In situ formation and electron-spectroscopic study of bis(arene) V and Cr compounds on a graphite surface

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Thin layers of bis(arene) transition metal (TM) compounds have been formed in situ in ultra-high vacuum by depositing Cr or V metal on top of a film of benzene (Bz) or toluene (Tol) ice at 100 K on a graphite substrate. The species thus formed are Cr(C\textsubscript{6}H\textsubscript{6})\textsubscript{2}, V(C\textsubscript{6}H\textsubscript{6})\textsubscript{2}, or Cr(C\textsubscript{6}H\textsubscript{5}-CH\textsubscript{3})\textsubscript{2} (termed CrBz\textsubscript{2}, VBz\textsubscript{2}, or Cr(Tol)\textsubscript{2}), and the valence structures have been examined using electron energy loss and ultraviolet photoemission spectroscopies (ELS and UPS). The reaction is “clean” in that there is no indication of side reactions or unwanted by-products, although a small coverage of unreacted TM atoms appears unavoidable. A simple ring substituent (CH\textsubscript{3}) remains intact during the reaction. Thus, it should be possible to synthesize and study species that are not readily available (or cannot easily be made) in bulk form or that have too low vapor pressure to allow easy in situ deposition. Data have been obtained for VBz\textsubscript{2} and Cr(Tol)\textsubscript{2}, the valence structures of which have not previously been studied in detail using UPS and ELS. Although deeper-lying arene orbitals are essentially unperturbed by formation of the bis(arene)TM sandwich, subtle differences in the TM-related orbitals have been observed and discussed in comparison to CrBz\textsubscript{2} with the aid of density functional theory. In the case of VBz\textsubscript{2}, clear evidence is seen for a molecular reorientation during annealing, based on the ELS polarization dependence. Electron transfer between an adsorbed bis(arene)TM and graphite depends on the occupancy of the highest occupied molecular orbital (HOMO) and on its energy relative to the Fermi level (E\textsubscript{F}). The small amount of unreacted TM resulting from in situ synthesis causes a large decrease in work function, which shifts the adsorbate HOMO to below E\textsubscript{F} and thus impedes electron transfer to highly oriented pyrolytic graphite. This is an obstacle to forming doping layers by this method.

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I. INTRODUCTION

The doping of semiconducting single-wall carbon nanotubes (SWCNTs) and graphene is a subject of significant importance since it enables the modification of electronic properties and, thus, the engineering of carbon nanostructures for specific applications. There has been extensive theoretical and experimental effort in this field, some of which is reviewed elsewhere.\textsuperscript{1–3} The term “doping” as used here includes manipulation of the band gap as well as the more traditional concept of modifying the free-carrier concentration. One very promising approach involves incorporating a transition metal (TM) or a TM compound by some means, either on the surface or by encapsulation within an SWCNT. An advantage of this approach is that an appropriately chosen TM structure will be stable against oxidation, whereas a bare TM atom is generally not. Another expected benefit\textsuperscript{4–6} is that the π-bonded network of the graphene or SWCNT remains intact, so that carrier mobility should not be significantly degraded. This contrasts with other methods in which sp\textsuperscript{3}-hybridized C atoms form at dopant bonding sites.

One particularly stable class of TM compounds\textsuperscript{7} is the bis(arene)TM “sandwich” in which a TM atom is bonded between two π-bonded organic rings, or arenes. An archetypal example is bis(benzene)Cr [{Cr(η\textsuperscript{6}-C\textsubscript{6}H\textsubscript{6})\textsubscript{2}, Fig. 1} where η\textsuperscript{6} indicates that the Cr is coordinated to all six C atoms in the benzene (Bz) ring, and theoretical studies have examined analogs of the bis(arene)TM sandwich in which one side is graphene\textsuperscript{4–6} and the other is an arene, typically Bz. A variant of this approach that has to some extent been demonstrated experimentally is to use a bis(arene)TM itself as the dopant. Ferrocene (Fe(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})\textsubscript{2} or FeCp\textsubscript{2}, where Cp \equiv cyclopentadiene) can be encapsulated into SWCNTs from solution\textsuperscript{8} or from the vapor,\textsuperscript{9,10} although the resulting electronic properties have not been characterized. Theory indicates n-type doping for cobaltocene (Co(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5})\textsubscript{2} or CoCp\textsubscript{2}) encapsulated in an SWCNT\textsuperscript{11,12} or adsorbed on graphene.\textsuperscript{13} This has been verified experimentally\textsuperscript{14} for CoCp\textsubscript{2} on highly oriented pyrolytic graphite (HOPG), which shows evidence for electron transfer from the adsorbate to the substrate.

Doping by means of a bis(arene)TM is closely related to the electronic structure of such species. The free Cr atom has the electronic configuration (Ar)3d\textsuperscript{5}4s\textsuperscript{1}, and the metal–ligand bonding in CrBz\textsubscript{2} has been analyzed quantitatively\textsuperscript{15} in terms of specific orbital interactions. The Cr 3d\textsubscript{z}\textsuperscript{2} orbital transforms as the a\textsubscript{1g} representation of the D\textsubscript{5h} point group describing CrBz\textsubscript{2} in the eclipsed structure (cf. Fig. 1). The 3d\textsubscript{xz} is a non-bonding orbital (NBO) and is the highest occupied molecular orbital (HOMO). The 3d\textsubscript{yz} and 3d\textsubscript{xy} orbitals (HOMO-1) belong to e\textsubscript{g} and are strongly δ-bonding, while the Cr 3d\textsubscript{zx} and 3d\textsubscript{xy} orbitals (HOMO-2) transform as e\textsubscript{g} and are weakly π-bonding. The resulting system has a very stable 18-electron “Kr-like” valence structure (six electrons from Cr and six from each of the rings), which gives a \textsuperscript{1}A\textsubscript{1g} ground state.

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related to the synthesis and deposition of bis(arene)TM species
which are addressed here.

The purpose of the present work is to examine the feasibility of a novel
approach to adsorption of bis(arene)TM species, using CrBz2 and VbZ2 as representative
compounds and HOPG as a simulant for graphene. Since the valence
structure is of most interest, this work uses UPS and electron energy loss spectroscopy (ELS) performed
in ultra-high vacuum (UHV). Such data are necessary for comparison with the theoretical results cited above. Forming a sample in situ under UHV conditions raises the issue of the low vapor pressure of bis(arene)TM species (e.g., 4.56 × 10−4 Torr for CrBz2 at 50 °C, Ref. 19). This will be circumvented using a method, first reported by Sklarek et al.,20 in which the metal of interest is vapor-deposited onto a layer of solid
arene ice. This technique is conceptually similar to metal-vapor synthesis (or co-condensation), in which vapors of the metal and the organic reagent are condensed together on a substrate. However, the process described by Sklarek et al.20 is more compatible with an UHV environment since only a small arene dose is needed to form the required ice layer. This was demonstrated for the in situ synthesis of CrBz2 but to our knowledge has not been reported for other TM or arenes. In addition to overcoming the problem of low
organometallic vapor pressure, this allows the easy synthesis of thin layers of bis(arene)TM species that are not available (or cannot be made) in bulk form. Thus, quite apart from any interest in doping, in situ spectroscopic studies can be performed on species not readily obtainable by conventional means.

II. METHODS
A. Experiment

All experiments were done in a standard stainless-steel UHV chamber with a base pressure of ∼7 × 10−11 Torr. The electron spectrometer was a double-pass cylindrical mirror analyzer (CMA) which, for UPS, was operated in the “retard” (constant-resolution) mode with electron-counting detection. The excitation source was the HeII (hν = 40.81 eV) line of a differentially pumped dc discharge in He gas, and the CMA pass energy was 25 eV, giving a total instrumental resolution of ∼0.40 eV. Binding energies (BEs) were referenced to the Fermi edge of metallic clusters22,23 formed on HOPG at room temperature and also to the HOPG slow-secondary peak.24 The sample work function (φs) was measured using the kinetic energy threshold for secondary-electron emission with a small negative bias applied to the sample and the CMA resolution increased to ∼0.16 eV. The threshold was obtained by a linear extrapolation of the low-energy edge to zero counts. The work function of clean, undamaged HOPG thus obtained was φs = 4.6 ± 0.1 eV at 100 K, which is in reasonable agreement with a previous result14 of 4.4 eV.

For ELS, data were obtained with an Ep = 90 eV, i0 = 0.3 μA/cm2 electron beam from the coaxial gun of the CMA. The current density was kept low to avoid damage to the organic species, the absence of which was verified by repeated scans of the same area of the surface. The resolution, given by the full-width at half-maximum (FWHM) of the

Figure 1 shows gas-phase ultraviolet photoemission spectroscopy (UPS) data,16 which are very similar to those for a condensed multilayer.17 The distinguishing characteristic of Cr–C6H6 bonding is the appearance of the a1g and e2g features, while deeper-lying structure is similar to that of molecular benzene.17 V(η6-C6H6)2 (or VBZ2) also forms an eclipsed structure but is a 17-electron system with a single unpaired
electron in the a1g NBO, which gives a2A1g ground state.

For a given TM the NBO can act as a donor or acceptor level depending on occupancy and on the energy separation from the SWCNT or graphene band edges, as has been shown theoretically.11–13 For CoCp2, Cobaltocene has a 19-electron structure but is a 17-electron system with a single unpaired
electron. Other theoretical work18 has shown that adsorption of FeCp2 and of ruthenocene, the Ru analog of FeCp2, can modify the electronic properties of graphene that has been doped with foreign atoms such as B or N. Further advances might be achieved by investigating other potential bis(arene)TM species as graphene dopants beyond CoCp2, which to date is the only such species to have been experimentally demonstrated14 for this application. Actually forming such systems, however, raises certain practical issues

![Figure 1. (Color online) (a) Staggered and (b) eclipsed Cr(η6-C6H6)2; (c) experimental UPS data for Cr(η6-C6H6)2 vapor (hν = 30 eV) from Ref. 16 (with permission). The binding energy reference is the vacuum level. The very sharp features are artifacts incurred during digitization of the published spectrum.](Image 78x456 to 271x751)
elastic peak, was 0.5 eV, and data were recorded as N(E) vs E using electron counting. Auger electron spectroscopy (AES) data were obtained in the form of d(E-N(E))/dE in the nonretard, first-derivative mode using a 3 keV, ~4 µA primary beam with a 2 eV peak-to-peak modulation. In all experiments, the sample normal made an angle of 25° with the CMA axis.

A sample of HOPG was mounted on a variable-temperature stage and cleaned in situ by annealing at 1200 K, which has been shown to yield a high-quality surface. The sample temperature was measured using an optical pyrometer, and following this treatment no impurities were detected in AES. Cr was deposited in situ using a resistively heated Cr-plated W wire, and V was deposited from a resistively heated ribbon (99.8% purity) which had been etched briefly in 1:1 HNO3:H2O prior to mounting to remove any gross surface contamination. The chamber pressure remained below 2 × 10⁻⁹ Torr during metal deposition, and residual gas analysis showed that H₂ was the main component in the UHV ambient during deposition. Metal deposition was controlled using a quartz crystal oscillator thickness monitor, and the actual coverages were determined using AES (see the supplementary material). The purity of the metal layers was evaluated after deposition at ~100 K on bare HOPG (i.e., with no arene ice layer). The O KLL spectrum overlaps the V and Cr LMM spectra but, in the case of Cr, is sufficiently separated to detect contamination can be detected directly. For V, the main O KLL feature, at ~510 eV, overlaps the V peak near 511 eV. Hence, O was detected on V by observing the relative peak-to-peak heights of the V transitions at 511 and 475 eV, which is 0.25 for clean V at E₀ = 3 keV. No O was detectable in the freshly deposited metal layers.

Exposure to reagent vapor was done using a calibrated-pinhole molecular-beam doser. The reagent-grade liquids were previously degassed by repeated freeze-pump-thaw cycles with freezing being done in dry ice (Bz) or liquid N₂ (toluene (Tol)). The nude ionization gauge was switched off before dosing in order to avoid excitation of molecular species. The sample temperature was measured using a chromel/alumel thermocouple attached to the cooled Cu block in thermal contact with the sample. The temperature reading was checked by noting the point at which condensed Bz disappeared in AES and UPS experiments. This occurred within 10 K of the reported desorption temperature (152 K) for a Bz monolayer (ML) on HOPG.

After each series of experiments, the Cr was thermally desorbed at 1200 K to re-clean the surface. This removed all but a small residue, ~0.05 ML, which is thought to represent Cr retained in fissures in the HOPG surface or strongly adsorbed at defects. Here, one ML means one Cr per surface C atom (i.e., 3.83 × 10¹⁵ atoms/cm²). In the case of V, metallic deposits could not be completely removed by heating in UHV to 1300 K, the highest temperature attainable with the present apparatus. Formation of V carbide might occur at this temperature, but the coverage was not sufficiently high that a distinct change in the C KLL line shape could be seen. V was removed using 1 keV Ar⁺-ion bombardment at room temperature (at a total dose of ~10 Ar⁺ per surface C) followed by annealing at 1200 K. It should be noted that the Cr experiments were all performed on HOPG that had never been ion bombarded.

B. Computation

Density functional theory (DFT) calculations for free molecules were done, mainly for the purpose of obtaining model UPS spectra, using the Gaussian 09 program suite. The TPSS functional was used since it has been shown to give good structural and bond-energy results for CrB₂ and related species. For C and H, 6–311G(d,p) basis sets were used, and larger basis sets (6–311++G(2d,2p)) gave no significant difference in the optimized geometries. Some calculations were also done for anions, and for these 6–311++G(d,p) basis sets were used for C and H since diffuse functions are generally required in this case. For TM's, the Stuttgart-Dresden relativistic effective-core pseudopotentials (ECPs) of Dolg et al. were used since these have been shown to give good results for CrB₂. These are small-core ECPs that replace only the metal 1s, 2s, and 2p shells. Spin-unrestricted calculations were done for species having an unpaired electron, and all results were checked for wavefunction instabilities and for imaginary vibrational frequencies. “Tight” convergence criteria and an “ultra-fine” integration grid were used in all calculations.

Model UPS spectra were computed using the one-electron energies of the occupied orbitals. A Gaussian of unit area was placed at each energy and the sum of all such peaks obtained. Thus, all orbitals are assumed to have the same photoionization cross section. A Gaussian FWHM of 0.40 eV plus additional contributions from “solid-state effects” (intermolecular interaction and disorder in the condensed layers).

III. RESULTS

A. Energy loss spectroscopy

The ELS data [Figs. 2(a) and 2(b)] for bare HOPG and for solid Bz in the range of valence and π plasmon excitation show, respectively, a π plasmon at ~6.5 eV and a π → π* excitation at 7.0 eV. The Bz spectrum shows an additional weak feature at 10 eV that has been associated with the extent of crystallinity. Sklarek et al. have reported the in situ synthesis of CrB₂ by deposition of Cr onto a layer of Bz ice and characterized the product using core-level x-ray photoemission spectroscopy. We have repeated this process, depositing ~0.20 ML of Cr on Bz ice at 100 K, and have studied the valence excitations of the resulting material using ELS and UPS. The ice thickness is estimated to be a few tens of MLs, based on the Bz dose and the assumption of unity sticking coefficient at 100 K. In this case, an ML refers to a close-packed layer of flat-lying Bz rings. When necessary, the sample was warmed to ~170 K to desorb unreacted Bz and then cooled back to 100 K for data collection. For thinner ice layers, this was not needed since most of the Bz either reacted with the metal or desorbed due to the energy released in the deposition. A recent study of Ag, Mg, and Al deposited on Bz ice at 30 K reports a complex mix of reaction
products for Al but not for Ag or Mg. The controlling factor is thought to be the metal ionization potential (IP) which is low for Al (5.98 eV) but higher for Ag and Mg (7.57 and 7.64 eV, respectively). The IPs for V and Cr (6.74 and 6.76 eV, respectively) are roughly midway between these values, and no indication of products other than VBz2 and CrBz2 was seen here or in Ref. 20.

With Cr added, a new feature is seen [Fig. 2(c)] at 4.0 eV. The absorption spectrum of CrBz2 vapor in the 2.7–5.3 eV range shows relatively narrow Rydberg transitions at 3.3 and 4.4 eV and a broad feature at ~4.0 eV, which is assigned to a valence excitation. If the initial state is the a1g NBO, then the final state in the valence excitation would be either a2u or e1u under the electric-dipole selection rules for D6h symmetry. A recent calculation using time-dependent DFT places the CrBz2 a1g → a2u transition at 3.3 eV, but the a1g → e1u energy was not given. VBz2 was synthesized in the same manner as for CrBz2, which suggests that this may be a general approach for the in situ synthesis of simple bis(arene)TMs. Data presented below will show that bis(toluene)Cr (Cr(Tol)2) can also be formed by this means.

The effect of annealing on the 2.6 and 3.8 eV losses can be understood in terms of a molecular reorientation. Rubloff has shown that, in the case of dipolar scattering, a polarization selection rule can be formulated for ELS whereby the intensity due to excitation of an adsorbate dipole parallel to the surface is reduced in magnitude by a factor of (ε1 + ε2) relative to one that is normal to the surface. Here, ε1 and ε2 are the real and imaginary dielectric constants of the substrate at an energy equal to that of the transition being excited. Using the optical constants for HOPG at 3 eV for polarization parallel to the surface gives a reduction factor of ~70; hence, only an excitation polarized perpendicular to the surface can be detected for purely dipolar scattering.

Both assignments of the VBz2 optical spectrum agree that the 3.8 eV transition is e2g → e2u. In the molecular D6h point group, e2g ⊗ e2u = a1u + a2u + e2u, of which only a2u is electric-dipole allowed, and therefore the transition is polarized parallel to the sixfold rotation axis (C6x). Hence, the effects shown in Fig. 3 can be understood if VBz2 is initially formed in an essentially random orientation and then reorients upon annealing so that C6x is normal to the surface (i.e., with the Bz rings lying flat). The 2.6 eV transition shows the opposite annealing dependence and is therefore polarized perpendicular to C6x so that it loses intensity when the Bz rings lie flat. This would be consistent with the a1g → e1u transition. The π → π* transition should also be polarized parallel to C6x since it is e1g → e1u or e1u → e1g, and e1g ⊗ e1u = a1u + a2u + e2u. In Fig. 3 the π → π* is weak and
broad, as in Fig. 2(d), and difficult to separate from the same transition in unreacted Bz; however, it is still clearly present after the 258 K anneal, which is consistent with the polarization assignment discussed above.

Deviations from complete polarization could indicate a degree of disorder in the molecular alignment or a contribution from impact scattering. The latter is a possibility since the scattering geometry in these experiments was off-specular (see Sec. II A). Theoretical studies have shown that both orientations are possible for TM(Cp)2 species on HOPG, depending on the TM, and that the energy difference is often small (<20 meV in some cases). However, a thermally induced reorientation such as that observed for VBz2 has not to our knowledge been previously seen experimentally. The reason for the preferred orientation in the case of VBz2, but not CrBz2, is uncertain and will require further theoretical study. It is speculated that the effect may result from a weak interaction between the singly occupied V 3dz2 HOMO, which lies parallel to C6, and the HOPG π-band.

Temperature-programmed desorption (TPD) data show desorption of CrBz2 from a Ni(100) surface and from a CH3-terminated n-alkanethiol self-assembled monolayer (SAM) at about 250 and 265 K, respectively, and the CrBz2-related structure in Fig. 2(c) disappears at about this temperature. Other TPD peaks are seen at similar structures on HOPG below 150 K. The reason for the preferred orientation in the case of VBz2, but not CrBz2, is uncertain and will require further theoretical study. It is speculated that the effect may result from a weak interaction between the singly occupied V 3dz2 HOMO, which lies parallel to C6, and the HOPG π-band.

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B. Ultraviolet photoemission spectroscopy

Figure 4(a) shows UPS data for clean HOPG that agrees well with previous HeII results; although, the major peak at ~8 eV is not as sharp, which may be due to the roughness of the present surface. Figure 4(b) shows data for a layer of Bz ice, which agree with previous results except that the BEs relative to the Fermi level (E2) are ~1.5 eV higher on Ni(100) than on HOPG. This represents the combined effects of differences in the work function of the two substrates (with a Bz overlayer) and in relaxation (molecular polarization plus image-charge screening).

The UPS data for CrBz2 formed in situ [Fig. 4(c)] agree well with those for a multilayer grown by vapor deposition on Ni(100), although in the latter case, the a1g and e2g features are better resolved and the BEs about 0.5 eV higher. The CrBz2 BEs are found, here and in Ref. 17, to increase with coverage, and therefore the UPS features are less well resolved until the layer is sufficiently thick to obscure the interface. Since the amount of Cr deposited in obtaining the data in Fig. 4(c) was equivalent to only ~0.16 ML, the data represent at most a single close-packed CrBz2 layer (see the supplementary material). The shift to lower BE with decreasing thickness arises from an increased relaxation shift of the photoionized molecule when in direct contact with the substrate. Features marked with an asterisk in Fig. 4 may be “ghosts” due to excitation of the HOMO by the 23.09 eV HeI satellite; however, they also correspond to theoretically predicted CrBz2 and VBz2 features (see below). For CrBz2 on Ni(100), secondary electrons damage the adsorbate during UPS data collection. For HOPG, repeated scans of the same area of the surface showed that such effects are negligible, which suggests that HOPG is a less efficient secondary-electron emitter than Ni under HeI and HeII irradiation.

There are, to our knowledge, no previous UPS data for either gas-phase or condensed VBz2 except for a tabulation of the gas-phase BEs, which shows the HOMO, HOMO-1,
and HOMO-2 all falling within a range of 0.75 eV. The data in Fig. 4(d) are very similar in all respects to those for CrBz2 except for the slightly higher BE for the e1g,e1u peak and the absence of any clear a1g feature. There is also a small splitting of the peak at ~10 eV BE, which is reproducible and which vanishes after annealing at ~260 K. The temperature dependence suggests that the splitting may be related in some way to the molecular reorientation discussed above.

Figure 5 shows data for a thin layer of Tol ice and for the same layer after depositing ~0.10 ML of Cr. The Cr coverage was reduced, relative to the CrBz2 experiments, in consideration of the larger “footprint” of flat-lying Tol versus Bz. There are, to our knowledge, no published UPS data for toluene ice; however, the results can be discussed with reference to HeI-excited gas-phase spectra. The main difference between Bz [Fig. 4(b)] and Tol [Fig. 5(a)] ices is in the region of BE = 8–9 eV, which in Bz is assigned to the σ-bonding 3e1u and 1b2u orbitals. In Tol, these orbitals are perturbed by the CH3 group, and the asymmetrically broadened Bz peak is seen to split in the Tol data. This effect, which is clearly seen in a comparison of gas-phase UPS data for CrBz2 and Cr(Tol)2, appears in Fig. 5(b) as a distinct broadening in comparison to the corresponding CrBz2 feature. This is taken to indicate that the bonding of the CH3 to the Bz ring remains intact since no similar broadening is seen for CrBz2 at any coverage.

To our knowledge, Cr(Tol)2 is not commercially available; hence, Fig. 5(b) illustrates the use of in situ synthesis as a simple method for obtaining spectra for new molecular species. Compared to CrBz2, the HOMO and HOMO-1 are broadened, even for a Cr(Tol)1 multilayer (not shown). This could result from an unresolved splitting of the e3g level due to the symmetry-lowering effect of the CH3 group. Theory finds that the lowest-energy configuration places the two CH3 groups 180° apart but that there is only a small (4.5 kJ/mol or less) barrier for the relative rotation of the two rings. Hence, rotational disorder is expected in the Cr(Tol)1 layer, which could contribute to broadening. In ELS data (not shown), a transition is found at 4.0 eV that is also broadened relative to that for CrBz2.

C. Search for doping effects

Doping via adsorption of CrBz2 involves formation of the cation, [CrBz2]⁺. As noted in the Introduction, an analogous process was observed for CoCp2 and ascribed to the low IP of the free molecule. Electron transfer to the substrate was indicated by the decrease in the sample work function (φ3), due to the formation of a dipole layer with the positive end above the surface, and by the emptying of the singly occupied HOMO. Furthermore, a sub-ML of CoCp2 remains adsorbed on HOPG at room temperature, unlike in the case of CrBz2 and VBz2, which suggests a strong bond that is consistent with electron transfer. CoCp2 has also been incorporated into organic electronic materials as an n-type dopant.

The experimental (i.e., vertical) ionization potentials (VIPs) of gas-phase CrBz2 (5.40 eV, Ref. 16), VBz2 (5.95 eV, Ref. 52), 5.78 eV, Ref. 57), and CoCp2 (5.55 eV, Ref. 58) are all similar. As a test of the computational methods used here, values of 5.40 and 5.32 eV were found for the VIPs of CrBz2 and CoCp2 which are in reasonable agreement with experiment. In electron doping, which forms a stable cation, the adiabatic IP (AIP) is more relevant than the VIP, and calculations performed here give AIPs of 5.44, 5.62 and 5.23 eV, respectively, for gas-phase CrBz2, VBz2 and CoCp2.

Here, the difference in zero-point vibrational energies between the neutral and the ionized species has been included. In agreement with previous DFT results, the lowest-energy configuration of the 16-electron [VBz2]⁺ cation is found to be a Jahn-Teller-distorted open-shell triplet rather than a closed-shell singlet. In the adsorbed state, the IPs will be reduced by ~1–1.5 eV due to screening and relaxation effects. Thus, if the AIP is the controlling factor, then electron transfer to HOPG should occur as readily for CrBz2 as for CoCp2, which was a motivating factor in the present experiments. It should be noted, however, that recent theoretical work suggests that it is the overlap of the bis(arene)TM HOMO with the graphene π orbitals, and not simply the AIP, that is critical in electron transfer.

Figure 6 shows UPS data for CrBz2 at 100 K together with DFT results for the neutral and cationic species. The CrBz2 coverage in Fig. 6(a) is somewhat higher than in Fig. 4(c), and the spectrum shows the sharper structure and slightly higher BEs associated with a multilayer. The [CrBz2]⁺ calculation was spin-unrestricted, and the results shown are for the total spin-up plus spin-down spectrum. Geometry optimization for [CrBz2]⁺ showed that the eclipsed structure is favored over the staggered by 3.1 kJ/mol. For the neutral molecule the computed energy difference is 4.1 kJ/mol, in good agreement with previous results. The relative intensities and BEs computed for VBz2 (not shown), which is isoelectronic with [CrBz2]⁺, are very similar to those in Fig. 6(c). Likewise, the computed UPS of [VBz2]⁻ (not shown) is similar to that of CrBz2.
Upon (computational) formation of \([\text{CrBz}_2]^+\) the now-singly occupied HOMO shifts higher in BE, to the point where it cannot easily be distinguished from the HOMO-1, and the HOMO-1 and HOMO-2 shift by about 0.7 and 0.4 eV, respectively, to higher BE. The computed BE shifts are assumed to be reliable, even though the absolute BEs are somewhat overestimated due to the difficulty in accurately describing strongly correlated TM 3d electrons in conventional DFT. This strong correlation accounts for the fact that all orbitals with a significant Cr 3d component shift in BE when a single electron is removed from the HOMO. In the experimental CrBz2 spectrum [both Figs. 4(c) and 6(a)] the a1g HOMO is clearly visible, with an a1g/e2g relative intensity similar to that in the computed CrBz2 spectrum. The appearance of the experimental HOMO and HOMO-1 (i.e., relative intensity and BE versus the Bz ring orbitals) is essentially the same, aside from additional broadening, for a thin layer in which the CrBz2 is in close proximity to the surface as it is for a multilayer or for the free molecule (Fig. 1).

Hole doping is considered unlikely for the present systems. A calculation for the \([\text{CrBz}_2]^+\) anion (not shown) resulted in a singly occupied HOMO centered at 2.8 eV above the e2g level (i.e., at E_p), which has no counterpart in the data. The adiabatic electron affinity (AEA) of gas-phase CrBz2, found computationally\(^{61}\) to be \(-0.14\) eV, indicates that the anion is unstable relative to the neutral species, although screening and/or image-charge effects could lower the energy of an adsorbed anion. In any case, the AEA is much less than \(\phi_S\) of bare HOPG (4.6 eV), which prohibits electron transfer from HOPG. VBz2 is a 17-electron system; hence, one might expect that electron transfer from HOPG, to form \([\text{VBz}_2]^+\), might be energetically favorable. However, theory\(^{61}\) and experiment\(^{62}\) show that the free anion is unstable against ejection of an electron, although \([\text{VBz}_2]^+\) has been prepared in solution\(^{63}\) through contact with K metal. A further discussion of this breakdown of the 18-electron rule, which is based on a simple one-electron description of the bis(arene)TM orbital structure, is beyond the scope of the present work.

In this work, any effect on \(\phi_S\) resulting from electron transfer to or from CrBz2 or VBz2 is difficult to detect due to the presence of small amounts of unreacted metal, which have a large effect on \(\phi_S\). Theoretical work\(^{64}\) for Cr on graphene finds a charge of \(+0.58\) e on an isolated Cr atom which, for a C–Cr distance of 1.95 Å (the sum of covalent radii), yields a dipole moment of 5.43 Debye. For the adsorption of \(n\) dipoles/cm\(^2\) with a surface-normal moment of \(\mu_S\) Debyes, \(\phi_S(eV) = 3.00 \times 10^{-10}/(4\pi\mu_S)\) gives the change in \(\phi_S\). Thus, \(\phi_S \approx -1.0\) e (a typical result for \(\text{in situ} \; \text{CrBz}_2\) formation) corresponds to \(n \approx 4.9 \times 10^{13} / \mu_S\), or about 0.013 ML (~5–10% of the total Cr in a typical experiment). This is only a rough estimate since it is based on \(\phi_S\) for a continuous layer of dipoles; however, it demonstrates the sensitivity of \(\phi_S\) to adsorbed TM atoms. The decrease in \(\phi_S\), due to the surface dipole layer formed by the unreacted TM, will shift all the TM(Bz)2 orbitals (which shift together with the vacuum level) to correspondingly higher BE relative to \(E_p\), which will then impede electron transfer to the HOPG. Adsorption of CoCp2 on HOPG also results in a large decrease\(^{14}\) in \(\phi_S\) (\(\phi_S = -1.2\) eV), but in this case it is due to the electron transfer itself rather than to a foreign species acting independently. Upon warming, \(\phi_S\) decreases somewhat in magnitude, presumably due to the clustering\(^{22,23}\) of unreacted TM atoms.

IV. CONCLUSIONS

In summary, thin bis(arene)TM layers on HOPG have been formed \(\text{in situ}\) in an UHV chamber by depositing the metal on top of a film of arene ice at 100 K. The valence electronic structure of the molecular species was then examined using ELS and UPS. The results are as follows:

1. Depositing a TM on a condensed layer of a simple arene\(^{20}\) appears to be a general method for \(\text{in situ}\) formation of a bis(arene)TM. The process is “clean” in that there is no indication of side reactions or unwanted by-products, although the presence of a small coverage of unreacted TM atoms appears unavoidable. A simple ring substituent (CH\(3\)) remains intact during the reaction. Thus, it should be possible to synthesize and study species that are not readily available (or cannot easily be made) in bulk form or that have too low a vapor pressure to allow easy \(\text{in situ}\) deposition.

2. Data have been obtained for VBz2 and Cr(Tol)2, the valence structures of which have not previously been studied in detail using UPS and ELS. Although deeper-lying arene orbitals are essentially unperturbed by formation of the bis(arene)TM sandwich, subtle differences in the HOMO and HOMO-1 have been observed and discussed.

Fig. 6. (a) UPS for CrBz2 (100 K, \(h\nu = 40.81\) eV), (b) Computed DOS for the free CrBz2 molecule, (c) Same as (b) but for the molecular cation. Both calculated spectra have been shifted in energy to bring the peak at 10.0 eV into approximate alignment with the experimental spectrum. This obscures any shift between the neutral and the cationic molecules and was done in order to make clear the relative shifts in the HOMO and HOMO-1. Note that \([\text{CrBz}_2]^+\) and VBz2 are isoelectronic.
in comparison to CrBz$_2$ with the aid of DFT modeling. In the case of VBr$_2$, clear evidence is seen for a molecular reorientation during annealing, based on the ELS polarization dependence.

3. Charge transfer between an adsorbed bis(arene)TM and HOPG depends on the occupancy of the molecular HOMO and on its energy relative to EF. The small amount of unreacted TM that results from in situ synthesis causes a large decrease in work function, which shifts the adsorbate HOMO to below EF and thus impedes electron transfer to the HOPG. This is an obstacle to forming doping layers by this method.

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