Comparison of Adsorbed Orthocarborane and Metacarborane on Metal Surfaces

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We compare the adsorption, bonding, and electronic structure of *closo*-1,2 dicarbadodecaborane (orthocarborane, $C_2B_{10}H_{12}$) and *closo*-1,7 dicarbadodecaborane (metacarborane, $C_2B_{10}H_{12}$) on metal surfaces. The electronic structure (molecular orbitals) of these two isomer molecules are calculated to be very similar, but there are significant differences in the experimental binding energies for each isomer as an adsorbed species. Metacarborane adsorbs on both Co and Au with the Fermi level (chemical potential) placed closer to the lowest unoccupied molecular orbital than is observed with orthocarborane adsorbed on Co and Cu.

There is a resurgence in the study of the electronic structure of gaseous (isolated)[1−11] and adsorbed[6−13] cage borane compounds. In part, this interest has been motivated by the applications of borane cage molecules as source compounds for boron−carbon semiconductors and boron-carbide semiconductor device fabrication.[8,14−24] Orthocarborane is now the source molecule of choice for making heterojunction diodes,[17−20] transistors,[22] tunnel diodes,[23] homojunction diodes,[23] and solid-state neutron detectors[24] that exploit semiconducting boron carbide. The *closo*-dicarbadodecaborane icosahedral cage molecules orthocarborane(1,2), metacarborane(1,7), and paracarborane(1,12) are isomers with the stoichiometric composition $C_2B_{10}H_{12}$, differing only by carbon placement within the cage.

Some experimental electronic structure studies of orthocarborane adsorbed on Cu(100),[8−10,12,24] and a limited overlayer band mapping[13] have been undertaken. Nonetheless, only the electronic structure of gaseous molecular isomers have been compared experimentally.[1−3] Herein we compare the adsorbed species of two icosahedral cage molecule isomers that share C_{2v} point group symmetry: metacarborane and orthocarborane, schematically indicated in Figure 1. We show that some surprising differences exist for these molecules, when adsorbed on metal surfaces.

Combined photoemission and inverse photoemission were undertaken to study the molecular orbital placement of both occupied and unoccupied orbitals of the adsorbed molecules on metal surfaces. The adsorbed molecular films were prepared by adsorption from vapor on substrates cooled to the vicinity of 200 K. Both orthocarborane and metacarborane were admitted to the vacuum system through a standard leak valve. The metal substrates include the Cu(100) surface, a 1000 Å Au(111) surface grown on Si(111), and Co surfaces, prepared by physical vapor deposition of Co on the gold coated silicon wafers. Where appropriate, the metal surfaces were cleaned before each adsorption by argon ion sputtering. The photoemission spectra were, generally, undertaken using a He I line source (21.2 eV)

in combination with hemispherical electron energy analyzer with photoelectrons collected normal to the surface. The polarization dependent photoemission studies, used to determine molecular orientation, were obtained from the polarized synchrotron radiation dispersed by a 3 m toroidal grating monochromator, at the Center for Microstructures and Devices, as described elsewhere.[12,13,25] With the highly plane polarized synchrotron light, photoemission experiments were undertaken with polarization varied from p-polarization (65 degrees off normal), with the vector potential oriented more normal than parallel to the surface, to s+p polarization (40−45° measured from normal) with the photoelectrons collected along surface normal. The He I (21.2 eV) ultraviolet photoemission (UPS), angle-resolved inverse photoemission (IPES), and XPS were undertaken in a single UHV chamber.[9,10] The inverse photoemission studies were performed using a Geiger-Müller detector with a SrF_2 window, with a pass energy of 9.5 eV. The overall energy resolution was approximately 500 meV. All IPES spectra were obtained with the electron gun at normal incidence and the detector positioned at 35° off the surface normal, as described elsewhere.[12,13] All binding energies are referenced to the Fermi level and were calibrated by tantalum foil in intimate contact with the sample surface, and the gold substrate. Inner shell energy loss spectroscopy, of the vapor, was also undertaken as a complimentary technique to inverse photoemission.[2,3]

The calculated molecular orbitals, undertaken to illustrate the molecular electron structure, are from semiempirical calculations based on an MNDO (modified neglect differential overlap) code similar to that undertaken on other carborane cluster molecules.[6−8] The molecular orbital symmetries were assigned by assuming a C_{2v} point group symmetry, which may not be applicable to the adsorbed molecule. Nonetheless, the wealth of experience from small weakly chemisorbed adsorbates,[26] e.g., CO[27] and N_2,[28,29] suggests that surface symmetry breaking will not result in large changes in molecular orbital binding energies or molecular orbital level ordering changes between the different surfaces of copper and gold.

As indicated by Figure 1, metacarborane and orthocarborane are isomers of C_{2v} symmetry, differing only by placement of the carbon atoms. The model calculations of the occupied and unoccupied molecular orbitals, shown in Figure 1, indicate that

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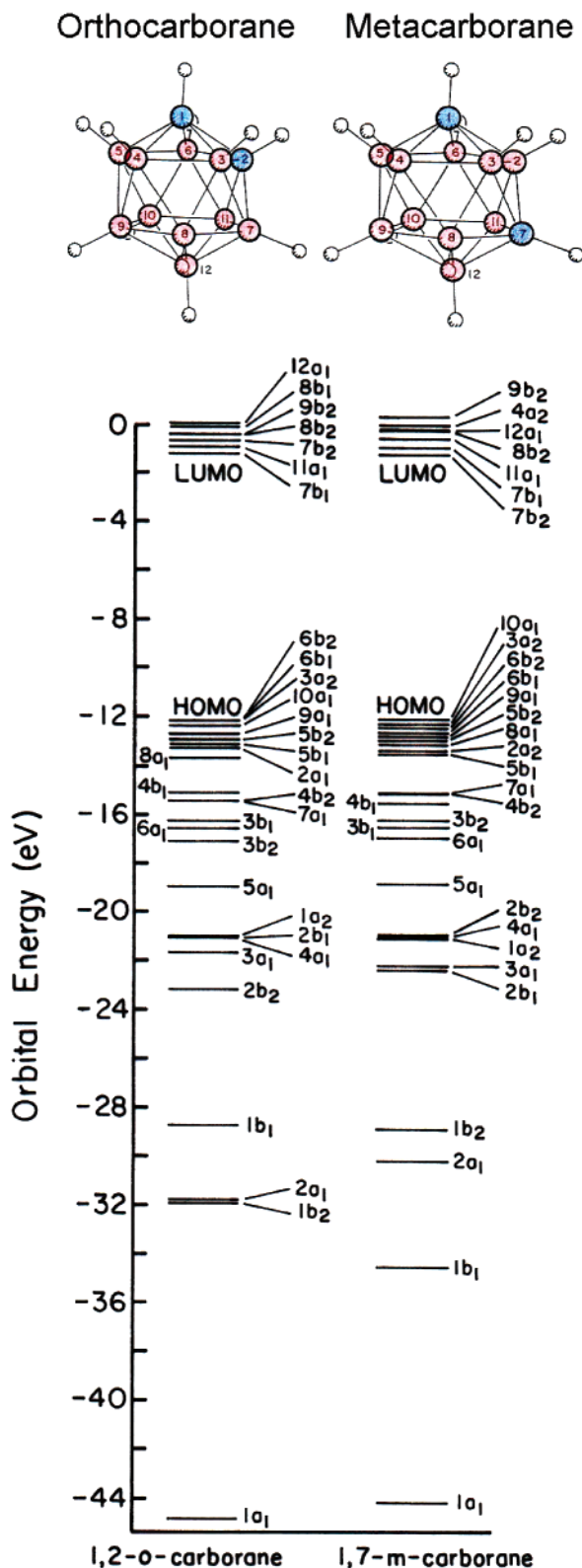‡ École Polytechnique Fédérale de Lausanne.

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Figure 1. Schematic models of orthocarborane or *closo*-1,2-dicarba-dodecaborane (left) and metacarborane or *closo*-1,7-dicarbadodeca-borane (right) are shown with the calculated ground-state molecular orbitals and their level ordering. Carbon atoms are highlighted in blue and the boron atoms in red.

Figure 2. Photoemission comparison of adsorbed orthocarborane on Cu(100) as a function of coverage (black) compared with a three monolayer molecular film of adsorbed metacarborane on gold (red). Photoemission (left) and inverse photoemission (right) are referenced to the Fermi level of the substrate. The estimated HOMO to LUMO gaps are indicated. The photoemission spectra for metacarborane on gold was taken with 32 eV photon energy and the spectra for orthocarborane on Cu(100) were taken with 30 eV photon energy and the synchrotron radiation includes both s- and p-polarization components with the photoelectrons collected normal to the surface with an angular acceptance of ±1.5 degrees.

orthocarborane and metacarborane exhibit very similar electronic structure, with almost identical placements of the highest occupied molecular orbital (HOMO) and lowest molecular orbital (LUMO) edges and the majority of other molecular orbitals. This is not observed in experiment.
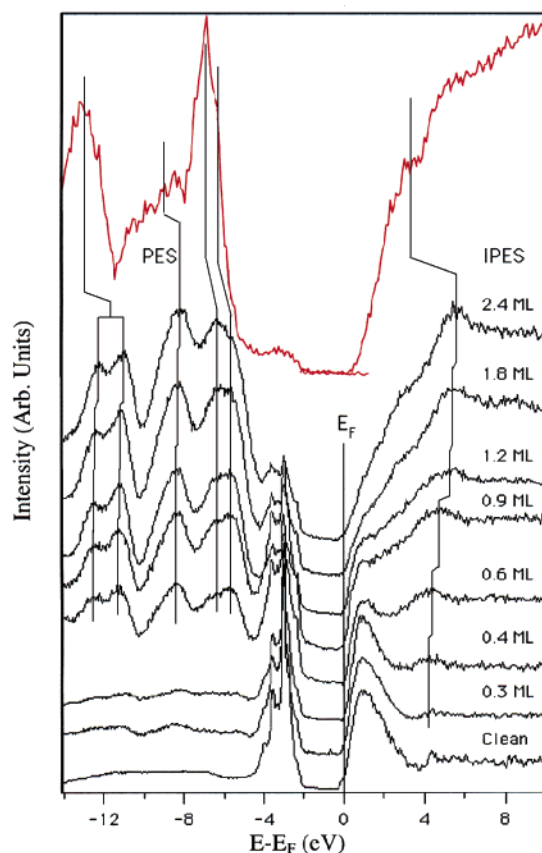
In Figure 2, we compare orthocarborane adsorption on Cu(100) with metacarborane adsorption on Au(111). With increasing molecular coverage, the substrate copper and gold d-band features are suppressed. By about 3 monolayers cover-age, the photoemission and inverse photoemission features due to the molecular orbitals of orthocarborane and metacarborane dominate, leaving only a small d-band density of states of the substrate Cu and Au. A similar process is observed with ortho-carborane and metacarborane adsorption on cobalt (Figure 3).

A number of occupied and unoccupied molecular orbitals can be identified and compared with theory, as summarized in Tables 1 and 2. A rigid shift from the calculated ground-state molecular orbitals with respect to the molecular orbitals observed for orthocarborane on Cu(100) and metacarborane on Au(111) in photoemission by about 6.7 and 5.5 eV, as expected from previous work,[8-10,12-13] is observed. The shift is somewhat less between calculated unoccupied orbitals and those observed in inverse photoemission. Despite the addition of a fragment or defect state appearing in inverse photoemission some 3 eV above the Fermi level at higher coverages for orthocarborane on Cu(100),[9,10] the general agreement of the photoemission and inverse photoemission with theory is a compelling indication of molecular adsorption, as has been previously noted.[9,10,12,13] These molecular orbitals are also evident with orthocarborane

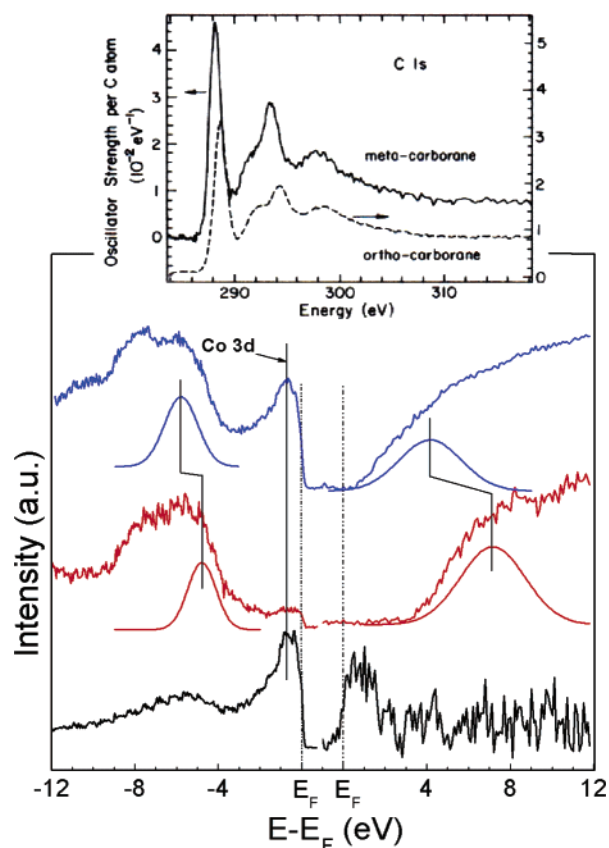**9622** *J. Phys. Chem. B, Vol. 107, No. 36, 2003*

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Figure 3. Photoemission and inverse photoemission of metacarborane (blue) and orthocarborane (red) on clean cobalt (black). The cobalt d-band intensity (as indicated) is dramatically reduced with carborane adsorption. The photoemission spectra were taken using a helium I (21.2 eV) line source. The inset shows the inner shell adsorption spectra of gaseous metacarborane and orthocarborane compared for the carbon 1 s edge, as described elsewhere.[3]

TABLE 1: Calculated Orbital Binding Energies for Orthocarborane Compared to the Observed Molecular Orbital Binding Energies for Orthocarborane on Cu and Co[a]

symmetry representation	theory	ortho on Cu	diff[b]	ortho on Co	diff[b]
12a$_1$	−0.11				
8b$_1$	−0.41				
9b$_2$	−0.43	5.6	−6.2	3.4	−4.1
7b$_2$	−0.70				
11a$_1$	−0.93				
7b$_1$ (LUMO)	−1.21				
6b$_2$ (HOMO)	−12.18				
6b$_1$	−12.2				
3a$_2$[c]	−12.36	−5.7	−6.7		
10a$_1$	−12.37				
9a$_1$	−12.71			−4.9	−7.9
5b$_2$	−12.93				
5b$_1$	−13.15				
2a$_2$[c]	−13.23	−6.7	−6.7		
8a$_1$	−13.68				
4b$_1$	−15.1				
4b$_2$	−15.4	−8.5	−6.8	−7.5	−7.8
7a$_1$	−15.43				
3b$_1$	−16.25				
6a$_1$	−16.57	−11.4	−5.2	−	−
3b$_2$	−17.1				
5a$_1$	−18.96	−12.5	−6.9	−	−

[a] The adsorbed molecular binding energies are all referenced with respect to the substrate Fermi level ($E - E_F$), whereas the calculated gas-phase binding energies are referenced with respect to the vacuum level. For the adsorbed phase, orbitals with negative binding energies ($E - E_F$) are occupied, whereas orbitals with positive binding energies represent unoccupied states. The HOMO and LUMO states are indicated. Note that all energy values are in electronvolts. [b] The binding energy differences are the calculated binding energies minus the experimentally observed binding energies uncorrected for work function and photoemission final state effects. [c] States that are forbidden by dipole selection rules, namely a$_2$ symmetry, in photoemission and inverse photoemission.

and metacarborane adsorption on Co, but the molecular orbitals are somewhat shifted in binding energy.

For both metacarborane and orthocarborane adsorption on Co, the HOMO to LUMO gap is substantially decreased from the expected values and the molecular orbitals are shifted toward the Fermi level, as summarized in Tables 1 and 2. This is consistent with the generally accepted greater reactivity of cobalt and suggests that cobalt acts as a charge donor to the molecular film or better screens the photoemission and inverse photoemission finals states. Because the molecular orbitals are perturbed for adsorption on cobalt, closing the HOMO to LUMO gap, final states effects, particularly electron delocalization related screening effects, likely dominate these shifts[30] rather than initial state effects that include fragmentation.[8]

On the basis of the binding energies, the HOMO to LUMO gaps for orthocarborane on copper (11.3 eV) and metacarborane on gold (10.0 eV) are in reasonable agreement with theory (10.97 and 10.92 eV, respectively). Nonetheless, there is an unexpected shift between the orthocarborane and metacarborane edges with respect to E_F. Although it is known that a lowering of orbital symmetry can occur with molecular adsorption,[26] and Cu(100) is not identical in reactivity compared to Au(111), this cannot account for the large binding energy shifts observed between metacarborane adsorption on Au(111) and orthocarborane adsorption on Cu(100). Because the HOMO−LUMO gap center is offset, with respect to the Fermi level, differently for the two molecules by more than ∼1.5 eV, significant

differences in the electronic structure of adsorbed metacarborane and orthocarborane are indicated, even for adsorption well beyond a monolayer on Cu(100), Au(111), or Co(111).

This shift in the HOMO−LUMO gap center offset with respect to the Fermi level is even more apparent when comparing orthocarborane and metacarborane adsorption on cobalt (Figure 3). In all cases studied, the LUMO is significantly closer to the Fermi level for adsorbed metacarborane than adsorbed orthocarborane. These results suggest that metacarborane forms a molecular insulating thin film that is far more n-type than the slightly p-type orthocarborane.

This shift in the lowest unoccupied molecular orbital seems to be intrinsic to the differences between metacarborane and orthocarborane that are not evident in our simple ground-state calculations. As seen in the inset to Figure 3, the inner shell excitation spectra[3] show a shift of about 1 eV in the C 1s to LUMO excitation. The greater excitation energy for orthocarborane has been suggested to be a result of weaker carbanion character[3] or a localized C=C bond.[31] This intrinsic difference between metacarborane and orthocarborane could be enhanced in the molecularly adsorbed films due to electronic differences induced by bonding orientation and due to molecular packing.

An enhancement in molecular orbital contributions with b$_1$, b$_2$ symmetry is observed with polarization dependent photoemission of s+p over p polarization for orthocarborane, but an enhancement in p over s+p for the corresponding photoemission

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TABLE 2: Calculated Orbital Binding Energies for Metacarborane Compared to the Observed Molecular Orbital Binding Energies for Metacarborane on Au and Co[a]

symmetry representation	theory	meta on Au	diff[b]	meta on Co	diff[b]
	1.19				
	1.0				
	0.8	4.7	−4.0	−	−
9b1	0.7				
8b1	0.54				
9b2	0.27				
4a2[c]	−0.08				
12a1	−0.22				
8b2	−0.26	3.2	−3.7	2.5	−3.0
11a1	−0.58				
7b2	−1.0				
7b2 (LUMO)	−1.25				
10a1 (HOMO)	−12.12				
3a2[c]	−12.27	−6.7	−5.6		
6b2	−12.45				
6b1	−12.67			−5.6	−7.2
9a1	−12.77				
5b2	−12.93	−7.7	−5.4		
8a1	−13.12				
2a2[c]	−13.41				
5b1	−13.51				
7a1	−15.13				
4b2	−15.16				
4b1	−15.54	−10.9	−5.0	−7.8	−8.1
3b1	−16.24				
3b2	−16.54				
6a1	−16.97				
5a1	−18.86	−13	−5.9	−	−

[a] The adsorbed molecular binding energies are all referenced with respect to the substrate Fermi level ($E - E_F$), whereas the calculated gas-phase binding energies are with respect to the vacuum level. For the adsorbed phase, orbitals with negative binding energies ($E - E_F$) are occupied, whereas orbitals with positive binding energies represent unoccupied states. The HOMO and LUMO states are indicated. Note that all energy values are in electronvolts. [b] The binding energy differences are the calculated binding energies minus the experimentally observed binding energies uncorrected for work function and photoemission final state effects. [c] States that are forbidden by dipole selection rules, namely a2 symmetry, in photoemission and inverse photoemission.

features for adsorbed metacarborane. This is a very strong indication that orthocarborane and metacarborane exhibit different preferential bonding orientations when adsorbed on metal surfaces. This is not surprising because the bonding configuration of both carbon atoms toward the surface, observed for orthocarborane,[12] is sterically forbidden with metacarborane.

Through a comparison of experimental photoemission and inverse photoemission results with theoretical calculations, we have shown that although the electronic structure of metacarborane and orthocarborane are expected to be similar, there are profound differences. These differences suggest the number of different polytypes observed for boron carbide[19] may exhibit huge differences in electronic structure as well, if the carbon cage positions are altered.

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