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Electronic structure of benzene on Ni(100) and Cu(110): An x-ray-spectroscopy study

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The valence electronic structure of benzene chemisorbed on Ni(100) and Cu(110) has been studied using angle-dependent x-ray emission and x-ray absorption spectroscopy. These techniques allow us to resolve the benzene *p* contributions involved in the chemical bond. Symmetry selection rules observed in resonant inelastic x-ray scattering are applied for the adsorbate case to identify the symmetry of new π states formed in the chemical bond. Based on x-ray absorption results we conclude that benzene adsorbs with the molecular plane parallel to both surfaces. On Ni a new, third π state is observed 1.8 eV below the Fermi level. Comparing resonant and nonresonant excitation its symmetry character is identified as being of e_{2u} type. The corresponding $\pi^* e_{2u}$ x-ray absorption intensity is strongly reduced. This is attributed to a splitting of the previously unoccupied e_{2u} orbital into bonding and antibonding states due to adsorbate π-substrate $3d$ interaction leading to a π backdonation bond. Moreover, a broad distribution of σ-symmetric states is observed all the way up to the Fermi level, indicating that despite of rehybridization σ states also contribute to the chemical bond. On Cu(110) in contrast a new, third π state is cut by the Fermi level. This indicates a resonancelike broadening of the e_{2u} orbital due to interaction with the Cu *sp* band. Additional benzene σ density of states is observed that tracks π emission and is attributed to weak hybridization in the chemisorbed state. The presented results give insights in the bonding of benzene to metal substrates and suggest that the usual π-donation bonding model of benzene to metal surfaces has to be extended.
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I. INTRODUCTION

One of the goals in surface science is to understand the interaction between a gas particle and a surface in terms of the chemical bond formed upon adsorption. For chemisorbates this bond is naturally mediated via the valence states present on both the adsorbate and the substrate. The identification of the modified electronic structure is therefore a key ingredient for the understanding of the adsorbate-substrate chemical bond.

The technical importance of hydrocarbon adsorption on metal surfaces has led to great interest in these systems and there exist numerous studies, addressing both fundamental and applied issues.[1] Benzene has been used for a long time as a prototype system to study these effects for a somewhat larger, aromatic hydrocarbon molecule. While most of these studies address structural topics, such as the symmetry of the adsorption complex, i.e., the orientation of the molecule with respect to the substrate, still little is known about the electronic structure in view of the chemical bond itself. It is generally accepted that the molecule adsorbs with the aromatic ring parallel to almost all metal surfaces (for a compilation see, e.g., Refs. 1 and 2). This adsorption geometry has led to the conclusion that the bond to the substrate involves mainly the benzene out of plane π orbitals. Upon benzene adsorption a decrease of the work function was found that suggests a negative dipole moment of the adsorbed species. While work-function changes are certainly a rather indirect indication they nevertheless were used to argue that benzene bonding involves a charge transfer from the adsorbate to the substrate, i.e., a dominating π donation bond in contrast to π backdonation. Moreover, it was suggested that rehybridization is weak, compared to, e.g., olefinic hydrocarbons, and despite weak rehybridization the contribution of σ symmetric states to the bonding is negligible.

Today knowledge of the valence electronic structure of benzene on metal substrates is mainly based on photoemission measurements (see Ref. 2 and references therein) and some theoretical studies.[3–6] Photoemission reveals that only the occupied out of plane π orbitals ($1e_{1g}$ and $1a_{2u}$) of the molecule exhibit significant differential shifts upon adsorption, usually interpreted as a signature for the involvement of these states in the chemical bond.

There is no uniform model of benzene chemisorption from theoretical studies, however, all calculations reveal changes in the benzene π system. In line with the experimental observations, mainly a modification of the occupied π states was found. From semiempirical molecular orbital calculations Anderson *et al.* predict a shift of the empty e_{2u} (π) orbital to lower energies. They do, however, not find evidence for electron transfer from the metal to the adsorbate for their cluster models of the Pt and Ni(111) surface.[3] Jing and Whitten investigated benzene chemisorption on Ni(111) by ab initio calculations using a cluster approach.[5] The authors find π donation and backdonation contributions, where charge transfer from the adsorbate to the substrate dominates. They conclude, that the strongly interacting π orbital is located 7.6 eV below the Fermi level and that benzene σ orbitals do not participate significantly in the bonding. Tight-binding calculations studying mainly structural aspects predict that benzene ring distortions on Rh(111) and Pt(111) result from π donation-backdonation bonding.[7] It should be mentioned that all calculations cited are restricted to fixed positions of the surface atoms. Recent LEED studies of the saturated benzene layers on Ru(001) (Ref. 8) and Ni(111) (Ref. 9) however, demonstrate that benzene chemisorption causes a significant substrate reconstruction, while the benzene ring is almost unaffected. This indicates the difficulties that might occur by modeling benzene chemisorption with a fixed, bulk terminated surface structure.

While some occupation of the unoccupied π states (e_{2u} and b_{2g}) is thus predicted by theory, no direct evidence was found experimentally. However, a considerable fraction of electronic states that are formed in the surface chemical bond can hardly be probed with photoemission, since they overlap with the metal valence band and are therefore obscured by substrate emission. It has recently been demonstrated, that this particular limitation can be overcome using x-ray emission spectroscopy (XES).[10–14] In XE the contribution of states located on the adsorbate can be separated from substrate emission, since the valence density of states is probed via an intermediate, core-excited state and the energies of emission lines from different elements (adsorbate and substrate) are thus separated by the respective corehole binding energies. The final state of the emission process, however, is a one-hole, quasiparticle state as in valence-band photoemission (UPS).

Thus selective excitation of different core levels, e.g., in a heteronuclear molecule, allows to project out the valence electronic structure on each individual atomic site. More specific, for carbon the *p* components of the valence orbitals in the excited state are projected on the 1*s* core hole. States of different symmetry are furthermore identified by use of angular dependent XES (see, e.g., Ref. 13).

As already mentioned contrary to photoemission the intermediate state in the XE process contains a core hole, while the initial state (prior to absorption of the exciting photon) corresponds to the ground state and the final state to a one-hole quasiparticle state. Thus the energies of emission lines can be directly related to the binding energies measured in valence-band photoemission. Note that differences in the line shape may still occur due to different vibronic coupling in UPS and XES. The important question remains, however, what influence the core hole has on the intensities of the XE spectrum. Based on experimental results from XES on simple metals, van Barth and Grossmann formulated what is known as the final-state rule.[15] In accordance with the theory of Grebennikov, Babanov, and Sokolov[16] they found that the spectral distribution is governed by the final-state electronic configuration (i.e., without the core hole) weighted by a dynamic factor resulting in a singular behavior near the Fermi level. These dynamic effects correct for the influence of the core hole. Model calculations for an homogeneous electron gas demonstrate that dynamic effects become more important for metallic systems with nearly empty bands.[17,18] In the case of filled bands the core-hole effects can be neglected.

Recent cluster calculations of the XE process for CO on Cu give no significant modification of the interpretation using ground-state frozen orbitals (without core hole) or a fully relaxed core-hole state for the more tightly bound valence electrons, respectively.[19] However, the calculations show a large enhancement in intensity for the states close to the Fermi level when the fully relaxed core-hole state is used. This enhancement resembles the singular behavior close to the Fermi level described in the above-cited electron gas calculations. In contrast, this effect is not seen in the experimental spectra.[20] Instead, the structures close to the Fermi level are well reproduced using frozen orbitals in the core-hole state. There are additional effects not taken into account in the calculations, such as valence-hole relaxation and differences in electron correlation, which might cancel the model-induced core-hole effects. We can argue that adsorbate systems containing carbon are close to the case of nearly full bands with weak or even negligible singular behavior. Further theoretical as well as experimental investigations are definitely necessary to provide a deeper understanding of all these effects and to set a limit for the use of the final-state rule. While it is tempting to use XE intensities to describe the chemical bonding and thus ground-state properties, we have restricted the analysis of benzene bonding in the following discussions to arguments concerning the energetic positions of the XE emission lines and their symmetry while complementary information on intensities is derived from the x-ray absorption spectra.

In this work we compare angular-dependent XES studies of the electronic structure of benzene on the Ni(100) and Cu(110) substrates. Changes of the emission spectra with excitation energy are discussed in terms of symmetry conserving resonant inelastic x-ray scattering (RIXS) and used as a tool to determine the origin of states formed in the chemical bond. A brief discussion of benzene on Ni(100) is given in a previous publication.[14] From thermal desorption spectroscopy it is known that benzene chemisorption is stronger on Ni than on Cu surfaces.[21,22] A detailed picture of the bonding on a microscopic level however is still missing. Due to the different energetic positions of the *d* bands with respect to the Fermi level and thus to the benzene π system one generally expects changes in the coupling of the benzene π orbitals to the substrate *d* and *sp* band.

II. EXPERIMENT

The experiments were carried out at beamline 8.0 of the advanced light source (ALS), Lawrence Berkeley Laboratory. This beamline combines a 89×5 cm period undulator with a modified spherical grating monochromator. The beam size, critical for XES, is measured to be smaller than 100 ×100 μm. The end station consists of two UHV chambers for sample preparation and analysis. The base pressure in the system was 1×10^{-10} mbar. The analyzer chamber is rotatable around an axis parallel to the incoming beam and houses an electron energy analyzer (Scienta SES 200),[23] an x-ray emission spectrometer (both mounted perpendicular to the incoming beam) and a multichannel plate detector for x-ray absorption measurements (XAS).

The XA spectra were recorded in partial yield mode and doubly normalized to the signal of the clean sample and to the photon flux as measured by the photocurrent from a fresh evaporated gold mesh placed close to the final refocussing optics of the beamline. The undulator gap and monochromator were scanned in parallel and the resolution of the exciting radiation was set to about 50 meV. The sample surface is tilted with respect to the incident beam by 3°. Thereby excitation geometries with the field vector aligned parallel and nearly perpendicular (3° tilt) to the surface are realized by rotating the crystal by 90° around the axis of the incoming light. For an undulator beamline we expect a degree of linear polarization around 90–100 %. This was confirmed experimentally by the XA spectra of CO on Ni(100) and format on Cu(110) with well-known adsorption geometries.

By rotation of the spectrometer chamber grazing and normal XE spectra are recorded for a fixed excitation geometry. For the present experiment the field vector of the incident radiation was aligned parallel to the surface normal. XE spectra for normal emission are collected along the surface normal, while grazing emission spectra were recorded with the spectrometer (entrance slit) rotated by 80° with respect to the sample normal (see also the inset of Fig. 3). The XE spectrometer is based on gratings operating in grazing incidence and a movable multichannel detector.[24] The acceptance angle of the spectrometer defined by the entrance slit, oriented along the axis of the beam, and the illuminated area of the gratings is about 3°. The resolution of the spectrometer was set to 0.5 eV, corresponding to a slit size of 20 μm. The bandwidth of the exciting radiation was 0.8 eV. The sample is mounted on a computer controlled manipulator and was cooled by liquid nitrogen to 80 K. 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 with fixed excitation geometry. All measurements were performed in grazing incidence (3°) to enhance the surface sensitivity.

Saturated benzene overlayers on Ni(100) were prepared by annealing predosed multilayers to 200 K. On Cu(110) the monolayer was prepared by dosing 3 L at 80 K via a prefilled volume with a multicapillary array outlet. For the saturated benzene layer on Ni(100) a $c(4\times4)$ low-energy electron diffraction (LEED) pattern was observed in accordance with the findings in Ref. 25. The layers were characterized by high-resolution x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS).

III. RESULTS AND DISCUSSION

A. XPS

XPS spectra recorded with a photon energy of 420 eV are depicted in Fig. 1. The $C1s$ line appears at 284.1 eV for benzene on Ni(100) and at 284.9 eV on the Cu(110) surface. For the Cu surface the mainline is significantly broadened [full width at half-maximum (FWHM) 1.15 eV] as compared to benzene on Ni (FWHM 0.7 eV). We can distinguish between homogeneous and heterogeneous broadening. Different mechanism of homogeneous line broadening in core-level spectra from adsorbed molecules are discussed in the literature, such as dynamic screening of the final core-ionized state and vibrational broadening (see, e.g., Ref. 26). The magnitude of this effects depends on the coupling to the substrate in the core exited state and the corrugation of the initial- and final-state potential, respectively. For larger molecules like benzene the molecule extends already over several adsorption sites and thus site-specific changes of the potential in the initial and final core-ionized state will lead to an additional line broadening. This effect should be more pronounced for an open (110) substrate and is likely to explain the observed line broadening on the Cu surface. A similar sampling effect could arise from different adsorption sites of the molecule.

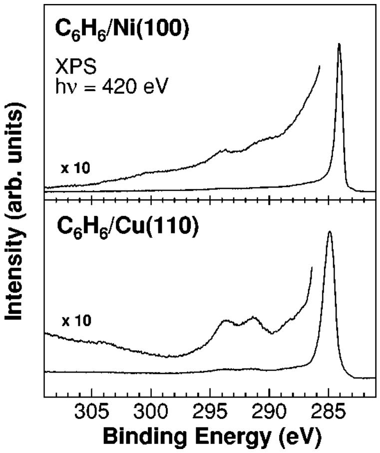

FIG. 1. XPS spectra for benzene on Ni(100) (top) and Cu(110) (bottom) measured at a photon energy of 420 eV. The respective shakeup regions are shown on an enlarged intensity scale.

The shakeup regions for the two systems are compared on an enlarged intensity scale. Two peaks, more pronounced for benzene on Cu(110) (6.2 and 8.8 eV),[27] shifted towards higher energies on the Ni(100) surface (6.7 and 9.8 eV) are observed. For free benzene several shakeup peaks, which are assigned to transitions within the π system, are found in the energy range between 5 and 11 eV.[28] Note that for the free molecule monopol transitions in the π system require that the ground-state D_{6h} symmetry is reduced to C_{2v} upon creation of the core hole. This lowering of the symmetry from D_{6h} to C_{2v} is accompanied by a splitting of the former degenerated π and π^* levels, leading to several, energetically separated, allowed monopol shakeup transitions.[28] From the shakeup spectra rather indirect conclusions of the electronic structure of the adsorbed molecules can be drawn. Overall the shakeup spectra are strongly influenced by the bonding of the benzene molecule to the substrate. By comparison to the XP spectrum of the free molecule the two resolved peaks for benzene on Cu(110) are attributed to transitions in the π and π^* manifold. For Ni these transitions are smeared out and shifted to higher energies. The more pronounced structures on Cu indicate, that the benzene π system closer resembles that of the free molecule. This is in line with the expected weaker interaction of benzene with the Cu substrate and thus smaller hybridization with metal states and will be corroborated by the XA results.

B. XAS

To independently characterize the orientation of the molecules and to determine excitation energies for resonant inelastic x-ray scattering XA spectra were recorded for two excitation geometries. Spectra measured with out of plane (top) and in plane polarization (bottom) are depicted in Fig. 2 for benzene on Ni(100) (solid line) and Cu(110) (dashed line). The excitation geometries are illustrated as icons in the figure.

The spectra have been aligned on a common energy scale by measuring the Fermi edge at the start of each scan and

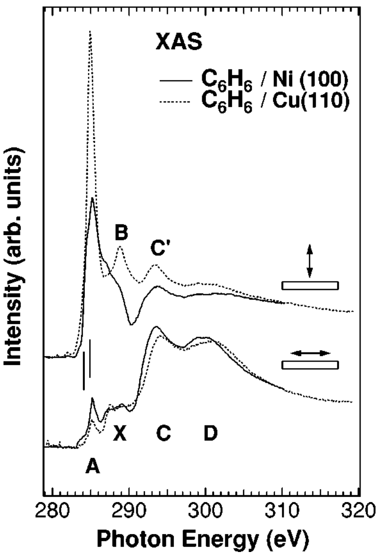

FIG. 2. Comparison of XA spectra for benzene on Ni(100) (solid lines) and Cu(110) (dashed lines). The icons indicate the orientation of the field vector with respect to the surface. The vertical lines mark the respective XPS binding energies; the labels are explained in the text.

cross checked using a characteristic carbon structure of the monochromator. From this procedure we estimate an relative error of the energy scale below 0.1 eV. The spectra are normalized to provide comparable edge-jump intensities.

Overall the strong polarization dependence indicates a well-oriented adsorption complex on both substrates.

Six structures (*A*, *X*, *B*, *C*′, *C*, and *D* following the labels in Refs. 29 and 30) can be distinguished. Even though there exist a large number of experimental[29–35] and theoretical[29,36–38] studies, the assignment of these transitions is still controversial.

The strong peak *A* at threshold [285.2 eV on Ni(100) and 284.9 eV on Cu(110)] is universally assigned to the $C1s \rightarrow \pi^*(e_{2u})$ transition. Based on $X\alpha$ calculations peak *C* and *D* are assigned to molecular shape resonances (σ symmetry).[29] The pronounced, opposite polarization dependence of peak *A* versus *C* and *D* is therefore a clear indication that benzene is adsorbed with the ring plane oriented parallel to the Ni(100) as well as to the Cu(110) surface. This adsorption geometry is in line with previous near-edge x-ray-absorption fine strucutre measurements for C_6H_6 on Cu(110) (Ref. 33) and the results for Ni(111),[2,39] Ni(110),[40] and Cu(111).[41]

While the spectra for benzene on Ni exhibit only one structure *C* at 293.5 eV, two peaks *C*′ (293.4 eV) and *C* (294.1 eV) are clearly separated for the Cu surface. From the polarization dependence and energy position peak *C* is identified as the shape resonance (σ symmetry), while peak *C*′ is assigned to a π shake up transition in line with multiconfiguration Hartree-Fock (MCHF) calculations,[36] which predict an admixture of π shakeup transitions in this energy region. The somewhat weaker polarization dependence of peak *C* as compared to peak *D* observed for benzene on Ni(100) and reported for other substrates[32] supports the given assignment.

The "out of plane" spectrum for Cu shows a distinct peak at 288.7 eV, *B*, not separable for benzene on Ni(100), which according to its π symmetry character was first attributed to the $C1s \rightarrow b_{2g}$ transition (second empty π orbital).[29] Schwarz *et al.* concluded that, due to configuration interaction, this transition has substantial amount of highest occupied molecular orbital-lowest occupied molecular orbital $[C(1s) \rightarrow e_{2u},\ e_{1g} \rightarrow e_{2u}]$ shakeup character.[36] Recent static exchange (STEX) calculations by Pettersson *et al.* of the benzene XA spectrum predict that the oscillator strength of the b_{2g} transition is too weak to account for peak *B*.[37,38] Accordingly peak *B* has to stem mainly from shakeup contributions. We therefore attribute the absence of a distinct transition *B* for benzene on Ni to a decrease in shakeup intensity, as already observed in XPS.

With the deduced orientation the double peak structure *X* has to have σ symmetry. A C-H character of the first transition (*X*) has been proposed by Menzel *et al.*, based on an enhanced hydrogen desorption yield in the condensate, while broadening of the $n \geqslant 3$ Rydberg series could account for the residual intensity.[30] The mentioned STEX calculations for the free, planar molecule[37,38] predict in line only significant intensity for σ symmetric transitions above the mainline.

Finally we have to explain the nonzero intensity around the position of the main line (*A*) in the in-plane geometry (σ channel), seen both for Ni and significantly smaller for Cu. This additional feature in the σ channel is somewhat narrower compared with the π resonance. A simple interpretation of the structure *A* would imply a small inclination of the ring plane with respect to the surface. As recently pointed out by Mainka and co-workers there is, however, a feature in virtually all *XA* spectra reported for planar aromatic molecules and moreover unreasonable large tilt angles would usually result in contrast to other experimental observations.[34] The authors therefore conclude that the additional intensity in the σ channel has to be attributed to a rehybridization of the molecules, i.e., an (upward) bending of the benzene C-H bond. This is in line with the calculations in Ref. 38, where already for the free molecule π intensity in the σ channel was predicted upon bending up the hydrogen atoms of the benzene molecule. For the adsorbed molecule this π derived intensity is not evenly redistributed in the σ spectra,[38] i.e., one cannot simply scale the π intensity and add it as a whole to the σ channel. We therefore attribute the π-derived intensity in the σ channel to a rehybridization of the molecule or a distortion of the molecular frame, rather than a tilt of the molecular plane. The larger effect on Ni is in line with the expected stronger coupling to the substrate. As will be discussed below further evidence for a rehybridization of the benzene molecule upon adsorption is found in the emission spectra.

We cannot, however, completely rule out that part of the observed π^* intensity stems from a small fraction of molecules adsorbed on defect sites and tilted with respect to the surface plane as discussed in Ref. 32 or a small tilt of all molecules. In the latter case we would, however, expect a comparable shape and width of the π contribution in the σ channel. More likely, small amounts of (re)adsorbed molecules in the second layer could lead to a physisorbed, tilted benzene species, giving rise to some π intensity in the σ channel with narrower linewidth.

The deduced flat adsorption geometry for benzene on Cu(110) is in contrast with a recent investigation by Lomas *et al.*[42] Based on angle-resolved UPS and high-resolution vibrational spectroscopy the authors propose a significant tilt (10–20°) of the benzene ring plane on Cu(110) for all coverages. We note that none of the techniques (including XAS) allows us to determine the magnitude of the tilt without certain assumptions[43] and that further structural investigations are necessary to clarify these contradictions.

While for the Cu surface the benzene XA spectrum immediately starts with peak *A*, a small structure at the onset of the spectrum is observed for benzene on Ni(100) in the σ and π channel. From careful experiments we can rule out that this additional intensity is due to atomic carbon, which exhibits a structure at somewhat lower photon energy (283 eV).[44] One might argue that this additional intensity is due to the broadening of the π resonance. However, the similar intensity in the σ channel is unlikely to be explained by rehybridization only. Thus we observe some additional benzene σ density at the onset of the absorption spectrum on Ni, but not on Cu. We will see, that this σ contribution has a counterpart in the XE spectra.

XA spectra can be interpreted by the use of the so-called final- and initial-state rules, which state that the shape and position of XA resonances is governed by the final, core-excited state (final-state rule), while the total intensity of a given transition reflects the occupancy of the corresponding initial state, i.e., the ground state (initial-state rule).[45] It is beyond the scope of this paper to discuss the quantitative validity of the initial-state rule and we will use it therefore only for a qualitative analysis.

The comparison of the NEXAFS spectra for benzene on Ni(100) and Cu(110) reveals immediately significant differences. The major features *A*, *B*, *C*, and *D* for benzene on Cu resemble the gas-phase spectrum.[46] This suggests that the overall weak interaction with the substrate leads to small changes of the electronic and geometric structure, i.e., little hybridization and distortion of the molecule. In contrast significant changes are observed for benzene on Ni(100). As compared to the Cu surface the σ shape resonances *C* and *D* are shifted to lower photon energies. This indicates an expansion of the ring and thus a weakening of the C-C bond.[35] An expansion of about 0.1 Å of the molecular radius was determined in a recent LEED study of the $(\sqrt{7}\times\sqrt{7})R19.1°$-benzene overlayer on Ni(111) (Ref. 9) and is thus not unexpected for the Ni(100) surface. In addition the benzene π^* resonance is broadened and reduced in intensity as compared to Cu. A similar intensity reduction is also seen for peaks B and C', which involve π shakeup transitions.[36] Overall the strong coupling will lead to a hybridization of the π system with substrate states and we expect a broadening of the involved molecular transitions. As discussed in Ref. 38 an additional distortion of the molecular frame can give rise to new features, such as the observed shoulder of the mainline. Moreover, the significant decrease of the total benzene π intensity on Ni suggests a change in occupancy of the corresponding states. In contrast, for benzene on Cu only modest broadening of the π resonance is observed and we expect only slight changes in occupancy and weak distortion of the molecular frame upon chemisorption. These observations are further corroborated by the XES results.

C. XES

Angle-resolved XES in combination with simple dipole selection rules allows us to determine the orientation of adsorbed molecules. More important for oriented molecules, states of different symmetry can be separated and the nature of new electronic states formed in the chemical bond is identified. Since the emission process involves a core hole, the same dipole selection rules as in XAS are appropriate and to the same extent the symmetry of the adsorbed molecule, rather than the symmetry of the adsorption complex, i.e., the symmetry group of molecule and substrate, is probed. For the present case, a benzene molecule adsorbed with the molecular plane parallel to the surface, it follows that in normal emission only states with σ symmetry are observed, while in grazing emission both σ and π orbitals are probed. Since the excitation and decay process are coupled via the intermediate state even more restricted selection rules may apply for resonant x-ray emission. This has recently been shown to be the case for condensed benzene.[47] For excitation to the lowest unoccupied $\pi(e_{2u})$ orbital RIXS reveals that the emission follows mainly dipole selection rules according to the D_{6h} point group of the ground state.[47] In other words, the core hole in the intermediate state can be described by the $1e_{2g}$ representation and therefore only dipole transitions from b_{1u}, b_{2u}, e_{1u}, and e_{2u} valence orbitals are allowed. Due to vibronic coupling in the intermediate state these selection rules are, however, not strictly fulfilled, and still some emission for symmetry forbidden orbitals is observed. Fluorescence spectra for higher excitation energies are in contrast reported to be quite nonresonantlike and emission from all valence states is observed.[47] In the present study these observations are used to unequivocally determine the symmetry character of states involved in the bond and to address the question of symmetry breaking due to the adsorbate-substrate chemical bond. Therefore excitation energies at the position of the $C1s\rightarrow e_{2u}$ transition and 5 eV above resonance with the polarization perpendicular to the surface were chosen. Before we discuss the spectra in more detail a brief description of the raw data and the steps to obtain pure spectra for σ and π states seems appropriate. For this purpose we will concentrate on the emission spectra recorded for benzene on Ni and point out conclusions immediately evident from a revision of the raw data only. The corresponding spectra for normal and grazing emission are depicted in Fig. 3. The experimental geometries are sketched in the inset.

In addition to emission from the benzene monolayer detected in the first order of the x-ray grating spectrometer, Ni substrate emission is seen in third order. The well-known Ni emission lines $L_3M_{4,5}$ (851.5 eV), L_2M_4 (868.8 eV), and the inner transition L_3M_1 (742.7 eV) (Ref. 48) result from bulk excitation due to third and higher harmonics of the undulator and monochromator. Despite the fact that substrate emission lines are useful to calibrate the energy of adsorbate XE spectra within one measurement, the overlap of the Ni emission lines with the benzene signal in this particular case is certainly an experimental limitation. However, since the interaction of the outgoing photons with the adsorbate layer is negligible the obtained XE spectrum is a pure sum of adsorbate and clean substrate emission and subtraction of the Ni

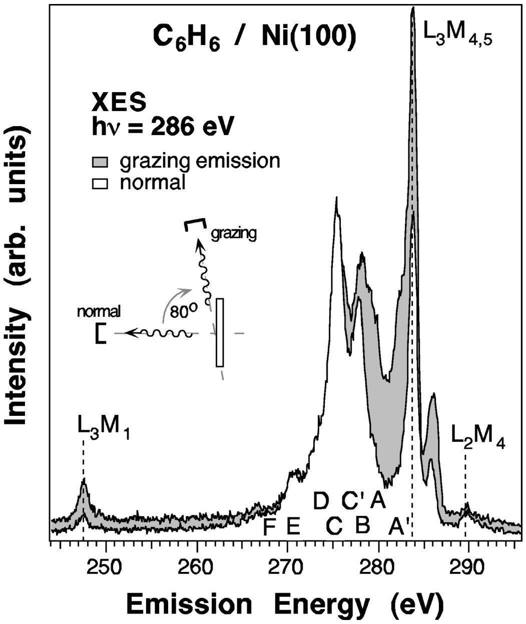

FIG. 3. X-ray emission raw spectra for the $c(4\times4)$ monolayer of benzene on Ni(100). The excitation energy of 286 eV corresponds to the $1s\rightarrow\pi^*(e_{2u})$ transition. The field vector was aligned perpendicular to the surface (*xy* plane). Emission spectra are shown for grazing emission (*x* and *z* polarization, filled area) and normal emission (*x* and *y* polarization, plain area). Benzene emission bands are labeled as described in the text and summarized in Table I.

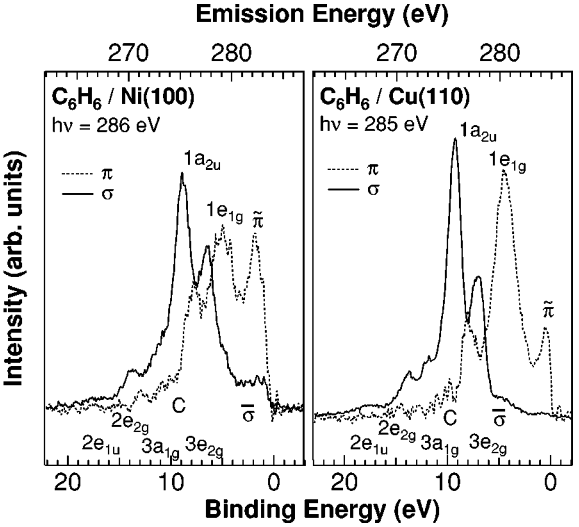

FIG. 4. *Left:* C_6H_6/Ni(100); The XE spectra of Fig. 3 decomposed in π (dashed line) and σ (solid line) symmetric contributions as described in the text. Spectra are normalized to unit area. The emission energy scale (top) is converted to a binding energy scale with the Fermi level at 0, as described in the text. The assignment of the benzene valence orbitals is indicated at the top (π states) and bottom (σ states). *Right:* C_6H_6/Cu(110).

background does not generate genuine artifacts. The additional peak at 286 eV stems from (quasi)elastic scattered photons.

For photonenergies below 281 eV seven structures can be identified as benzene emission bands labeled A, B, C, C', D, E, and F in Fig. 3, respectively. By comparison to recent calculations[47] for the free molecule and to the gas-phase UPS spectrum[49] these bands are assigned to the valence orbitals of benzene as summarized in Table I. In addition, seen in the raw spectra, a shoulder around 282.5 eV (A'), not seen for the condensed phase,[47] is observed. Comparing both measurement geometries reveals that the $1e_{1g}$ and $1a_{2u}$ π orbitals (bands A and C') give rise to additional intensity for grazing emission (gray area), while in normal emission only orbitals of σ symmetry (bands *F*, *E*, *D*, *C*, and *B*) are seen.

As mentioned above this angular dependence of the XE spectra confirms that benzene is adsorbed with the molecular plane parallel to the Ni(100) surface. Based on the adsorption geometry a spectrum displaying states with pure π symmetry can be extracted from the raw data. A spectrum showing mainly π contributions was obtained by normalizing the spectra to the same area and subtracting 50% of the normal emission spectrum (*x* and *y* polarization) from the grazing emission spectrum (*x* and *z* polarization). This normalization relies on the assumption that the emission intensities are dominated by atomic like p_x, p_y, and p_z to 1s dipole transitions and are of equivalent intensity independent of the polarization (*x*, *y*, or *z*).

The subtraction was also tested with somewhat different intensity ratios of the recorded normal and grazing emission spectra with the resulting spectra being, however, little influenced. The described procedure is also justified by frozen-orbital one particle calculations for the free molecule.[50] We like to emphasize that while the subtraction might still affect details of the spectrum, i.e., the exact energetic position of individual emission lines (in particular the exact weight and position of the $1a_{2u}$ π band), the gross features are little influenced. Spectra modified in that way are depicted in Fig. 4 for C_6H_6/Ni(100) (left panel) and C_6H_6/Cu(110) (right panel).

The amount of substrate intensity was determined from the Ni L_3M_1 (247.56 eV) and the L_2M_4 (289.6 eV) lines, which do not overlap with the benzene emission. For Cu only the weak L_3M_1 transition (270.4 eV, excited with fifth-order radiation from the undulator) falls in the energy range of benzene emission and subtraction of substrate emission is thus not critical.

The spectra are transferred to a valence-state binding-energy scale with the Fermi level at 0 using the fact that for systems with metalliclike screening, such as chemisorbed molecules, the position of the Fermi level on an emission scale corresponds to the XPS core-level binding energy[51] [284.1 eV for benzene on Ni(100) and 284.9 eV for benzene on Cu(110)]. We estimate an absolute error of $\leqslant 0.2$ eV due to uncertainties in the calibration of the XE spectrometer. Overall good agreement with binding energies determined by UPS is found (see Table I and II).

For benzene on Ni(100) [Fig. 4(a)] the spectrum for π symmetry (dashed line) reveals now three distinct peaks, the $1a_{2u}$ and $1e_{1g}$ out of plane π orbitals and a third state not seen for the free molecule 1.8 eV below the Fermi level (labeled $\tilde{\pi}$). For normal emission (σ symmetry, solid line) in addition to the already assigned five benzene emission bands (see Table I) intensity is observed all the way up to the Fermi level (labeled $\bar{\sigma}$). This spectrum is obtained by subtracting the Ni substrate contributions only, leaving therefore no doubt that the additional feature $\bar{\sigma}$ is genuine. Comparing the

TABLE I. Assignment of the emission bands of benzene on Ni(100): E_{em} is the measured photon energy, E_B is the binding energy related to the Fermi level as described in the text, E_B (UPS) are UPS values for the saturated benzene layer on Ni(111) taken from Table 2 in Ref. 2, E_{gas} are photoemission results for gaseous benzene relative to the vacuum level (Ref. 49) and ΔE is the derived shift between gas phase and adsorbed molecule.

Band	Orbitals (symmetry)	E_{em} (eV)	E_B (eV)	E_B (UPS)	E_{gas} (eV)	ΔE (eV)
A'	$e_{2u}(\tilde{\pi})$	282.3 (0.1)	1.8			
A	$1e_{1g}(\pi)$	279.0 (0.1)	5.1	5.1	9.3	4.2
B	$3e_{2g}$	277.8 (0.1)	6.3	6.2, 6.8	11.7	5.4
C'	$1a_{2u}(\pi)$	276.3 (0.3)	7.8	8.1	12.2	4.4
C	$3e_{1u}$ $1b_{2u}$ $2b_{1u}$	275.4	8.7	8.3 8.7 10.1	14.1 14.7 15.5	6.0
D	$3a_{1g}$	272.9 (0.3)	11.2	11.3	17.0	5.8
E	$2e_{2g}$	270.6 (0.1)	13.5	13.5	19.3	5.8
F	$2e_{1u}$	267.1 (0.2)	17.0		22.8	5.8

energetic positions of all valence states to the gas-phase photoemission spectrum reveals that the $1e_{1g}$ and $1a_{2u}$ π orbitals are shifted with respect to the σ levels by 1.6 eV and 1.4 eV to higher binding energies (see Table I).

For better comparison the π and σ contributions of Fig. 4 are separated for both substrates in Fig. 5. For benzene on Cu(110) again another, third π state is observed but this state is now located at the Fermi level and the emission intensity is weaker as compared to the Ni substrate. This state has recently been observed by two photon photoemission confirming the proximity to the Fermi level.[52] Moreover, no σ intensity is observed at the Fermi level, while weak additional emission (labeled $\bar{\sigma}$) is found in the binding-energy range of 3–5 eV.

TABLE II. Assignment of the emission bands of benzene on Cu(110): E_{em} is the measured photon energy, E_B is the binding energy related to the Fermi level as described in the text, E_B (UPS) are UPS values taken from Table 1 in Ref. 42, E_{gas} are photoemission results for gaseous benzene relative to the vacuum level (Ref. 49) and ΔE is the derived shift between gas phase and adsorbed molecule.

Band	Orbitals (symmetry)	E_{em} (eV)	E_B (eV)	E_B (UPS)	E_{gas} (eV)	ΔE (eV)
A'	$e_{2u}(\tilde{\pi})$	284.5	0–0.4			
A	$1e_{1g}(\pi)$	280.5	4.4	4.6	9.3	4.9
B	$3e_{2g}$	277.8	7.1	7.1	11.7	4.6
C'	$1a_{2u}(\pi)$	277.0	7.9	8.3–10.3	12.2	4.3
C	$3e_{1u}$ $1b_{2u}$ $2b_{1u}$	275.6	9.3	8.3–10.3	14.1 14.7 15.5	5.4
D	$3a_{1g}$	273.2	11.7	11.8	17.0	5.3
E	$2e_{2g}$	271.2	13.7		19.3	5.6
F	$2e_{1u}$	267.4	17.5		22.8	5.3

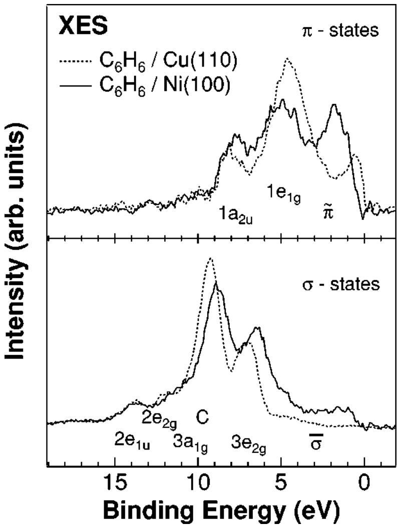

FIG. 5. The x-ray emission spectra of Fig. 4 separated in π and σ symmetric contributions for C_6H_6/Ni(100) (solid line) and C_6H_6/Cu(110) (dashed line).

In addition, we observe smaller differential shifts of 0.4 eV for the $1a_{2u}$ and 1.0 eV for the $1e_{1g}$ π orbitals indicative of a weaker interaction of the molecule with the substrate.

This shift is usually explained as a chemical shift due to a bonding interaction of the π orbitals with the substrate. The term ''bonding'' in this context is, however, somewhat misleading, since it implies that the higher binding energy of the π orbitals indicates a stabilization of the bond between benzene molecule and substrate. While the observed shifts will qualitatively reflect the interaction strength of the occupied π orbitals with substrate states, the net contribution to the chemical bond is not obvious.

On the other hand, the XE spectra demonstrate that new π states are formed below the Fermi level. To further clarify the nature of these states emission spectra excited at the π resonance and 5 eV above are compared in Fig. 6. No further change of the emission spectra on Ni was observed at an excitation energy of 315 eV, i.e., 30 eV above the π^* resonance.

The intensity ratios between the different bands depend obviously on the excitation energy, while within experimental errors no energetic shifts are observed. Normalizing the in plane spectra to band C ($2b_{1u}$, $1b_{2u}$, and $3e_{1u}$ orbitals) results in an enhancement of the remaining emission peaks ($3e_{2g}$, $3a_{1g}$, $3e_{2g}$, and to some extent $\bar{\sigma}$). The same effect is observed for the π states. The emission intensity from the $1a_{2u}$ and $1e_{1g}$ orbitals increases as compared to the $\tilde{\pi}$ state as the excitation energy is switched. This change can be understood by reviewing the results for the condensed phase.[47] The excitation to the $\pi^* e_{2u}$ resonance results in emission from b_{1u}, b_{2u}, e_{1u}, and e_{2u} valence orbitals, while other transitions are significantly suppressed. This can be described in terms of a conservation of the D_{6h} symmetry in the excited state, i.e., by assuming a distinct symmetry of the core-hole ($1e_{2g}^{-1}$) state according to the dipole selection rules for the D_{6h} point group. Similar to the condensate for the chemisorbed molecule states belonging primarily to the above representations are enhanced at off-threshold excita-

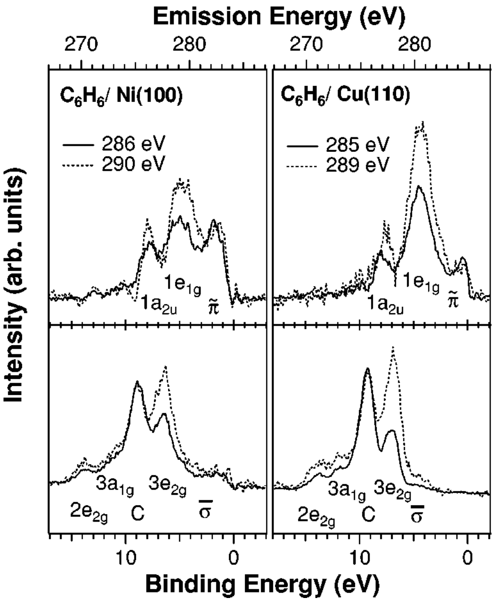

FIG. 6. Comparison of x-ray emission spectra for benzene on Ni(100) (left) and Cu(110) (right) for excitation at the π^* resonance (solid line) and 5 eV above (dashed line). Top: π symmetric states. Bottom: σ symmetric states.

tion. This effect is more pronounced for benzene on the Cu substrate, i.e., where the interaction between substrate and adsorbate is weaker.

There are several mechanisms that will lead to a breakdown of these selection rules. Due to the bonding to the substrate, the symmetry of all wave functions is altered and has strictly to be described in the combined point group of molecule and substrate, i.e., without inversion symmetry. Furthermore, the inversion symmetry of the molecule itself can be perturbed by a static distortion of the benzene ring. Such small distortions have been, e.g., proposed for benzene chemisorbed on Pt(111),[53] Ru(001) (Ref. 8), and coadsorbed with CO on Rh(111) (Ref. 54) and were predicted by recent calculations modeling benzene bonding on Cu(110).[38] A comparison of the benzene σ states for chemisorption on Ni and Cu reveals indeed an indication for an expansion of the benzene ring on the Ni(100) substrate. The occupied σ states for benzene on Ni(100) are shifted towards lower binding energies (see Fig. 5). As discussed a similar shift to lower binding energies is also observed for the unoccupied σ states (peaks *C* and *D* in Fig. 2). In a simple model the energetic distance between occupied an unoccupied states that are not involved in the bond to the substrate can be viewed as a ruler for the bond length: a smaller gap corresponds to a longer bond length. Since the XA spectra for benzene on Cu are similar to that of the free molecule, we expect little distortion of the molecule on Cu, while the observed shifts indicate some C-C ring expansion on Ni(100). As will be discussed this C-C bond weakening is in line with the observed changes in the benzene π system. In addition, these static changes will alter the intramolecular vibrations and any change in symmetry the coupling of the normal modes of the molecule in the intermediate state.

All of these effects will be more pronounced when the coupling to the substrate gets stronger and we conclude therefore that the breakdown of inversion symmetry upon bonding is stronger on Ni as compared to Cu.

We like to emphasize that the expected symmetry reduction, in particular in the horizontal mirror plane ($D_{6h} \rightarrow C_{6v}$) and thus the loss of inversion symmetry, due to the bonding of the molecule to the substrate is in both cases present, but manifests itself only gradually in the spectra. This is not too surprising, since in the XE process the valence wave functions (*p* contribution) are probed close to the core, where the influence of distortion and bonding will be weaker.

On both substrates the emission behavior of the state $\tilde{\pi}$ is different from that observed for the other π states but agrees with that expected for a state with e_{2u} symmetry. We thus conclude, that for both substrates the π (e_{2u}) orbital becomes partially occupied in the chemisorbed state. Since the enhancement of the σ symmetric $3e_{2g}$ state and the π symmetric $1e_{1g}$ state for off-resonant excitation is of similar magnitude, the π state has to have predominantly e_{2u} character. We therefore expect minor contributions of the occupied π states ($1a_{2u}$ and $1e_{1g}$) to the emission feature $\tilde{\pi}$.

X-ray emission enables us now to elucidate the differences in benzene interaction with the Ni(100) and Cu(110) surfaces.

For Ni the additional $\tilde{\pi}$ emission line is clearly separated from the Fermi level and can thus be viewed as a distinct molecular orbital formed upon adsorption. The occurrence of a single state of π symmetry well below the Fermi level can be understood in a simple frontier orbital picture. Due to the interaction of the e_{2u} orbital with Ni states a pair of bonding and antibonding adsorbate-substrate hybrid states is formed. The bonding combination is pushed below the Fermi level and consequently occupied. Evidently this leads to a stabilization of the adsorbate-substrate bond. The molecular character of the bonding state implies that the respective antibonding combination has significant metal character. As a consequence we observe a strongly reduced π^* intensity in XAS. The formation of a single bonding state rather than a band suggest that the e_{2u} orbital interacts mainly with localized states, i.e., the narrow Ni *d* band.

In contrast on Cu the observed additional π intensity is weaker and cut off by the Fermi level. We thus can understand the bonding in a simple resonance model.[55,56] The π (e_{2u}) orbital is broadened upon interaction with the Cu substrate and the tail that reaches below the Fermi level gets occupied. The model implies an interaction with a broad band of states. This appears reasonable since the Cu *d* states are located well below the Fermi level and interaction of the π (e_{2u}) orbital with the substrate should thus be dominated by the Cu *sp* band.

The simple model derived for benzene bonding to Ni and Cu does not involve the occupied π states. We observe, however, a differential shift of the occupied $1e_{1g}$ and $1a_{2u}$ π orbitals to higher binding energies indicative of an involvement of these states in the chemical bond. This is usually described in terms of a π donation bond. In line with the stronger coupling to the substrate a larger shift is observed for benzene on Ni. Some mixing of Ni character in the $1e_{1g}$ orbital may be envisaged by the decrease of $1e_{1g}$ emission intensity seen for Ni as compared to the Cu substrate. There is a possibility that some of the original $1e_{1g}$ and $1a_{2u}$ orbitals have been pushed above the Fermi level forming antibonding states with the Ni *d* band. The π resonance seen in XAS is substantially broadened and could contain many different states of π symmetry. Furthermore, part of the reduction in the parity selection rule on Ni could be related to an excitation not only in the states of e_{2u} symmetry but also to states of e_{1g} symmetry. However, based on the decrease of the π resonance in absorption we can conclude that on Ni the π backdonation is more prominent than the π donation. In the case of Cu most of the evidence indicates only a small backdonation but we cannot completely rule out π donation.

While the observed backdonation of the e_{2u} orbital, even so far not experimentally proven, fits well in the usual picture of π bonding of the benzene molecule to metal surfaces, a contribution of benzene σ states to the bond is surprising.

For Cu the additional shoulder $\overline{\sigma}$ falls in the region of strong π emission. The two weak structures at energies below 5 eV appear at the same binding energies as the $1e_{1g}$ and e_{2u} orbitals seen in the π symmetry spectrum. We can therefore anticipate some symmetry mixing due to rehybridization.

In contrast, for Ni the situation is different. As for Cu and similar to olefinic hydrocarbons[1] an admixture of σ symmetric states to the π bond will result from a rehybridization towards a tetrahedral configuration of the benzene molecular bonds upon adsorption. This is in line with some of the π contributions observed in the σ channel in the absorption spectra. Nevertheless, symmetry mixing cannot entirely explain the σ spectra. We find significant σ intensity in x-ray emission all the way up to the Fermi level and, not as conclusively, some σ intensity at the onset of the x-ray absorption spectra. A simple admixture of π states seems, however, not sufficient to explain the appearance of distinctive σ states in the XE spectrum, since then we would expect a σ electron distribution that resembles the π state with a peak at 1.8 eV and weak intensity close to the Fermi level and not a flat emission feature.

The origin of benzene σ symmetric states occupied up to the Fermi level on the Ni substrate cannot be understood in a simple orbital-orbital interaction scheme. The broad band $\overline{\sigma}$ indicates a contribution of more delocalized states to the bond and is thus likely due to an additional interaction of benzene σ states with the Ni sp band.

The formation of adsorbate-substrate bonds leads generally to a destabilization of the internal molecular bonds. While the occupancy of the e_{2u} orbital will thus result in a destabilization of the C-C ring, the contribution of σ states to the bond should lead to a C-H bond weakening. The relative weight of these contributions will play a crucial role for reaction paths at higher temperatures and might be generally important for hydrogenation and dehydrogenation reactions of aromatic hydrocarbons on metal surfaces. This might explain that for the Ni substrate a dissociation of the benzene molecule is observed at higher temperatures, while for Cu desorption of the intact molecules occurs.

IV. SUMMARY

To summarize, the present investigation of benzene on Ni(100) and Cu(110) demonstrates that angular resolved x-ray emission is a powerful tool for separating relevant features of the electronic structure of even larger molecules on surfaces, not detectable with other techniques. The molecules are found to adsorb with the aromatic ring parallel to the Ni(100) and Cu(110) surfaces. The suggested π bonding with metal surfaces for such an adsorption geometry can be specified: a strong π backbonding and splitting of the π (e_{2u}) orbital is found on Ni, while a resonance like broadening of the e_{2u} state occurs on Cu. These differences are discussed in terms of the Newns-Anderson model, i.e., an interaction with the narrow Ni *d* band and the broad distribution of *sp* states on Cu, respectively. The experimental result for benzene on Cu fits with theoretical calculations of the nonresonant benzene emission spectrum. The calculations reveal a peak close to the Fermi level, which was interpreted as due to states of e_{2u} symmetry.[38] In addition to the π state for Ni a significant σ density of states is resolved all the way up to the Fermi level, which indicates a contribution of σ states to the adsorbate-substrate bond. On Cu in contrast additional σ intensity is only observed, where benzene π emission is seen and therefore attributed to weak rehybridization upon bonding.

While without further detailed theoretical calculations it is not possible to specify the contribution of these σ states to the chemical bond, it is obvious that a simple frontier orbital picture is not sufficient to describe benzene bonding with metal substrates.

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