An Atom-Specific Look at the Surface Chemical Bond

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High resolution x-ray emission spectroscopy is shown to reveal unprecedented details of the chemical bond formed between a molecule and a transition metal surface. An atom and symmetry projected view of the bonding orbitals is obtained. We find that all outer and inner valence orbitals of the molecule change due to the surface interaction. New types of molecular states are observed which are a direct signature of the surface chemical bond. [S0031-9007(97)02814-7]

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It is generally assumed that the bonding of molecules to transition metals can be explained in terms of the interaction of the frontier orbitals, i.e., the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals of the free molecule with the metal d orbitals [1–4]. This model of the surface chemical bond implicitly assumes that the intramolecular bond is stronger than the molecule-substrate bond so that the molecule can be treated as a unit. In principle, however, it is more appropriate to use an atom-based, or linear combination of atomic orbitals (LCAO) type, description. Because conventional experimental techniques, in particular ultraviolet photoemission spectroscopy (UPS), do not allow an atom-based view of bonding effects, an LCAO-based look at the surface chemical bond has not been possible experimentally. Another complication has been the energetic overlap of the most important signatures of the surface chemical bond with the metal d states. The dominance of the d states in the electronic spectra has made it difficult to observe the direct signature of the surface chemical bond in all but a few selected cases [5].

Using monochromatic x rays from an undulator beam line on the advanced light source (ALS), we have obtained angle dependent x-ray emission (XE) spectra which allow an atom-specific look at the surface chemical bond. The atom specificity in XE is due to the localization of the core-excited intermediate state [6]. Thus the molecular contributions to the valence electronic states can be separated from those of the substrate. Furthermore, angle dependent measurements allow the determination of the symmetry of the molecular states, e.g., the separation of π and σ states [7]. We have obtained detailed results for two prototype "σ" and "π" bonding systems, standing up N_2 on Ni(100) and lying down C_6H_6 on Ni(100). The upright adsorption geometry of N_2 on Ni(100) [8] in an on top site [9] is usually explained in analogy with the isoelectronic CO molecule in terms of the Blyholder model [1], i.e., a synergetic σ (HOMO) donor and π (LUMO) backdonation bond. We show here that this model is incorrect. On the other hand, benzene has long served as an example of π bonding [4,10]. Again, our results indicate that this picture is greatly oversimplified.

The experiments were performed on beam line 8.0 at the ALS which is equipped with a spherical grating monochromator. The resolution of the exciting radiation was set to 0.4 eV for N_2 and 0.8 eV for C_6H_6. XE spectra were measured with an energy resolution of 0.5 eV using a grazing incidence spectrometer [11] which can be rotated around an axis parallel to the incoming beam. A $c(2 \times 2)$ overlayer of N_2/Ni(100) was prepared by a 10 L dose at temperatures below 110 K [12]. Saturated benzene overlayers, exhibiting a $c(4 \times 4)$ LEED pattern, were prepared by annealing predosed multilayers to 200 K [13]. To avoid damage of the overlayer during the XE measurements the spectra were collected by scanning the sample in front of the spectrometer entrance slit. X-ray absorption (XA) spectra were recorded with an energy resolution of $\leq$50 meV using partial yield detection [4].

In order to avoid multielectron (shake-up) effects, the XE spectra for both adsorption systems were recorded following excitation of a K-shell electron in the molecule to the lowest unoccupied π^* orbital. To maximize the x-ray absorption cross section for the π^* system, the exciting radiation was incident at a grazing angle on the sample with the $\vec{E}$ vector parallel to the surface for N_2 and perpendicular for C_6H_6. XE spectra were recorded at both grazing and normal emission directions by rotating the x-ray spectrometer around the sample. In normal emission, orbitals with a maximum amplitude parallel to the surface are probed while in grazing emission orbitals both parallel and perpendicular to the surface contribute to the spectrum [7,14]. The contributions from orbitals perpendicular to the surface can then be obtained by a substraction procedure, assuming equal contributions from both types of orbitals in the grazing emission spectrum. Since the initial state in the XE process involves a $1s$ core hole we observe only the $2p$ density of states in all spectra. Because of the core-hole localization, the transition matrix element in the

XE process will be dominated by $2p \rightarrow 1s$ transitions on the specific atomic site where the core-hole was created.

Previous work has shown that the XA spectrum for $N_2/Ni(100)$ exhibits two $1s \rightarrow 2\pi^*$ resonances at 400.6 and 401.0 eV [15], corresponding to the outer and inner N atoms, respectively. Hence by using slightly different excitation energies, atom-specific XE spectra can be recorded. The resulting XE spectra for the outer and inner N atoms are shown in Fig. 1. The spectra are plotted on a common binding energy scale relative to the Fermi level, obtained by subtracting the N 1s core-level photoemission binding energies of the two atoms (outer atom: 399.4 eV; inner atom: 400.7 eV, [12]) from the emitted photon energies [16]. The figure is divided into an upper part, displaying states of σ symmetry (obtained by substracting the normal emission spectra scaled by 0.5 from the grazing emission spectra [14]), and a lower part, displaying states of π symmetry (the normal emission spectra). From the symmetry and binding energies of the spectral features, it is straightforward to assign all features above 5 eV binding energy in analogy with UPS measurements [17,18]. In order to facilitate the comparison with the much studied CO molecule we shall use $C_{\infty v}$ symmetry notation for the molecular orbitals.

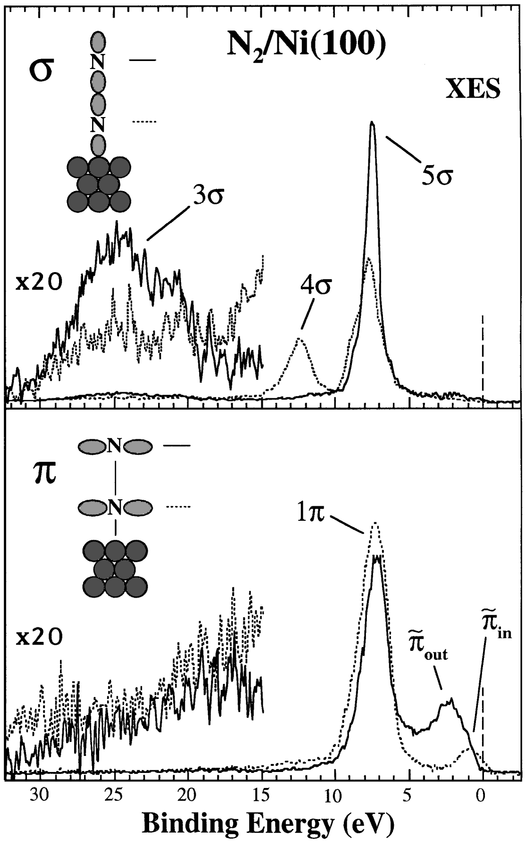

FIG. 1. Symmetry resolved x-ray emission spectra for the inner (dashed line) and outer (full line) N atoms for $N_2/Ni(100)$. The two N atoms were separated by selected x-ray excitation at 400.6 eV (outer atom) and 401.0 eV (inner atom). The π symmetry spectrum is the normal emission x-ray emission spectrum. The σ symmetry spectra were obtained by substracting the normal emission spectra scaled by 0.5 for the grazing emission spectra. Peaks in the spectra are labeled by the corresponding molecular orbitals. New orbitals arising from the surface chemical bond are indicated by a tilde symbol.

The novel information contained in Fig. 1 is the large difference in the states located on the inner (dashed line) and outer (full line) N atoms and the clear resolution of the structure within 5 eV binding energy, i.e., in the Ni d band region. All spectral peaks, representing the 2p atom-projected molecular orbitals, exhibit different intensities or shapes for the inner and outer N atoms. Even the 3σ state, located about 25 eV below the Fermi level, shows an intensity difference for the two atoms demonstrating that the chemisorptive bond affects even the inner valence levels. Other interesting findings are the localization of the 4σ state on the inner N atom, with no visible intensity on the outer N atom, and the larger 5σ localization on the outer N atom. Near the Fermi level we observe the molecular states which are most important for the surface chemical bond. These states arise from interaction of molecular π states with the Ni d band. The state located on the outer N atom is centered at about 2.5 eV binding energy, while the state located on the inner N atom is centered at about 1 eV. No significant states of σ symmetry are observed in the Ni d band region near the Fermi level.

In Fig. 2 we illustrate how our results compare with the Blyholder model, where the surface chemical bond is described by the interaction of the 5σ and $2\pi^*$ molecular states with the metal d states in a donation and backbonding picture. The backbonding should give rise to an occupied $2\pi^*$-Ni 3d hybrid orbital. This is not what we see in our spectra. Instead we observe the appearance of two new states $\tilde{\pi}_{\mathrm{in}}$ and $\tilde{\pi}_{\mathrm{out}}$. These states can be generated only through a linear combination of the original 1π and $2\pi^*$ orbitals. We picture the $\tilde{\pi}_{\mathrm{in}}$ state to be strongly Ni-N bonding and the $\tilde{\pi}_{\mathrm{out}}$ state is essentially a N 2p lone pair. It may contain some nonbonding Ni contribution. The observed changes in the π system upon chemisorption resemble those between free CO and H_2CO. When two hydrogen atoms are added to CO to form H_2CO one of the π orbitals breaks up into a local C-H bonding orbital ($1b_1$) and an O 2p nonbonding lone pair orbital ($2b_1$), in analogy to the $\tilde{\pi}_{\mathrm{in}}$ and $\tilde{\pi}_{\mathrm{out}}$ states, respectively.

In the spectra we do not see any new occupied states of σ symmetry and in previous XA spectra of adsorbed N_2 there is no indication of any new states above the Fermi level [19]. Thus we do not observe any bonding and antibonding states indicative of a significant 5σ contribution to the surface chemical bond. This supports the cluster calculations of Bagus *et al.* [20], which show the σ contribution to be mainly repulsive. Our spectra show the repulsion effects as a redistribution of the molecular σ system upon formation of the surface chemical bond. The 4σ state becomes polarized on the

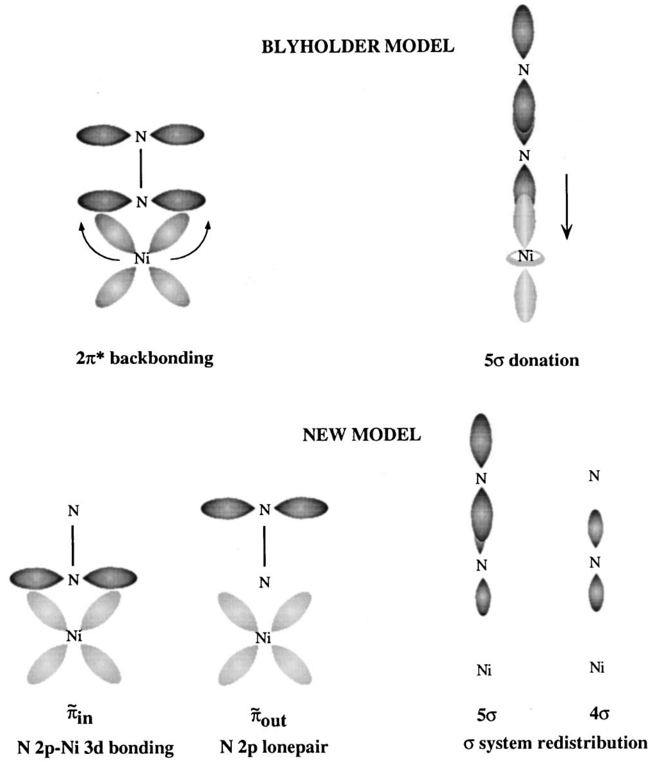

FIG. 2. Schematic illustration of the interactions of the π orbitals, to the left, and σ orbitals, to the right, with the Ni 3d band for the N_2/Ni(100) system in the Blyholder model and based on our new results.

inner and the 3σ and 5σ states on the outer nitrogen atoms. Surprisingly, all valence states, down to the 3σ state around 25 eV binding energy, are affected by the formation of the chemisorption bond. Despite the relative weakness of the chemisorptive (≈ 0.4 eV) relative to the intramolecular bond (≈ 8 eV) the intramolecular bonding is completely changed upon chemisorption. The resulting electronic structure of the chemisorption complex is best described in an atom-based picture.

The bonding of benzene to a transition metal is typically viewed to involve the π system. XE and XA spectra for benzene on Ni(100), shown in Fig. 3, support this picture. XE spectra were taken at an excitation energy of 286 eV [C 1$s \rightarrow \pi^*(e_{2u})$]. The spectra are plotted on a photon energy as well as binding energy scale, where zero energy refers to the Fermi level position. This position was obtained from a photoemission measurement of the C 1s core level binding energy [16], 284.1 eV for C_6H_6/Ni(100). The assignment of the XA features [4] and the XE features with binding energies larger than 4 eV [21] are known from the literature.

The pronounced polarization dependence of the XA spectrum clearly shows [4] that benzene is adsorbed with the molecular plane parallel to the Ni(100) surface. Based on this adsorption geometry, the XE spectra shown in Fig. 3, corresponding to pure σ and π symmetries, were obtained from the normal emission spectrum and by substraction of the normal emission spectrum, scaled by 0.5, from the grazing emission spectrum [14]. The spectrum for pure π symmetry (dashed line) reveals three distinct peaks, the $1a_{2u}$ and $1e_{1g}$ out of plane π orbitals and a third state, labeled $\tilde{e}_{2u}$, not seen for the free molecule. This state, located 1.7 eV below the Fermi level and hence overlapping the Ni d band region, originates from the surface chemical bond. It arises from the interaction of the e_{2u} orbital with Ni d states, resulting in an occupied $\tilde{e}_{2u}$ bonding state, observed in XE, and an empty antibonding $\tilde{e}^*_{2u}$ state, observed in XA. The strong molecular character of the bonding $\tilde{e}_{2u}$ state, revealed by its large spectral intensity, implies that the respective antibonding $\tilde{e}^*_{2u}$ state has significant metal character. This is confirmed by the reduced intensity of the $\tilde{e}^*_{2u}$ XA peak relative to the e^*_{2u} resonance in the gas phase spectrum [4]. The formation of a single bonding state rather than a band suggests that the e_{2u} orbital interacts mainly with localized states, i.e., the Ni d band.

For the σ symmetry XE spectrum in Fig. 3 (solid line) we observe the expected molecular orbitals at binding energies larger than 5 eV [10]. Here the interesting result is that there is significant σ intensity all the way to the Fermi level, marked $\tilde{\sigma}$ in Fig. 3. Similar states are also observed in the XA spectrum [22], indicating a significant σ contribution to the surface chemical bond.

While the observed backdonation of the e_{2u} orbital agrees with the conventional picture of π bonding of the benzene molecule to metal surfaces, the sizeable

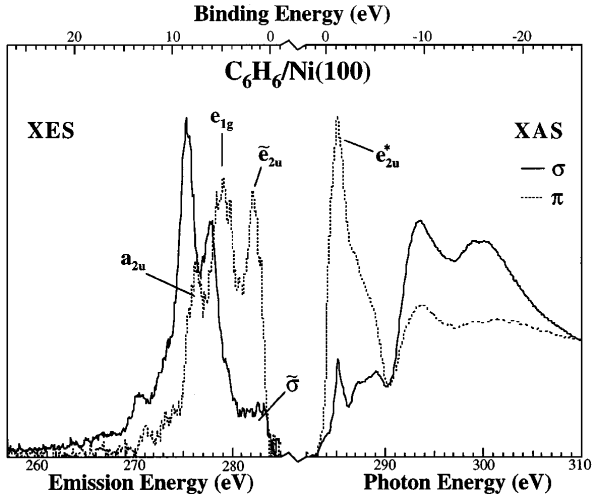

FIG. 3. Symmetry resolved x-ray emission and x-ray absorption spectra for benzene on Ni(100). The x-ray emission spectrum was recorded at an excitation energy of 286.0 eV. The σ symmetry XES spectrum (full line) is the normal emission x-ray emission spectrum, the π symmetry spectrum (dashed line) was obtained by a suitable linear combination of the grazing and normal emission spectra. The π symmetry peaks in the spectra are labeled by the corresponding molecular orbitals, empty states being designated by an asterisk. New orbitals arising from the surface chemical bond are indicated by a tilde symbol.

contribution of benzene σ states to the bond is interesting. A broken molecular symmetry would lead to a mixing of π and σ states [23] but a σ-π hybridization cannot entirely explain the smooth, bandlike character of the observed $\tilde{\sigma}$ states. Hybridization would impose a replica of the π density of states on the σ distribution, but no remainder of the pronounced $\tilde{e}_{2u}$ peak at 1.7 eV binding energy is observed in the σ geometry. The smooth, bandlike character of the $\tilde{\sigma}$ states indicates a contribution of delocalized states to the bond and is thus likely due to an interaction of benzene σ states with both the Ni *sp* and *d* bands. Since the HOMO and LUMO σ orbitals contain C-H contributions we can anticipate that the presence of these new states affects the C-H bond. Thus the σ contribution to the surface chemical bond, revealed by our experiments, has direct implications for the important hydrogenation and dehydrogenation reactions of aromatic hydrocarbons on metal surfaces.

In summary, the present experiments shed new light on the details of the surface chemical bond and provide direct evidence for interaction effects which have remained hidden in previous experimental work on this topic. They should stimulate new theoretical work which emphasizes an atom-projected description of the surface chemical bond.

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