figure 6 shows orbital plots with $1b_{2u}$ (π) character. Again, the lowest orbital plot, representing the state of highest binding energy, shows a strongly bonding combination of the ethylene $1b_{2u}$ with the d-orbitals of the two coordinated Cu atoms. Following the evolution of orbital character toward the Fermi level, a continuous rotation of the lobes of the Cu d-orbitals is observed, as for the π^* interaction in Figure 6. This is leading toward the Fermi level to states, which are less bonding between the ethylene and the two coordinating Cu atoms, and less antibonding between the two Cu atoms (middle panel of Figure 5). The unoccupied state, shown in the upper panel, is in complete analogy to the equivalent state of π^* symmetry in Figure 5 but introduces additional nodes between the substrate atoms.

On the basis of this analysis we can make a simplified model for the chemical bond of ethylene on Cu(110), shown in Figure 7: the HOMO ($1b_{3u}$) and the LUMO ($1b_{2g}$) of the ethylene interact with the t_{2g} and e_g Cu d-orbitals and form two manifolds of hybrid states. The lowest orbitals in both symmetries are bonding between the e_g 3d and ethylene orbitals and the highest is antibonding. The middle orbitals shown as t_{2g} represent a distribution of orbitals in the energy range around the Cu_{3d} band which consists of a mixture of different Cu d-orbitals. This mixing causes a rotation of the Cu_{3d} orbitals from having an amplitude toward the carbon atoms to an essentially nonbonding configuration with the d-orbital amplitude between the carbon atoms.

How do these observations fit into the Dewar−Chatt−Duncanson (DCD) model for the adsorption of unsaturated

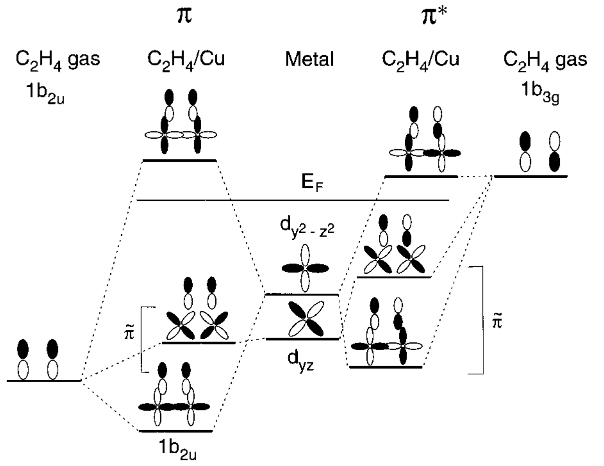

Figure 7. Schematic representation of the bonding mechanism of ethylene/Cu(110. (a) Top panel: Illustration of the π interaction with d-metal orbitals. (b) Bottom panel: Illustration of the π* interaction with d-metal orbitals.

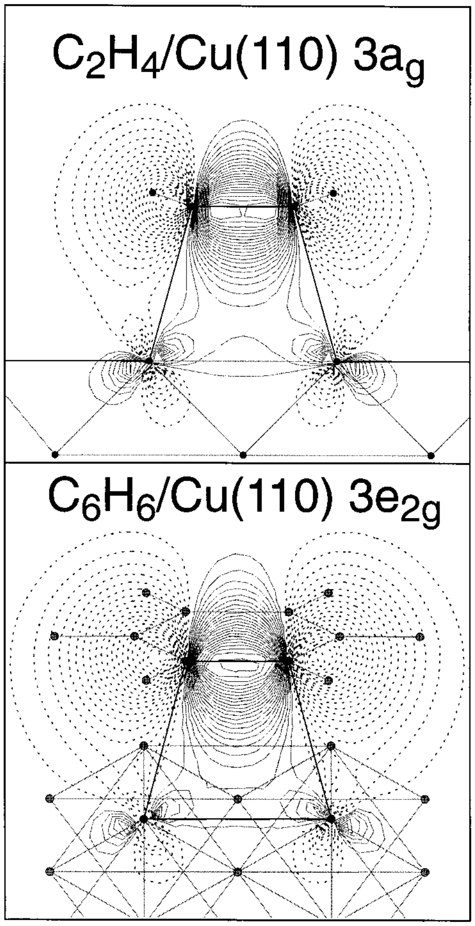

Figure 8. Molecular orbital plots of σ orbitals of ethylene and benzene adsorbed on Cu. The ethylene $3a_g$ orbital shows a significant distortion from the gas phase σ symmetry, due to strong $\sigma-\pi$ hybridization upon adsorption. The equivalent benzene $3e_{2g}$ orbital is less distorted due to weaker hybridization upon adsorption.

hydrocarbons? The π-donation in the DCD model corresponds to the unoccupied antibonding ($1b_{3u}$) orbital and the π*-back-donation to the occupied bonding ($1b_{2g}$) orbital. Since the XES process corresponds to an experimental population analysis we use the calculated spectra for each symmetry to quantify the degree of donation and back-donation. If we normalize the integrated intensities of each symmetry to the intensity of the ($1b_{3u}$) orbital of free ethylene we obtain an estimate of the total occupancy of each symmetry in electrons per atom. The result is an occupancy of the π ($1b_{3u}$) by 0.52 electron, equivalent to a donation of 0.48 electron, and an occupation of 0.22 electron of the π* ($1b_{2g}$), equivalent to back-donation. In comparison, for adsorbed benzene electron populations of 0.76 π electrons and 0.1 π* electrons per carbon atom are found which is only half the donation and back-donation per carbon atom obtained for ethylene. From this it is evident that adsorbed benzene, to a much larger degree than ethylene, keeps the orbital structure of the free molecule intact upon adsorption. The orbital structure of adsorbed benzene is rather complicated, however, since benzene has many more π orbitals than ethylene. However, for both molecules an overall loss of π character takes place upon adsorption, which is in full agreement with the observed decrease in work function for hydrocarbon-adsorption.

Energetically, the adsorption of ethylene and benzene on Cu-(110) has been computed in a previous study,[4] where the chemisorption energy of ethylene was determined to be 13 kcal/mol and that for benzene to be 14 kcal/mol. Under the assumption that each carbon atom contributes equally to the total chemisorption energy we obtain for ethylene a chemisorption energy per carbon atom of 6.5 kcal/atom, while for benzene it is 2.3 kcal/atom. This trend in chemisorption energetics per carbon atom follows the degree of donation and back-donation for adsorbed ethylene and benzene.

In the spin-uncoupling mechanism[4] the interaction energy per molecule upon adsorption is seen as a balance of the rehybridization cost and the gain from the formation of bonds to the surface. The rehybridization cost is obtained by explicitly considering the excited state of the adsorbate that corresponds to the bonding state. Adsorbed ethylene corresponds to the eclipsed conformation of the triplet gas-phase ethylene, where the electron occupation of the π orbital per carbon atom is equal to 0.5. To achieve the same π occupancy per carbon atom for the benzene molecule the benzene molecule must be promoted into the septet state with an excitation energy exceeding 300 kcal/mol. This large excitation energy cannot be compensated by the C−Cu bonds.[4] Consequently, the planarity of the free benzene molecular carbon ring is largely maintained upon adsorption as no direct covalent carbon−copper bonds to the substrate can be formed and the bonding must take place only through a polarization of the π-system.

The large difference in the degree of donation/back-donation and in particular the degree of $\sigma-\pi$ mixing for ethylene and benzene upon adsorption can be illustrated through molecular orbital plots of characteristic σ orbitals of the chemisorbates, i.e., the ethylene $3a_g$ and benzene $3e_{2g}$ orbitals. For ethylene (upper panel Figure 8) a significant distortion of the ethylene $3a_g$ gas-phase orbital due to the interaction with the d-orbitals of the two neighboring Cu atoms is found. For benzene, in the lower panel of Figure 4, the distortion of the benzene $3e_{2g}$ gas-phase orbital upon adsorption is much smaller in comparison to the corresponding state of ethylene. Our observations of strong $\sigma-\pi$ mixing for adsorbed ethylene, but weak mixing for benzene, can also be put into perspective of the known elongation δr of the C−C bonds upon adsorption. For ethylene, δr is three times larger ($\delta r = 0.06$ Å) than for benzene ($\delta r = 0.02$ Å).[4]

IV. Conclusion

In summary, the XE spectroscopy allows the symmetry of the adsorbate states to be identified in terms of π and π* and consequently the suitability of the Dewar−Chatt-Duncansson model to be verified. This model captures the overall mechanism of the interaction of unsaturated hydrocarbons with metal surfaces well, by postulating donation and back-donation between frontier orbitals. The charge transfer upon adsorption from the molecular π into the unoccupied metal orbitals and the back-donation from the occupied metal orbitals into the π^* is found to be twice as large for ethylene as for benzene. In particular, the degree of donation/back-donation is accompanied by the internal $\sigma-\pi$ mixing within the adsorbed molecules. These results give an experimental verification of the DCD donation/back-donation bonding model for unsaturated hydrocarbons on metal surfaces.

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