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Adsorption of Benzene on Coinage Metals: A Theoretical Analysis Using Wavefunction-Based Methods[†]

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The interaction of benzene with a Ag(111) surface has been determined using reliable ab initio electronic structure calculations. The results are compared to a recent detailed analysis of the interaction of benzene with copper and gold surfaces, thus making it possible to derive a consistent picture for the electronic structure changes encountered when benzene is brought into contact with the densely packed coinage metal surfaces. To avoid the problems encountered when the presently most frequently employed computational approach, density functional theory (DFT), is applied to adsorbate systems where dispersion (or van der Waals) forces contribute substantially, we use a wavefunction-based approach. In this approach, the weak van der Waals interactions, which are dominated by correlation effects, are described using second-order perturbation theory. The surface dipole moment and the work function changes induced upon adsorption are also discussed.

Introduction

The adsorption of aromatic molecules on transition metal surfaces is a topic of still growing interest in materials science and surface science because of the importance of understanding the interaction and the character of the bonds at the adsorbate/metal interface. Benzene, the prototype aromatic compound, has been extensively studied since the 1980s both theoretically and experimentally. An extensive list of references to experimental work done in those years is reported in ref 1. The recent renewed interest in the interaction of aromatic compounds with metal surfaces has been motivated in part by the importance of noble metals as catalysts for hydrogenation and cracking reactions. The precise electronic structure at the interface between metals and organic molecules is also relevant for organic electronics where, quite frequently, the mismatch of the electronic levels at this interface severely limits the total amount of electrons that can be injected into an organic semiconductor. In addition, a number of papers have appeared recently where two-dimensional supramolecular structures formed by molecules weakly adsorbed on metal surfaces have been studied. The main interest has been on molecular species where this interaction is noncovalent in nature, most notably being brought about by hydrogen bonds formed between neighboring molecules.[2,3] In these systems, there is a competition between adsorbate−adsorbate interactions and adsorbate−substrate interactions. The currently most commonly used theoretical method to compute cases where noncovalent interactions are present between adsorbate and substrate,[4] density functional theory, is well suited to describe hydrogen bonds. However, the interaction of saturated and unsaturated molecules with metal surfaces can presently only be described reliably with DFT in the case of strongly interacting systems. In cases where the interaction between molecule and substrate has important contribution from van der Waals interactions, DFT methods are, at present, not sufficiently accurate.[5] A prominent current example of this problem for DFT is the interaction of water with a close-packed ruthenium surface where all available DFT methods report a nonwetting situation (ref 6, see also discussion in ref 7), whereas in the experiment a wetting of ruthenium by water is clearly observed.[8] Although the problems encountered with DFT for the description of adsorbate/substrate interactions are best documented and understood for weakly interacting systems, there is a significant discrepancy also for more strongly interacting systems. For example, in recent work on benzene bound to Pt surfaces, the experimental values for the adsorption energy have been found to be twice as large as the results from DFT calculations.[9−11]

The limitations of DFT for determining the equilibrium geometries and adsorption energies of weakly bound adsorbates do not prevent the use of DFT to obtain valuable information about these systems. Thus, Vázquez et al.[12] and, more recently, Neaton et al.[13] have used DFT to examine charge transport across the interface between organic adsorbates and metal electrodes. However, in these papers, the authors recognized that Kohn−Sham orbital energies do not correctly describe the ionization and affinity levels of the adsorbate. Furthermore, Vázquez et al.[12] showed that these levels depend strongly on the distance between adsorbate and substrate, and they point out that DFT calculations are not reliable for determining the equilibrium distance. In addition, Da Silva et al.[14] have shown for Xe/Pt that the binding energies obtained with two different density functionals were different by more than factors of 4. Because our principle concern is to study the detailed character of the interaction of benzene with noble metal surfaces, we have not supplemented our ab initio HF and MP2 studies with DFT.

In the case of benzene adsorption on close-packed coinage metal surfaces, most experimental work reported today has found a planar adsorption geometry.[15] Early work showed that benzene adsorbs preferentially on 3-fold sites on the (111)

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surface of silver, nickel, and platinum.[16−18] A compilation of results has been reported in ref 19. Among the metal surfaces, silver has received less attention, both experimentally and theoretically, with regard to benzene adsorption. Recently, a femtosecond study of electron dynamics at the benzene/Ag(111) interface has been reported;[20] in an older study, the interaction with UV photons and low-energy electrons has been investigated.[21] Also, in that paper data from thermal desorption spectroscopy (TDS) have been reported.[21] In previous theoretical work, the interaction of benzene with Cu and Au surfaces has been studied using a wavefunction-based approach.[15,22] In case of gold,[15] the interaction of benzene was found to be essentially exclusively determined by correlation effects (or van der Waals interactions), whereas on copper small contributions from the charge transfer from the substrate into the molecule were proposed.[22] A small charge transfer in case of benzene interacting with Cu surfaces basically fits with the Dewar−Chatt−Duncanson model,[23,24] which has been developed for the interaction of unsaturated hydrocarbons with metal surfaces as well as with more recent theoretical work by Pettersson and co-workers reported for DFT studies on unsaturated hydrocarbons adsorbed on the more open Cu(110) surface; see, for example, refs 25−29.

At present, the main reason for an increased interest in the interaction of benzene molecules with metal surfaces results from the fact that the interaction of this prototype aromatic molecule with metals represents an important benchmark for the field of organic electronics where the charge injection across interfaces between metals and aromatic systems represents a formidable problem.[15] Previous work has demonstrated that a naive description assuming a vacuum level alignment (Schottky−Mott model) fails even for noble metal surfaces, as first realized by Seki and co-workers.[30] Systematic studies reported later by the groups of Kahn[31] and Seki[32] have allowed one to conclude that generally the adsorption of molecules on metal surfaces, including noble metals, is accompanied by the formation of an interface dipole, which leads to a lowering of the work function of between 0.5 and 1.0 eV. Recently, in the case of saturated and unsaturated hydrocarbons on Cu(111), a pure physical mechanism, Pauli exclusion, could be identified to cause these unexpected, strong work-function changes.[15,22,33] The relative contributions of charge transfer, covalent chemical bonding, and the Pauli exclusion principle may be different for other combinations of adsorbates and substrates. Thus, Vázquez et al.[12] have argued for PTCDA, a large, planar organic molecule, on Au that the interface dipole arises mainly from charge transfer. However, it is important to stress that, in our analyses, we will use a theoretical method of constrained variations[34] that permit us to decompose the interaction into the contributions of individual chemical and physical mechanisms. This method is special in that it allows us to provide quantitative estimates of the importance of the various mechanisms; such a decomposition is not made, for example, in ref 12.

The current theoretical approaches to investigate interactions occurring during molecular adsorption on metals employ either DFT methods or wavefunction-based methods. Metal surfaces interacting with open-shell systems or unsaturated molecules, for which the formation of covalent bonds and/or a substantial charge transfer is observed, are well described by DFT-based approaches. However, closed-shell adsorbate/metal substrate interactions where dispersion forces contribute substantially or even dominate over “chemical” effects like charge transfer can be better described by a wavefunction-based approach where correlation effects are considered explicitly and with known accuracy. Because of the importance of correlation effects, we report in the present work results obtained with an ab initio wavefunction-based method using self-consistent field theory with second-order Møller-Plesset correction (MP2) for the interaction of benzene with an Ag(111) surface. It is of interest to extend the previous theoretical investigation reported for benzene on Au and Cu to Ag for two reasons. First, it should be noted that the work functions of Cu(111), Au(111) are almost equal (4.94 and 5.07 eV, respectively[35]), whereas the work function of Ag(111) is substantially, by about 0.5 eV, smaller (4.54 eV[35]), and it should be interesting to see whether the calculations can reproduce the fact that the work-function shift induced by the adsorption of benzene on Ag(111) is the smallest for the noble metal (111) surfaces. Second, the density of states at the Fermi-edge is significantly smaller for Ag(111) than for Au(111) and Cu(111),[36] and it should be interesting to see how this affects the interaction with adsorbed benzene. It is also of interest to investigate whether a weak chemical interaction can be detected for benzene on Ag(111), because recently a substantial chemical interaction including charge transfer and rehybridization has been observed for perylene-tetracarboxylic acid dianhydride (PTCDA) adsorbed on this surface.[36]

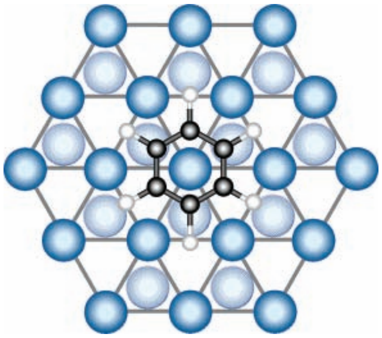

Figure 1. View of the AgC_6H_6 cluster model of C_6H_6/Ag(111) with the benzene center of mass located at an on-top site above the central Ag atom.

Computational Methods

The Ag(111) surface is modeled by a 32 atom cluster, with a geometry similar to that used in previous calculations for Cu and Au clusters.[15,22] The Ag−Ag distances are taken from those for bulk Ag[37] where the lattice constant is 4.090 Å; surface reconstruction was not considered. The benzene molecule is added parallel to the surface with the center of the C_6 ring at an on-top site directly above the central Ag atom. The bond distances and planar geometry of the C_6H_6 are fixed at their equilibrium values for the isolated molecule with C−C and C−H bond distances fixed at 1.396 and 1.083 Å, respectively. However, the distance, z, of the C_6H_6 molecule from the surface is varied to determine a potential curve and an equilibrium distance, z_e, from the surface. A schematic representation of the Ag_{32} cluster with C_6H_6 is given in Figure 1. We have calculated the adsorption energy of benzene on this cluster modeling an Ag(111) surface at the Hartree−Fock self-consistent field[38,39] (SCF) and second-order Møller−Plesset[40] (MP2) levels of theory. For both the SCF and the MP2 interaction energies, we have included a correction to account for errors due to the finite basis sets used, that is, to account for the basis set the superposition error (BSSE). This correction followed the Boys and Bernardi[41] procedure. While this Boys−Bernardi correction may contain artifacts and should only be regarded as approximate,[42] it avoids the too short bond lengths obtained when the correction is not used and gives a useful approximation for the overall shape of the potential curve. The SCF and MP2 calculations were made with the Turbomol suite of programs.[43] We have also decomposed the interaction using constrained variations of the wavefunction with the constrained space orbital variation (CSOV) method.[34] The CSOV decomposition was made for both the energy and the dipole moment at the z_e determined from the MP2 calculations. These CSOV calculations were made with the CLIPS program system.[44] In our previous work for the interactions of C_6H_6 with Cu(111),[22] the internal geometry of C_6H_6 was optimized and allowed to depart from being planar. We have redone the calculations for C_6H_6 on Cu keeping the benzene geometry frozen as for the new calculations on Ag(111) and the older calculations for benzene on Au(111)[15] so that we can directly compare the interactions of C_6H_6 with all three noble metal surfaces.

For the substrate cluster, two different treatments were used for the silver atoms. The seven Ag atoms nearest the adsorbate are treated with an 11-electron effective core potential (ECP) where the Ag 4d and 5s electrons are explicitly treated and included in the wavefunction; the ECP and basis set parameters were determined by Hay and Wadt.[45] Similar 11-electron ECPs were also used in our earlier work for C_6H_6/Cu(111)[22] and for C_6H_6/Au(111).[15] The other, more distant, Ag atoms in the first layer and all of the Ag atoms in the lower layers were treated with a one-electron ECP where only the Ag 5s electron is explicitly retained in the wavefunction. We have used the basis set and ECP parameters originally given by Hay and Martin.[46] One-electron ECPs were successfully used by Bagus et al.[22,47] to represent the contributions to the metallic conduction band that comes from the environmental atoms, while the substrate atoms that interact directly with the adsorbate are treated with a small core ECP. This same approximation has also been used in our previous work for C_6H_6/Cu.[22] For both the 11-electron and the one-electron ECP Ag atoms, we added a diffuse elementary Gaussian to the p-basis set and reoptimized the exponents and contraction coefficients of the p-basis set to have a better description of the Ag 5p contribution to the conduction band. For the 11-electron atoms, a (3s,4p,4d) set of elementary Gaussian basis functions was contracted, using an unsegmented contraction, to (2s,3p,1d) contracted Gaussian-type orbitals (CGTOs). The use of a minimal basis set for the Ag 4d orbital is satisfactory because the main purpose of including this shell explicitly in the wavefunction is to account for the steric repulsion and the Pauli exclusion between the Ag 4d orbital and the C_6H_6 adsorbate.[22] For the one-electron ECP Ag atoms (3s,4p), elementary Gaussians were contracted to (2s,3p) CGTOs. The carbon and hydrogen atoms are treated as all-electron atoms using a 6-311++G** basis set with a (12,6,1/5,4,1) CGTO set for C and a (10,4/3,2) set for H. For the CSOV calculations, somewhat different ECP and basis set parameters were used, but this is not expected to significantly affect the decomposition of the changes in the interaction energy and dipole moment. For the new calculations for $Cu_{32}C_6H_6$, the same basis set and ECP parameters were used as in our previous work.[22]

Results and Discussion

(A) Adsorption Energy and Electronic Properties. The potential curve, $V(z)$, for the distance of planar benzene from the metal surface is defined as

$$V(z;\mathrm{M}) = E(\mathrm{C_6H_6/M}) - E(\mathrm{M}) - E(\mathrm{C_6H_6})$$

where M is Cu, Ag, or Au and $E(C_6H_6/M)$, E(M), and $E(C_6H_6)$ are the total energies of the adsorbate system, $M_{32}C_6H_6$, of the cluster alone, M_{32}, and of the free benzene molecule, respectively. For the interaction energy, E_{INT}, we use the reversed sign so that $E_{INT} > 0$ corresponds to an attractive interaction while $E_{INT} < 0$ is repulsive; this convention is used to be consistent with the usual definition of interaction energies. In particular, the dissociation energy D_e is taken as E_{INT} at equilibrium, $D_e = E_{INT}(z_e)$. The benzene adsorption geometry that we have used, with benzene ring orientated parallel to the (111) surface, is the most common geometry for benzene adsorbed on metal surfaces in general and for coinage metal surfaces, including Ag, in particular.[1,48] Our previous work for benzene on Cu(111) and Au(111)[15,22] has shown that the deviations from planar geometry of the benzene are quite small for the weak interactions on the (111) face of noble metals, and this justifies our assumption of planar geometry for C_6H_6/Ag. Our theoretical values for D_e and z_e are given in Table 1 where they are compared to available experimental data for D_e. The experimental binding energy for benzene on Ag(111) has been computed using the Redhead formula for the desorption temperature of 160 K reported in ref 21 and using a pre-exponential of 10^{13} s^{-1}. Our calculated values of D_e are quite similar for all three of the noble metals, decreasing from 0.35 eV for C_6H_6/Cu(111) to 0.31 eV for C_6H_6/Au(111). These small D_e values are fully consistent with the view that the metal−C_6H_6 interaction is largely dominated by van der Waals, or dispersion, forces. Furthermore, our calculated D_e values are ∼0.1 to 0.2 eV smaller than the measured values. We have consistently found values of D_e in our previous cluster studies of weakly interacting adsorbates on metal surfaces that are smaller than experiment.[15,22,33,49−51] We have explained these smaller values as arising from the fact that the relatively small clusters that we use are not sufficiently large to represent the full polarizability of a metal surface. Indeed, as we increase the cluster size, the D_e values become larger and approach more closely to experiment. Thus, our theoretical results are consistent with experiment, and this lends considerable support to the validity of the analysis of the interaction energy and dipole moment that we present below. In Figure 2, we show the potential energy curve for benzene on Ag(111) as a function of z for two different levels of theory, SCF and MP2. We report in Figure 3 the potential energy curves of benzene adsorbed on Cu(111), Ag(111), and Au(111), obtained at the MP2 level. These potential energy curves have the form expected for a physisorption system, that is, a typical van der Waals type potential curve with a shallow minimum; see the inset of Figure 2.

TABLE 1: Different Properties of Benzene Adsorbed on the (111) Surfaces of Cu, Ag, and Au (Our Theoretical Values Are Compared to Experiment)

metal surface	D_e/eV	z_e/Å	$\Delta\Phi$/eV	results
Cu(111)	$+0.58^a$		-1.05^c	experiment
	$+0.35^d$	3.6^d	-1.08^c	theory
Ag(111)	$+0.42^b$		-0.70^c	experiment
	+0.33	3.7	−0.77	theory[d]
Au(111)	$+0.6^e$		-1.10^c	experiment
	$+0.31^d$	3.8^d	-0.87^c	theory

[a] See refs 22,30. [b] From ref 21; for conversion, see text. [c] From ref 15. [d] Present work. [e] Simon Lukas, Dissertation, Faculty for Chemistry, Ruhr-University Bochum, 2006.

The conventional description of the benzene bonding to a transition metal involves the π-system, and it is essentially based on the back-donation mechanism proposed by Blyholder[52] for the CO/metal interaction. This Blyholder model has to be

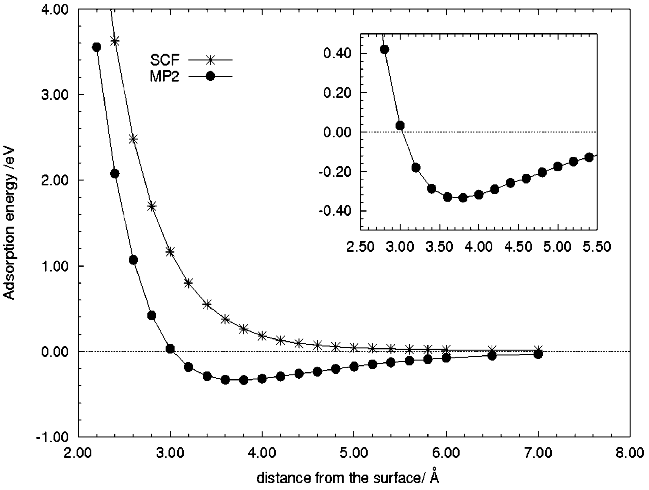

Figure 2. SCF and MP2 potential energy curves for benzene on the Ag(111) surface as a function of the distance of the benzene ring to the surface.

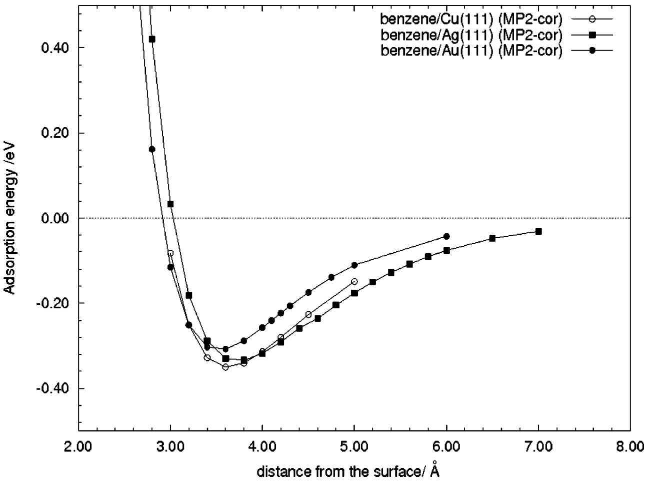

Figure 3. MP2 potential energy curves for benzene on Cu(111), Ag-(111), and Au(111) surfaces.

modified, however, for unsaturated hydrocarbons; the corresponding description is frequently referred to as the Dewar, Chatt, Duncanson model.[23,24] Of course, these simple models significantly oversimplify the benzene/metal interaction, as pointed out recently by the theoretical work of Pettersson et al.[26,29,53]

On more reactive transition metals like Pt, the adsorption of benzene is accompanied by a significant rehybridization of the C-atoms leading to a situation that bears some similarity to metal−organic compounds like bisbenzene-chromium,[54] which is accompanied by a substantial out-of-plane bend of the CH-bonds.[55] On Cu, the changes induced in the benzene geometry are smaller. However, on the more open Cu(110)-surface, there are also substantial, boatlike, distortions of the adsorbed benzene.[26] On the other hand, for benzene on the close-packed Cu(111)-surface, as well as for the other close-packed coinage metals, there is no evidence for a distortion of the CH-bonds out of the C−C−C plane, and the forces binding benzene to these surfaces are largely dominated by van der Waals (or dispersion) forces. In accord with this expectation for Cu(111), a detailed analysis reveals a small amount of charge back-donation.[22] The latter finding is corroborated by a detailed comparison between the unsaturated hydrocarbon benzene and the saturated hydrocarbon cylohexane.[22] On Au(111), the chemical interactions are even smaller than those on Cu(111).[15]

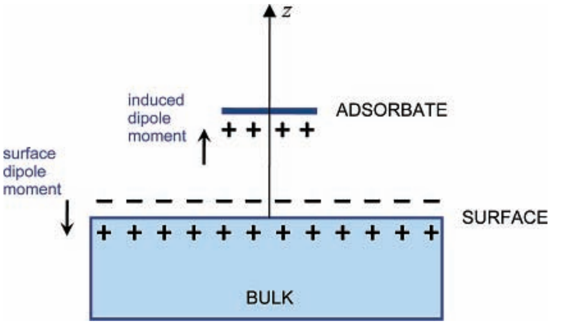

Figure 4. A schematic view of the dipole moments at a metal surface. The dipole of the clean surface is directed toward the bulk. The dipole moment induced upon adsorption (interface dipole) points outward and increases the dipole of the clean surface, thus leading to a lowering of the work function.

Although, as confirmed below for the cases of benzene on Ag(111) and on Cu(111), the direct chemical interactions between benzene and the close-packed surfaces of the coinage metals are weak, there are substantial changes of the substrate work function upon adsorption of benzene. An important effect when weakly bound adsorbates are present on a metal surface is that there is often a large change, a reduction, of the work function that can be ~1 eV; see refs 22 and 33 and references therein. A major origin of this change in the interface dipole is the Pauli exclusion principle,[15,22,33] a purely physical effect; the mathematical embodiment of this exclusion is the antisymmetry of the electronic wavefunction for exchange of the electron coordinates. There may also be chemical contributions to the interface dipole arising, in particular, from the polarization of the metal substrate due to the presence of the adsorbate. In the case of C_6H_6/Cu(111), there is also a small contribution due to π donation from C_6H_6 to Cu.[22] In the next subsection, we will present results for the different contributions of various mechanisms to the changes in the interface dipole for C_6H_6/Cu(111) and C_6H_6/Ag(111). In the following, we briefly review the interpretation of the interface dipole in terms of the dipole moment changes for our cluster models.

For the clean metal surface, the only nonzero component of the interface dipole, μ, is along the surface normal, μ_z; for our cluster models that all have C_{3v} point group symmetry, again μ_z is the only nonzero component. To simplify our notation, we refer to this nonzero component as μ. For a clean metal surface, electronic charge moves above the surface, and this leads to a dipole that is minus above the surface and positive below the surface, thus yielding a total dipole with $\mu < 0$.[56] When an adsorbate is added, an additional dipole moment is induced, which frequently is referred to as interface dipole.[32] For weakly bound adsorbates, like rare gases[33,57] and certain organic molecules,[22] this interface dipole is directed opposite from that of the metal surface (i.e., plus above and minus toward the surface); it thus reduces the work function.[56] The total dipole moment of a clean surface and the additional interface dipole induced by an adsorbate are shown schematically in Figure 4. For our cluster models, we consider the changes in the cluster μ between the cluster with benzene present and the bare cluster. This gives the interface dipole $\Delta\mu$ associated with a single adsorbate. This can then be converted to a change in the work function, $\Delta\phi$, by using the Helmholtz equation. Before we turn to the detailed analysis of the origins of the changes in the interface dipole induced by adsorption of benzene, we point out that the work-function changes due to this induced dipole

TABLE 2: CSOV Decomposition of the Interaction of C_6H_6

CSOV step	$E_{INT}/\Delta E_{INT}$		$\mu/\Delta\mu$	
	Cu(111)	Ag(111)	Cu(111)	Ag(111)
μ_{ref}			−2.05	−1.13
FO	−0.46/−	−0.38/−	−1.14/+0.90	−0.47/+0.66
vary(substrate)	−0.08/+0.39	+0.04/+0.43	−1.06/+0.08	−0.60/−0.13
vary(C_6H_6)	−0.03/+0.05	+0.07/+0.03	−0.71/+0.35	−0.28/+0.31
full SCF − nonadditive	−0.03/+0.00	+0.07/+0.00	−0.65/+0.06	−0.28/+0.00
total $\Delta\mu$			−/+1.40	−/+0.85

moment arising from adsorption of benzene on metal surfaces may be quite large and cases where $\Delta\phi$ exceeds 1 eV have been observed.[1]

(B) Decomposition of the Origin of the Interaction Energy and the Interface Dipole − A CSOV Analysis. To identify the detailed contributions of the benzene−Ag interaction to E_{INT} and to the interface dipole, we have used a constrained space orbital variation,[34,58] or CSOV, analysis to decompose the interaction into the contributions of individual physical and chemical mechanisms. The CSOV analysis, as applied to the interaction of C_6H_6 and C_6H_{12} adsorbed on Cu(111), is described in detail in ref 22; here, we shall review the essential features of the CSOV steps. The first, or frozen orbital (FO), step gives the properties of the superposition of the substrate and C_6H_6 charges to form an antisymmetric wavefunction as required by the Pauli exclusion principle. This step has a purely physical origin because there are no chemical changes taking place. At the FO step, the interaction energy, E_{INT}, reflects electrostatic forces and steric repulsion, and the dipole moment μ is modified from the sum of the dipole moments of the separated substrate and adsorbate by the Pauli exclusion. Typically, E_{INT}(FO) < 0 because the steric repulsion dominates and $\Delta\mu(\text{FO}) = \mu(\text{FO}) - \mu(\text{substrate}) - \mu(\text{adsorbate})$ is $\Delta\mu > 0$.[15,22,33] The next CSOV step, denoted vary(substrate), allows the metal cluster charge density to vary and to respond to the presence of the adsorbate. For C_6H_6, this step is dominantly determined by the substrate polarization to reduce the steric repulsion. We recall that at this step $\Delta\mu$ may be positive due to motion of σ charge below the surface or negative if the motion of π charge upward, especially at the edges of the adsorbate dominates.[22] Indeed, we shall see that the different cancellation of contributions to $\Delta\mu$ due to σ and π charge motion is one of the major differences between C_6H_6 on Cu and on Ag. The next CSOV step, denoted vary(C_6H_6), allows the C_6H_6 charge to polarize due to the presence of the surface charge of the metal substrate. In general, the effect of vary(C_6H_6) on E_{INT} is expected to be small,[22] but, surprisingly, the effect on the interface dipole at the vary(C_6H_6) is a significant fraction of the total $\Delta\mu$.[22] Finally, we examine the changes in E_{INT} and μ by allowing a full unconstrained, or full SCF, variation. Nonzero values of ΔE_{INT} and $\Delta\mu$ at this step indicate the extent to which the constrained variations are not additive; small values of ΔE_{INT} and $\Delta\mu$ show that the decomposition of the total interaction into individual terms is reliable, while large values indicate the need for additional CSOV cycles.[58] We also recall that the CSOV is based on Hartree−Fock, HF, SCF wavefunctions that do not include the vdW dispersion forces and the total interaction, except for small artifacts introduced by BSSE will be repulsive.[22] Despite this, the SCF wavefunctions give an excellent description of the chemical changes arising at the individual CSOV steps and, thus, form the basis for a reliable interpretation of how this chemistry affects both the interaction energy and the interface dipole.

Before we discuss the CSOV analysis of the interactions at the SCF level, we comment on the differences between the SCF and MP2 results for E_{INT} and μ. As can be seen from Figure 2, near z_e, the MP2 E_{INT} is ~0.65 eV stronger than the SCF E_{INT}. However, this large increase in E_{INT}, due to physical dispersion forces, is in addition to the chemical CSOV decomposition given in Table 2. It arises from the correlation of substrate and absorbate electrons, and it cannot be associated with one or the other as is done for the chemical terms in Table 2. The dipole moment induced by the adsorption of benzene, $\Delta\mu$, has also been computed taking into account the MP2 perturbations in the case of C_6H_6/Ag(111). For a wide range of distances about z_e, the MP2 $\Delta\mu$ differs by a nearly constant amount from the SCF $\Delta\mu$. This shows that the dispersion forces add a constant to the chemical SCF $\Delta\mu$ taken into consideration in Table 2.

The CSOV contributions to E_{INT} and to μ for the $Cu_{32}C_6H_6$ and $Ag_{32}C_6H_6$ clusters are given in Table 2. This analysis is made for distances of $z(C_6H_6/Cu) = 3.6$ Å and $z(C_6H_6/Ag) = 3.7$ Å the z_e obtained with MP2; see Figure 3. As noted above, the results for C_6H_6/Cu(111) are slightly different from those reported earlier.[22] Also, we do not include BSSE corrections because, while these corrections indicate the magnitude of the uncertainties in the calculated values due to the finite basis sets used, the quantitative values of the "so-called" corrections have been questioned.[42,49] In any case, these corrections are expected to be small for our SCF wavefunctions. Furthermore, we have used slightly different basis sets and ECPs, for the CSOV calculations than for the MP2 calculations. However, the changes in basis set and ECP should not significantly change the computed properties, especially at the HF-SCF level.[22] At each CSOV step, we give the E_{INT} and ΔE_{INT}, in eV, and the μ and $\Delta\mu$, in Debye. Except for the FO CSOV step, the ΔE_{INT} and $\Delta\mu$ are the changes with respect to the preceding CSOV step. At the FO step, ΔE_{INT} is not defined and $\Delta\mu$ is taken as the change from the sums of the dipole moments of the separated systems. Becauase the C_6H_6 is fixed to be planar, $\mu(C_6H_6) = 0$, and the reference dipole, μ_{ref} in Table 2, is simply the dipole moment for the bare Cu_{32} or Ag_{32} clusters. The μ and $\Delta\mu$ reported are the components of μ in the z direction, that is, along the normal to the surface.

For both Cu(111) and Ag(111), the FO results are similar, the steric repulsion is ~0.1 eV smaller for C_6H_6/Ag than for C_6H_6/Cu, and the decrease in the interface dipole, $\Delta\mu$, due to the Pauli exclusion principle is ~0.25 D smaller in magnitude for Ag than for Cu. The origin of these differences comes from the fact that the C_6H_6 is 0.1 Å closer to Cu than to Ag. The driving force for both the steric repulsion and the $\Delta\mu$ is the overlap of the charge distributions of the substrate and the adsorbate,[33] and this overlap increases exponentially as the distance between the surface and the adsorbate decreases. The polarization of the substrate charge at CSOV step V(substrate) leads in both cases to a decrease in the steric repulsion of essentially the same magnitude, $\Delta E_{INT} = 0.4$ eV. However, the effect of the substrate polarization on the interface dipole is quite different for the Cu and Ag surfaces. As shown in ref 22, the $\Delta\mu$ for the substrate polarization arises from a cancellation of the contributions of metal charge of σ symmetry and of π symmetry. The σ charge directly below the C_6H_6 moves below the surface leading to a $\Delta\mu > 0$, while the π charge at the edges of the C_6H_6 moves upward leading to a $\Delta\mu < 0$. For the Cu surface, the σ contribution is larger and the net $\Delta\mu > 0$, while for the Ag surface, the π contribution is larger and the total $\Delta\mu < 0$. From our analysis for Xe/Cu(111),[33] this different cancellation is related to the distance of the adsorbate from the surface with the σ contribution to increase μ becoming larger as the distance of the adsorbate from the surface becomes smaller. For both Cu and Ag surfaces, the ΔE_{INT} and $\Delta\mu$ $v(C_6H_6)$ CSOV step indicate a weak chemical bond due to π donation from C_6H_6 to the surface[22] with the bond being slightly weaker for the Ag surface than for the Cu surface. The terms contributing to the CSOV decomposition are clearly additive because the changes for the full unconstrained SCF calculation are quite small. The major difference between the effect of C_6H_6 adsorption on the interface dipoles is that the increase of $\Delta\mu$ is larger on a Cu than on an Ag surface; thus, the reduction in work function due to adsorption of C_6H_6 is larger for Cu than for Ag. The difference in the $\Delta\mu$ comes from a combination of changes in several of the CSOV contributions; see Table 2. The overall conclusion is that the reduction of the substrate work function by interface dipole formation is significantly larger for Cu than for Ag.

If we assume that the changes in the dipole moment of the cluster upon adsorption of benzene correspond to the dipole moment per adsorbed benzene molecule on Ag(111), we can compute the changes in the work function by using the Helmholtz equation.[1] If we take the coverage of benzene in the monolayer equal to that for Au(111), 2.4×10^{14} cm^{-2},[15] the change in dipole moment for Ag(111) (see Table 2) corresponds to a work-function change, $\Delta\phi$, of 0.77 eV, in good agreement with the experimental data (0.7 eV[20]).

The theoretical and experimental values of $\Delta\phi$ for C_6H_6/Cu(111) and C_6H_6/Au(111) are taken from our earlier work in ref 15. These prior values of $\Delta\phi$ together with our new value for C_6H_6/Ag(111) are collected in Table 1. We note that there is good agreement between our theoretical values for $\Delta\phi$ and the directly observed $\Delta\phi$ for benzene adsorbed on Cu(111) and Ag(111). The theoretical value of $\Delta\phi$ for benzene on Au(111) is a bit further from experiment, but still its error is not especially large. Because the calculations for C_6H_6/Au(111) are somewhat more computationally demanding than those benzene on Cu and Ag, we simplified the calculations of the wavefunctions, and this may have reduced the accuracy of our calculated $\Delta\phi$ by ~0.1 eV. However, the key point to be made is that our theoretical results track the observed $\Delta\phi$ quite closely, lending confidence that we have correctly described the physics and the chemistry of the interaction of benzene on the (111) faces of Cu, Ag, and Au.

Conclusions

In the present work, we have analyzed the interaction of benzene with the Ag(111) surface and compared the results to the case of the adsorption of this prototype aromatic molecule on the two other coinage metals, Cu(111) and Au(111). This theoretical analysis has been carried out using a wavefunction-based method where dispersion forces (or van der Waals interactions) are accurately described using second-order Møller−Plesset perturbation theory (MP2). Using this WF-based approach, we avoid problems encountered using DFT, which, at present, is not able to describe correctly substrate/adsorbate interactions where dispersion forces contribute substantially.[4,5] The calculated results reproduce the experimental observation in that the adsorption of benzene generally lowers the work function by about 1 eV. This significant effect is of considerable importance for the electronic level alignment at electrodes in electronic devices where charge has to be injected from metals into organic semiconductors. Our detailed analysis reveals that the displacement of charge at the metal surface due to the Pauli exclusion between the metal electrons and the electrons of the adsorbed benzene (frequently referred to as "cushion effect") causes this phenomenon, thus confirming earlier findings for benzene (and other weakly interacting adsorbates) deposited on Cu and Au surfaces.[15,22,33]

In addition, the chemical contributions to the benzene/Ag(111) interaction were analyzed in the framework of a step-by-step analysis of the adsorption-induced changes of the electronic structure. This analysis, which clearly allows us to separate "physical" contributions like Pauli Exclusion induced distortions of the electronic structure from chemical contributions like a charge transfer, points out that charge-donation from the adsorbate to the metal for Ag(111) is significantly weaker than that for Cu(111) and has about the same magnitude as that on Au(111).

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