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Cobaltocene adsorption and dissociation on Cu(1 1 1)

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Abstract: Photoemission results indicate that the initial adsorption of cobaltocene on Cu(1 1 1) at 150 K leads to molecular fragmentation, but with subsequent cobaltocene exposures, molecular absorption occurs. The molecularly adsorbed species is either adsorbed with only a fraction of molecules adopting a preferential orientation along the surface normal or adsorbed with the molecular axis away from the surface normal. This adsorption behavior is compared to nickelocene and ferrocene adsorption.

Keywords: Molecular adsorption, Cobaltocene, Photoemission, Organometallics

1. Introduction

The surface chemistry of many metallocenes, $M(C_5H_5)_2$ (M = Cr, Mn, Fe, Co, Ni) has been motivated by the possibilities of "direct writing" small magnetic features [1–12]. "Clean" magnetic features require the removal of the ligand species during decomposition, which may require the addition of hydrogen to the background, but the metallocene interaction with the substrate is also key.

Of the many studies of molecular ferrocene [13–22], nickelocene [20–31] and cobaltocene [32] adsorption, the initial adsorption is associated (molecular) on most surfaces, when the adsorption is undertaken at substrate temperatures in the region of 100–200 K. Molecular metallocene adsorption has been observed on Ag(1 0 0) [13–15], [21], [22], [26], and [27], Cu(1 0 0) [15], [19], [21–25], Mo(1 1 2) [17] and [22], graphite [16], [18], and [32] and Si(1 1 1)-2 × 1 [20]. Nonetheless, initial nickelocene adsorption on Ni(1 0 0) [25] and NiO(1 0 0) [25] is dissociative even for substrate temperatures of 135 K. We might expect that cobaltocene adsorption, like that observed for other metallocenes, would also be molecular on substrates well below room temperature, but in this work, we show that (perhaps surprisingly) this is not the case, even for the relatively inert Cu(1 1 1) surface.

2. Experimental details

The light polarization dependent angle-resolved photoemission experiments were carried out using synchrotron radiation, dispersed by a 3 m toroidal monochromator, at the Center for Advanced Microstructure and Devices (CAMD) in Baton Rouge, LA, as described elsewhere [33–35]. The measurements were performed in an ultra high vacuum (UHV) chamber employing a hemispherical electron energy analyzer with an angular acceptance of ±1°, as described elsewhere [35]. The combined resolution of the electron energy analyzer and monochromator varied between 0.10 and 0.25 eV. All angles (both light incidence angles as well as photoelectron emission angles) reported herein, are with respect to the substrate surface normal. Because of the highly plane polarized nature of the dispersed synchrotron light through the toroidal grating monochromator, the large light incidence angles result in a vector potential **A** more parallel to the surface normal (p-polarized light), while smaller light incidence angles result in the vector potential **A**

residing more in the plane of the surface (s-polarized light) in the geometry of our experiment. We compare the photoemission spectra taken with s + p-polarized light (a light incidence angle of 40° off the surface normal) and more p-polarized light (a light incidence angle of 65° off the surface normal). For the photoemission results reported here, the photoelectrons were collected normal to the surface ($\bar{\Gamma}$ or $k_{\parallel} = 0$) to preserve the highest possible point group symmetry. All binding energies given are with respect to the substrate Fermi level.

The Cu(1 1 1) crystal was cleaned by repeated Ar^+ ion bombardment and annealing treatment at 830 K. In studying the adsorption of cobaltocene, $Co(C_5H_5)_2$ was sublimed and admitted to the chamber through a standard leak valve and exposed to the clean Cu(1 1 1) at 150 K.

3. Cobaltocene adsorption on Cu(1 1 1)

There are strong indications that with initial exposure of cobaltocene to Cu(1 1 1) at 150 K, the adsorption is not molecular. The exposure dependent angle-resolved photoemission spectra of cobaltocene on Cu(1 1 1) at 150 K, are shown in Fig. 1, for a photon energy of 36 eV for both s + p-polarized light (a light incidence angle of 40° off the surface normal) and p-polarized light (a light incidence angle of 65° off the surface normal). Upon adsorption of cobaltocene, there is suppression of the Cu 3d bands and increase of a strong photoemission feature at approximately 9 eV binding energy, for cobaltocene exposures up to 12 Langmuirs (1 L = 1.0×10^{-6} Torr s). This is more characteristic of a graphitic species and not the expected photoemission features of adsorbed cobaltocene [32].

The photoemission features that appear with cobaltocene exposures of 14 Langmuirs and more, to Cu(1 1 1) at 150 K, are very characteristic of molecular cobaltocene [32], and other metallocenes [21–22]. The photoemission features observed at higher cobaltocene exposures (Fig. 1) at 9.0 ± 0.2 eV (peak B), 12.7 ± 0.2 eV (peak C), and 17.3 ± 0.2 eV (peak D) as well as the much weaker features at 0.9 ± 0.2 eV (peak A′) and 5.1 ± 0.2 eV (peak A″) are similar in relative intensities and binding energies to those assigned to cobaltocene adsorbed on cleaved graphite [32]. There is also a strong similarity between the gas phase photoemission spectra of cobaltocene [36–37], but with a shift of about 4 eV in the energy scale, as is typical of metallocenes [13–15], [17], [20–23], and [32], even though the molecule-substrate as well as intermolecular interactions may shift, or broaden the molecular orbitals.

Based on theoretical calculations of the ground-state molecular orbitals of cobaltocene [38], final excited states [38] and gas-phase photoemission studies [36–37], we can assign these photoemission features of the adsorbed species and the

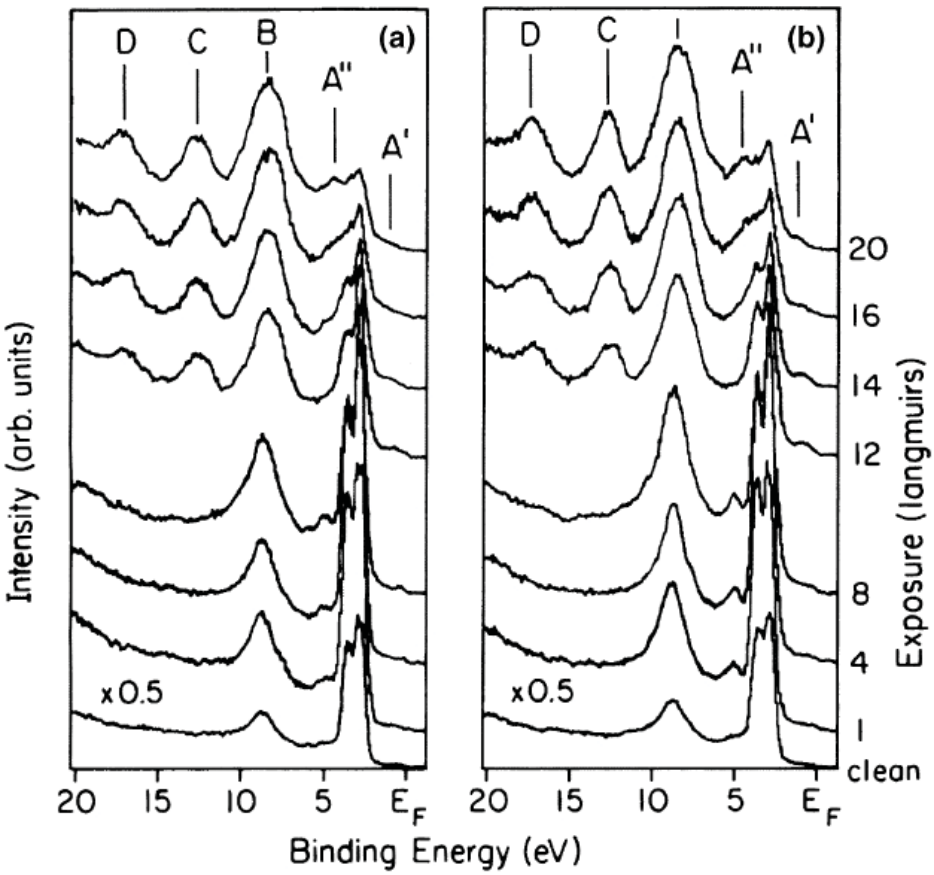

Figure 1. Coverage dependent angle-resolved photoemission spectra of cobaltocene on Cu(1 1 1) at 150 K. The photon energy of 36 eV and the photoelectrons are collected along the surface normal. The photoemission spectra were taken with s + p-polarized light (a) and more p-polarized light (b). The cobaltocene exposures are provided in units of Langmuirs (1 L = 1.0×10^{-6} Torr s).

induced photoemission features to the molecular orbitals of cobaltocene. With very large cobaltocene exposures (Fig. 2 and Fig. 3), the very weak photoemission features at binding energies 0.9 ± 0.2 eV (A′) and 5.1 ± 0.2 eV (peak A″) can be assigned to the $4e_{1g}$ molecular orbital (with combined 3d and cyclopentadiene π (Cp-π) character) and the $4e_{1u}$ molecular orbital (with largely cyclopentadiene π (Cp-π) character), respectively. A photoemission from the $3e_{2g}$ initial state can only be determined from difference spectra or at extremely large cobaltocene coverages where the Cu(1 1 1) d-band features are completely suppressed. This cobaltocene feature should be complicated by a number of final states [38], which cannot be resolved in our photoemission spectra. The cobaltocene photoemission features at 9.0 ± 0.2 eV (peak B), 12.7 ± 0.2 eV (peak C), and 17.3 ± 0.2 eV (peak D) are more easily observed and can be assigned to photoemission feature from a variety of molecular orbitals, as summarized in Table 1.

If cobaltocene adopted a preferential orientation, either with the molecular axis along the surface normal, or with the molecular axis parallel with the surface, then the relative photoemission intensities should depend significantly on light polarization, even with all the photoelectrons collected along the surface normal (as undertaken in these experiments) [21–22]. Such behavior has been observed for molecular ferrocene adsorption on Cu(1 0 0) [15], [21–22], Ag(1 0 0) [15], [21–22] and Mo(1 1 2) [17]. We see little evidence of changes in relative photoemission feature intensities in comparing photoemission spectra taken with s + p-polarized light (a light incidence angle of 40° off the surface normal) and more p-polarized light (a light incidence angle of 65° off the surface normal), even for several different photon energies, as seen in Fig. 2. The slight enhancement of the photoemission feature due to the combination of $4a_{2u}$, $2e_{2g}$, $2e_{2u}$, $3e_{1u}$, $2e_{1g}$, and $4a_{1g}$ molecular orbitals, at 9 eV binding energy, in more p-polarized light does suggest a slight preferential orientation for molecular cobaltocene at the high coverages (Fig. 2). This preferential orientation is with the molecular axis canted away from the surface normal, so that the light polarization dependent photoemission effects are small or, only a small fraction of cobaltocene molecules are oriented with the molecular axis along the surface normal. A canting of the molecular axis away from the surface normal would make the bonding orientation adopted by molecular cobaltocene, resemble that of nickelocene on Ag(1 0 0) at some coverages [26–27]. So that cobaltocene adopting a somewhat

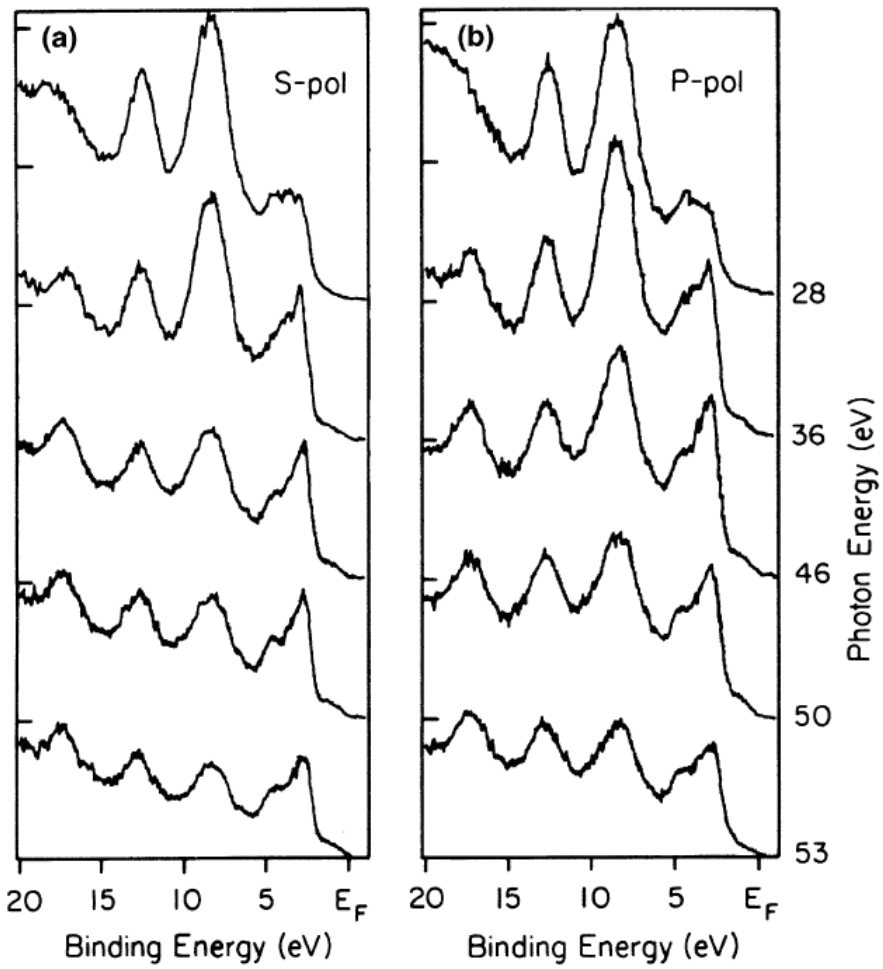

Figure 2. Valence band spectra as function of photon energy following 20 L cobaltocene exposured on Cu(1 1 1) at 150 K. The photoemission spectra were taken with s + p-polarized light (a) and more p-polarized light (b), with the photoelectrons collected along the surface normal.

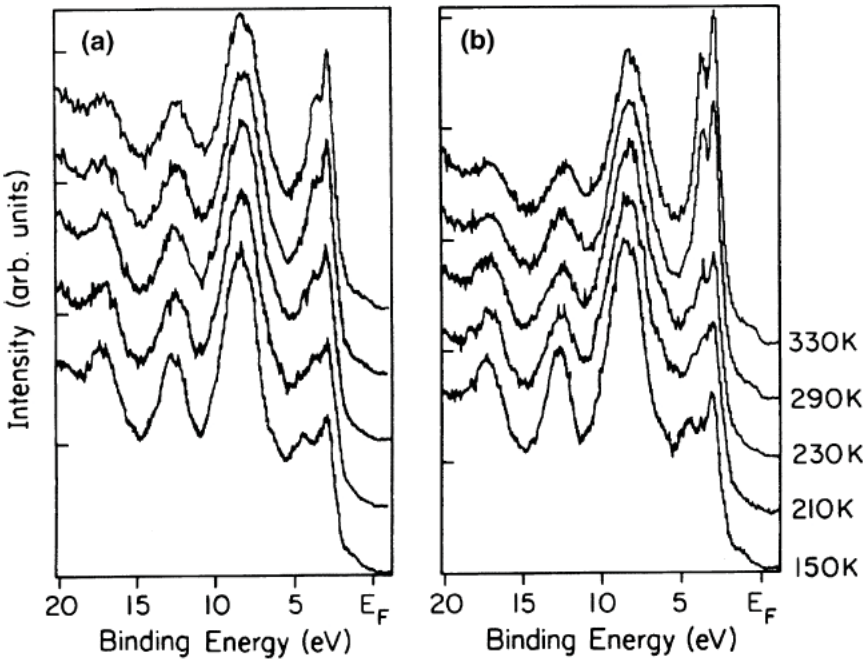

Figure 3. Temperature dependence of adsorbed cobaltocene on Cu(1 1 1), following an initial 20 L exposure of cobaltocene to Cu(1 1 1) at 150 K. Spectra were taken using a photon energy of 36 eV. The photoemission spectra were taken with s + p-polarized light (a) and more p-polarized light (b), with the photoelectrons collected along the surface normal.

Table 1
The molecular orbitals of cobaltocene

Molecular orbitals	Theory (eV)	Gas phase[a] (eV)	Cu(1 1 1)[b] (eV)	Graphite[b] (eV)
$4e_{1g}$ (d-π)	$^1A_{1g}$ 4.73 [38]	5.55 [36] 5.56 [37]	0.9	1.2 [32]
$3e_{2g}$ (d-δ)	$^3E_{1g}$ 6.8 [38] $^3E_{2g}$ 6.8 [38] $^1E_{1g}$ 7.08 [38]	7.15 [36] 7.18 [37]	3.2	3 [32]
$5a_{1g}$ (d-σ)	$^3E_{1g}$ 7.48 [38] $^1E_{2g}$ 7.48 [38] $^1E_{1g}$ 7.72 [38]	7.65 [36] 7.63 [37] 7.99 [36] 8.01 [37]	–	–
$4e_{1u}$ (Cp-π)	$^3E_{2g}$ $^3E_{1g}$	8.72 [36] 8.66 [37]	5.1	4.9 [32]
$3e_{1g}$ (Cp-π)	$^1E_{1g}$ $^3E_{1g}$ $^1E_{2g}$	9.92 [36] 9.88 [37]	–	–
$4a_{2u}$ $2e_{2g}$ $2e_{2u}$ (Cp-π) $3e_{1u}$ $2e_{1g}$ $4a_{1g}$		12.34 [36] 12.24 [37] 13.43 [36] 13.99 [37]	9.0	8.8 [32]
$3a_{2u}$ $3a_{1g}$ (Cp-σ) $1e_{2u}$ $1e_{2g}$		16.98 [36] 16.57 [37]	12.7	13.3 [32]
$2a_{1g}$ (C 2s)			17.3	18.4 [32]

[a] Indicates values with respect to the vacuum level.
[b] Indicates values with respect to the Fermi level.

canted molecular adsorption configuration need not be considered surprising even though most studies place the metallocene molecular axis along the surface normal of Ag(1 0 0) [15], [21–22] and graphite [16] and [18].

Annealing the Cu(1 1 1) substrate from 150 K to high temperatures, following the adsorption of molecular cobaltocene, may well result in greater preferential orientation of the molecular cobaltocene. With annealing, significant increases in photoemission intensity resulting from the substrate Cu(1 1 1) 3d bands are restored (largely between 230 and 290 K), but the residual photoemission features show much dependence on light polarization, as seen in Fig. 3. With annealing, the increase in substrate photoemission signal indicates that a considerable amount of desorption occurs (between 230 and 290 K, as indicated in Fig. 3). The combination of $4a_{2u}$, $2e_{2g}$, $2e_{2u}$, $3e_{1u}$, $2e_{1g}$, and $4a_{1g}$ cobaltocene molecular orbitals, that are the initial ground state molecular orbitals that contribute to the photoemission feature at 9 eV binding energy are more clearly enhanced in more p-polarized light, relative to the other photoemission features, when the Cu(1 1 1) substrate is annealed (Fig. 3). This indicates a much stronger preferential orientation with the molecular axis more parallel with the surface normal [21–22].

Much desorption of cobaltocene above 230 K may be facile because of island growth of the cobaltocene thin film, beyond the first few molecular layers. Desorption then occurs leaving a more ordered molecular films of only a few layers (or just a single molecular layer) of cobaltocene. Unfortunately, apart from the absence of a strong preferential orientation for molecular cobaltocene, we cannot say much about the structure of the multilayer molecular cobaltocene film on Cu(1 1 1) from the photoemission data alone.

4. The stability of adsorbed cobaltocene

When comparing initial cobaltocene adsorption on graphite [32] and Cu(1 1 1) (the work presented here) with other metallocenes, it seems fairly clear that cobaltocene is far less stable as a molecule on surfaces than ferrocene ($Z - 1$) [13–22] or nickelocene ($Z + 1$) [20], [23–27]. The big difference among these three metallocenes appears to be that the "nineteen electron" cobaltocene has a single unpaired electron resulting in a low ionization potential [32] of 5.56 eV [37] when compared to ferrocene (6.88 eV [37]) and nickelocene (6.51 eV [37]). This results in formation of a surface species that somewhat resembles $[Co(Cp)_2]^+$ on graphite [32] but apparently leads to fragmentation on Cu(1 1 1). Ferrocene, with greater stability as an adsorbate, is a paired electron system in a singlet state, while nickelocene, which exists as a triplet state as an isolated molecule, almost certainly adopts a singlet state on adsorption due to lowered molecular symmetry [26] and [27] and possibly localization of an electron pair on a double bond arising from ring slippage of the carbocyclic ligand [36]. With absorption other than end-on, nickelocene MUST adopt a singlet state as the off normal adsorption orientation has reduced the molecular symmetry to such an extent that a triplet state is simply not possibly.

On more reactive surfaces such as Ni(1 0 0), it is perhaps significant that the unpaired nickelocene shows dissociative adsorption behavior, even at substrate temperatures of 135 K [25], that resembles the dissociative adsorption behavior observed for cobaltocene on Cu(1 1 1), discussed here. More reactive surfaces, like Ni(1 0 0), may promote partial "ionosorption" to a greater extent (that is to say adsorption with very significant charge transfer with the substrate), so that the adsorbed metallocene has a greater tendency to adopt an "oxidized" configuration $[M(Cp)_2]^+$.

While induced decomposition of metallocenes certainly is possible, during photoemission [2], [3], [13–14], decomposition induced by absorption on the bare metal substrate is certainly more significant. Very little decomposition of the multilayer molecular cobaltocene species is observed on the time scale of our photoemission measurements, with much of the multilayer molecular cobaltocene desorbing below 290 K.

5. Summary

Molecular adsorption of cobaltocene, $Co(C_5H_5)_2$, on Cu(1 1 1) at 150 K, is initially adsorbed dissociatively. There appears to be only a slight amount of preferential orientation of subsequent molecularly adsorbed cobaltocene, but a preferential orientation along or close to the surface normal is increasingly adopted by molecular cobaltocene as the sample is annealed.

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