



Dependence of surface properties on adsorbate-substrate distance: Work function changes and binding energy shifts for I/Pt(1 1 1)

Paul S. Bagus^{a,*}, Christof Wöll^b, Andrzej Wieckowski^c

^a Department of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, TX 76203-5017, USA

^b Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780, FRG

^c Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

ARTICLE INFO

Article history:

Received 13 June 2008

Accepted for publication 12 November 2008

Available online 3 December 2008

Keywords:

Ab initio quantum chemical methods and calculations

Chemisorption surface electronic phenomena (work function, surface potential, surface states, etc.)

ABSTRACT

This paper presents an analysis of the character of the bond of I adsorbed at on-top and 3-fold sites of Pt(1 1 1). At both sites, the bonding is dominated by an ionic interaction supplemented with some covalent character due to donation from the adsorbed I anion to the Pt surface. The way in which the I–Pt interaction affects observed properties has been established. In particular, the origins of the anomalous work function changes induced by the adsorption of I and the shifts of I core level binding energies are explained. It is shown that the magnitudes of the changes in these properties can be directly correlated with the distance of the I from the Pt surface. Thus, these shifts can be interpreted to indicate adsorbate height. The fact that the negatively charged I adsorbate leads to a work function decrease, rather than the increase expected due to the charge of the adsorbate, may appear to be an anomaly. However, it is shown that this decrease arises from electronic reorganizations that cancel the dipole due to the charge of the adsorbate. Furthermore, the electronic terms that contribute to a lowering of the work function are larger as the adsorbate moves closer to the surface.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

For both their fundamental interest and their practical value, the interaction of halogens with metal surfaces has been studied extensively. Of particular relevance to our present study are the electrochemical studies of I/Pt by Hubbard and collaborators [1] and of I/Cu by Wandelt and collaborators [2–5] as well as the UHV study of I/Pt by Jo and White [6]. We have chosen to study I/Pt(1 1 1) because there is a detailed experimental study of the interaction as a function of coverage [6] against which our theoretical predictions can be compared. In particular, the properties of I/Pt at 3-fold and on-top sites were compared and contrasted in this experimental study [6]. The comparison included work functions, bond strengths, and the X-ray photoemission spectra, XPS, binding energy, BE, of the I 3d core level. The principle objective of this paper is to determine the character of the bond of I to Pt(1 1 1) and to interpret the properties described above in terms of the bonding character.

The ionicity of the I–Pt bond is not obvious. Based on the relatively large electron affinity, EA, of the I atom [7], 3.1 eV, one could argue that the chemisorption bond of I/Pt is ionic with the adsorbed I being I[−]. On the other hand, following Hubbard [8], the

electrochemical community has believed that neutral adatoms of iodine are chemisorbed on platinum following iodine adsorption from iodide media, and that such neutral iodine structures appear in UHV after emersion from aqueous iodide solutions. Two arguments can be quoted in favor of this claim. First, the high coverage iodine structures (above 0.4 ML) are hydrophobic, a property barely expected for anionic adlayers. Second, if the emersion is made from nearly neutral potassium iodide media, no potassium is retained in UHV. This is also a property that, in the first approximation, was not expected for anionic adlayers. It was therefore proposed that following the immersion of platinum into the iodide media, a reaction occurs:



If Pt(1 1 1) is immersed, an ordered layer of iodine atoms is formed. Basically the same structures were also found when Pt(1 1 1) was dosed with iodine in UHV (either with I₂ or HI). Strong iodine chemisorption was confirmed in all cases [8]. However, our present theoretical results for I/Pt raise serious questions about whether the I–Pt chemical bond is covalent. We present strong evidence for a dominantly ionic interaction, certainly at lower coverages, and we show that this strongly ionic character is consistent with the extensive set of measurements for I/Pt(1 1 1) reported by Jo and White [6]. We provide reliable theoretical evidence to quantify the extent of the departure of the adsorbed I from being

* Corresponding author. Tel.: +1 940 369 8001; fax: +1 940 565 4318.
E-mail address: bagus@unt.edu (P.S. Bagus).

an ideal anion. Of course, at sufficiently high coverages of I, one expects the bond to have more covalent character in order to reduce the Coulomb repulsions between the closely packed anions. However, the coverage at which the transition from an ionic to a covalent bond will take place is not known. Our work suggests that a dominantly ionic bond remains even at relatively high coverages.

Our conclusions about the iodine anionicity are similar to the conclusions reached in earlier theoretical work for I/Cu(111) [9] and for lighter halogens on Ag(111) [10] and Cu(100) [11]. An important extension in the present work is that we examine adsorption at both 3-fold and on-top sites while previous work had been restricted to only one site for a given surface. Furthermore, we demonstrate in the present work that many properties are strongly influenced by the distance of the adsorbate from the surface. This had been noted earlier as being important for the magnitude [11] and even for the sign [9] of work function changes, $\Delta\phi$. However, we show here, for the first time, that effects of different bond distances may allow one to distinguish the properties of adsorption at different sites.

It is not a simple matter, on the basis of either theoretical or experimental evidence, to determine the ionic character of the bonding of an adsorbate to a substrate. In the case of cationic adsorbates, one of the commonly used methods to determine an ionic interaction is to look for a large lowering of the work function, $\Delta\phi < 0$, upon adsorption [12]. This criterion has been used, quite extensively [13]. However, the assignment of alkali metal adsorbates as being cationic was questioned in the 1990s based on theoretical analyses [14–16]. Furthermore, this new theoretical analysis was supported by reinterpretations of experimental data; see, for example, Ref. [17]. This re-interpretation of the bond character stimulated additional theoretical work that explained observed properties of the adsorption of alkali metals in terms of their being cations; see for example, Refs. [18–20]. In part based on this theoretical work, it is, once again, accepted that alkali metal atoms on metal surfaces are cationic at low coverage. The situation is more complicated for anionic adsorbates where the behavior of the work function is not as simple as for cations [9,21–23]. In particular, the adsorption of Iodine on Pt [6], on Ni [24], and on Cu [9] has led to a lowering of the work function, $\Delta\phi < 0$, rather than the increase expected from the dipole layer induced by a negative charge. Recent work [9] explained this paradoxical $\Delta\phi$ as being due to cancelling terms from the electronic responses of adsorbate and substrate charge distributions. In the present work, we extend the earlier analysis to explain different $\Delta\phi$ for I at different adsorption sites. Our interpretation of the chemical and physical origins of the $\Delta\phi$ is based on a decomposition of the $\Delta\phi$ into changes due to different chemical mechanisms using a method of constrained variations of the molecular orbitals, the constrained space orbital variation, CSOV, method [25,26]. The CSOV decomposition has also been applied to understand the origins of the I(3d) BE shifts, ΔBE , for I at different sites.

Our theoretical approach, the surface cluster model, uses clusters to model the adsorbate-substrate system and *ab initio* wavefunctions, WFs, are determined for these clusters [27–29]. The results obtained with the cluster WFs are interpreted in terms of properties of the chemisorption system. The special advantage of the cluster model approach is that it allows us to use methods and concepts that have been developed for chemical interactions and chemical bonding to study surface interactions. For the determination of ionicity, the cluster model allows the use of reliable methods of analysis [30] that avoid the artifacts that may arise with more commonly used methods of population analysis [27,31]. One of these methods involves projecting adsorbate orbitals on the cluster WF and determining an orbital occupation, n_p , based on this projection. A value of $n_p \approx 2$ is compelling evidence that the orbital is nearly fully occupied [10,27,30,32]. We also

use dipole moment curves, $\mu(z)$, where the height of the adsorbate above the surface, z , is varied, to determine whether an interaction is dominantly ionic or dominantly covalent. When atomic units are used, the slope of $\mu(z)$ has the units of electronic charge. Hence, if the curve has a slope with a magnitude of ~ 1 , this is a strong indication of a dominantly ionic interaction [18,32,33].

However, the cluster model has a limitation in that one does not normally include adsorbate–adsorbate interactions in the cluster model. This is especially true when, as in the present case, we use clusters that contain only a single adsorbate. In the limit of a cluster with a large number of substrate atoms, a cluster with a single adsorbate models the limit of zero coverage. In order to obtain coverage dependent information, it is necessary to combine the theoretical results with measurements where the coverage dependence is examined [6] and this is what we have done in the present study.

The following section, on methodology, provides details about the theoretical and computational methods and treatments that are used in this paper. In Section 3, we discuss the calculated properties of the I/Pt(111) chemisorption bond for both 3-fold and on-top bonding sites. In Section 3.1, we show that the bonding at both sites is dominantly ionic. In Section 3.2, we analyze the origins of the I–Pt interaction and of the dipole moment change, $\Delta\mu$, induced by the adsorption of I in terms of CSOV decompositions. In Section 3.3, the origins of the I(3d) BE shifts are analyzed. In Section 4, the measurements for I/Pt(111) reported by Jo and White [6] are discussed and interpreted in the context of our theoretical results. Here, we consider three properties: (1) the bond energy difference between I at the 3-fold and on-top sites; (2) the shifts of the I(3d) BE between these sites; and (3) the $\Delta\phi$ as the on-top site becomes filled at higher coverages of I. In particular, we present a different interpretation of the interface dipole induced by I at the on-top site from that given earlier [6]. Our conclusions, especially about the direct correlation of $\Delta\phi$ and ΔBE with adsorbate distance, from the surface are summarized in Section 5.

2. Methodology: theoretical and computational details

A 31 atom cluster is used to model an unrelaxed and unreconstructed Pt(111) surface; this Pt₃₁ cluster has 12 atoms in the first, seven atoms in the second, and 12 atoms in the third layer of the Pt(111) surface and is denoted Pt₃₁(12,7,12). An I atom is placed above the central 3-fold site of the first Pt layer or above one of the equivalent Pt atoms that form the 3-fold site. These Pt₃₁I clusters model adsorption at 3-fold and on-top sites, respectively. The distance of the adsorbed I from the surface plane, denoted z or $z(1)$, is varied and the properties of the adsorption are studied as a function of z . Schematic views of this cluster are shown in Fig. 1. The cluster size and the approximations used in the WF calculations were chosen based on our extensive experience [27,28,34,35] with cluster model studies of surface properties. In particular, we have used a mixed treatment of the substrate atoms in order to reduce the computational burden of the WF calculations [36]. In this mixed treatment, we approximate the cluster atoms distant from the adsorbate with a large core pseudopotential, or effective core potential, ECP [34,37], where only a few electrons are explicitly included in the cluster WF. Since, these atoms represent the long range environment of the crystal and are not directly involved in the interaction with the adsorbate, the use of a large core ECP does not significantly affect the accuracy of the results [36]. On the other hand, the substrate atoms that are close to the adsorbate are treated more accurately with a small core ECP [38] where the valence and semi-core electrons are explicitly included in the WF. Furthermore, we have chosen a cluster sufficiently large that we could treat both the on-top and 3-fold sites with a single cluster in order

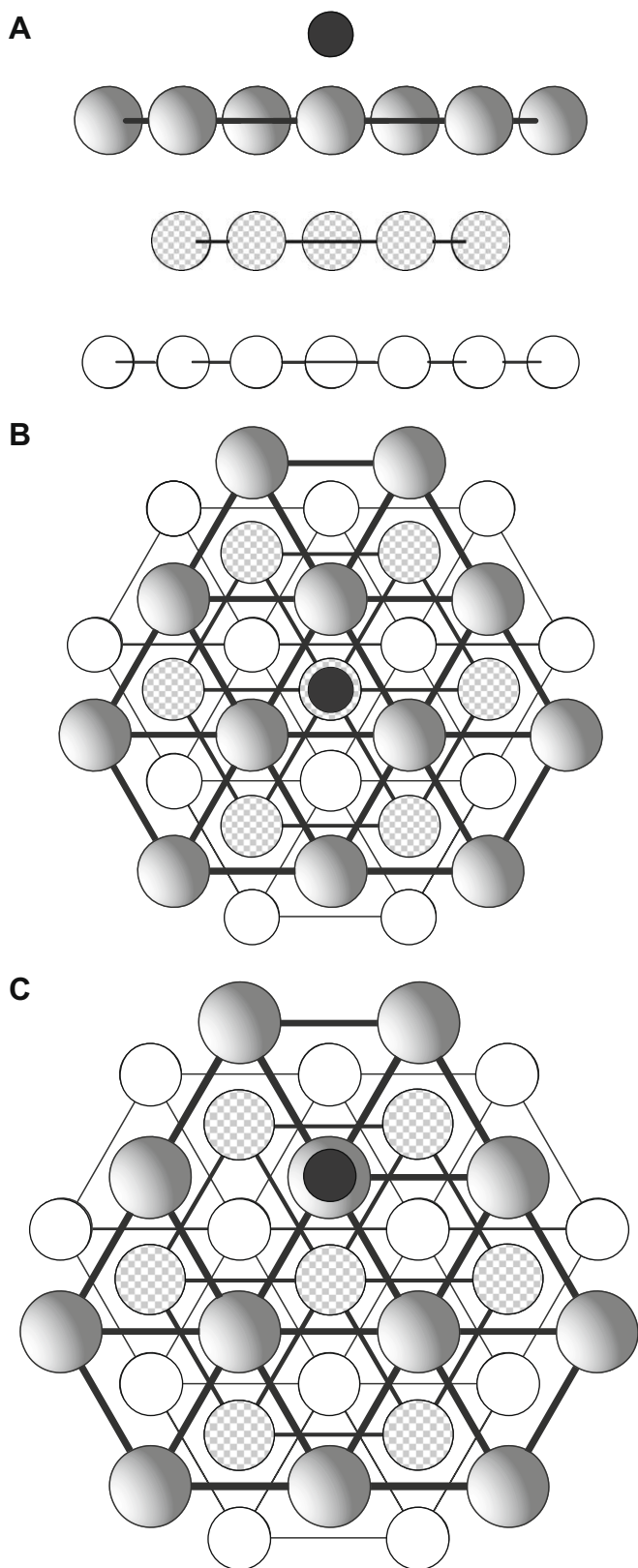


Fig. 1. Schematic views of I with the $\text{Pt}_{31}(12,7,12)$ cluster. The first layer Pt atoms are shaded, the second layer atoms are hashed, and the third layer atoms are open circles; the bonds that connect neighboring Pt atoms within a layer are drawn with progressively thinner lines for the lower layers. (A) side view at a 3-fold site; (B) top view at a 3-fold site; and (C) top view at an on-top site.

to be able to directly compare the adsorption properties at these two sites.

In the mixed treatment of Pt_{31} , the three central Pt atoms of the first layer were treated with an 18 electron ECP where the electrons arising from the 5s, 5p, 5d, and 6s shells are explicitly included in the WF [38]. The central atom of the second layer was also treated with this 18 electron ECP. The choice of a small core ECP for this atom was made for the initial, exploratory calculations with a small $\text{Pt}_4(3,1)$ cluster [10] and retained for the Pt_{31} calculations. The additional Pt atoms, nine in the first, six in the second and 12 in the third layers of the $\text{Pt}_{31}(12,7,12)$ were represented by a one-electron ECP where only the 6s and 6p space of the Pt is included in the WF. Certainly, this one-electron ECP is a major approximation since, for these Pt atoms, the 5d electrons are not allowed to participate in chemical interactions. However, as noted above, only the environmental Pt atoms, not directly involved in the interaction with I, are treated with the one-electron ECP. Furthermore, based on their tests of the one-electron ECP, Zurita et al. [39] conclude that this ECP can be used to model the environmental atoms for surface cluster models. Both ECPs treat the scalar relativistic effects of the electrons explicitly included in the WFs [38,39]. The ECP parameters and the basis sets for the 18 and one-electron ECP Pt atoms were taken from Refs. [38,39], respectively. Reasonably flexible unsegmented contractions of the basis functions were used and the basis set functions to describe the Pt 5d shell in the 18-electron ECP were not contracted at all. The size of the contracted Gaussian type orbital, CGTO, basis sets were (3s, 3p, 3d) and (2s, 1p) for the 18 and one-electron ECPs, respectively.

For the I adsorbate, an all electron treatment was used since we needed to study the I(3d) shell binding energies. The starting basis set exponents and contraction parameters were taken from Footnote.¹ However, we added one diffuse Gaussian function in each of the I s, p, and d symmetries in order to have an accurate description of the dipole polarizability of I^- . Since, as shown in the following section, I is adsorbed as essentially a full anionic species, an accurate description of the polarizability is necessary to correctly describe the I–Pt interaction [9–11].

All the WFs calculated for the Pt_{31} and Pt_{31}I clusters were *ab initio* Hartree–Fock, HF, self-consistent field, SCF, WFs. The point group symmetry of the bare Pt_{31} and the 3-fold site Pt_{31} clusters is C_{3v} and this symmetry was imposed on the SCF solutions; the symmetry is lower for the on-top site Pt_{31}I cluster, where it is only C_s . Since we did not include symmetry breaking effects for the C_{3v} clusters, there may be artifacts related to the calculation of the bond energy, D_e , at the on-top site; these are discussed in the following section. We analyze our results for several properties based on a CSOV [25,26] decomposition of the interaction into several steps where different chemical terms are selectively included or excluded from the interaction. Our use of the CSOV constrained variations to decompose and analyze the character and consequences of the Iodine interaction with Pt is accomplished most easily within the framework of HF theory. While constrained variations can, in principle, be used with density functional theory, DFT, it is necessary to introduce corrections to the kinetic energy operator when the DFT variations are constrained [40–42]. The uncertainties associated with these corrections are avoided by using HF theory.

As a test of the possible limitations of the Pt_{31} cluster model that we have used for Pt(111), we have studied two charge states of the clusters with I; namely, neutral, $[\text{Pt}_{31}\text{I}]^0$ and negatively charged $[\text{Pt}_{31}\text{I}]^-$. As we show in the next section, for both charge states, the dominant bond is ionic with the I being I^- . As a first approximation, we can view the two clusters as being $\text{Pt}_{31}[+]$ with

¹ The I basis set was kindly provided to us by Prof. Klaus Hermann, Fritz–Haber Institute, Berlin. It is included in the library of basis sets available with the StoBe program system for electronic structure calculations.

I^- in the case of $[Pt_{31}I]^0$ and $Pt_{31}[O]$ with I^- in the case of $[Pt_{31}I]^-$. When the cluster is sufficiently large, then the chemisorption bonding and properties will not change if we change the charge state of the cluster by one electron [43]. Specifically, we should find similar properties for the $[Pt_{31}I]^0$ and the $[Pt_{31}I]^-$ clusters since the main change between these clusters is that, for $[Pt_{31}I]^-$, there is an additional electron in the Pt_{31} “conduction band”. Thus, we can take the properties that are similar for the two charge states as describing the properties of $I/Pt(111)$ and we can take the differences between these properties for the different charge states as measures of the uncertainties of the values determined with the cluster model.

Since we have used HF theory, the possibility that our conclusions could be modified by electron correlation effects, which are neglected in HF, needs to be considered and we present a brief summary of the strong evidence that this is not a major concern. A part of this evidence comes from comparing HF with DFT results since DFT does include electron correlation. A very recent comparison of DFT with HF has been made for the interaction of covalently bonded CO with Au particles [44]. This comparison showed that shifts of bond distances and vibrational frequencies between the CO in different Au environments were quite similar between HF and DFT. On the other hand, the HF adsorption energies for the covalently bonded CO were significantly smaller than the DFT values. However, for cases where the bonding has considerable ionic character, the HF D_e are reasonably accurate [32,45], provided they are computed correctly and taken with respect to the ionic dissociation limits. This theoretical value is then corrected to the neutral limits with experimental values for the electron affinity, EA, and the ionization potential, IP, of the charged limits. For a surface, the IP is simply ϕ . Thus for the D_e of $I/Pt(111)$, modeled with $Pt_{31}I$, we would have

$$D_e = E(Pt_{31}^+) + E(I^-) - E(Pt_{31}I) - EA(I) + \phi[Pt(111)], \quad (1)$$

where $E(Pt_{31}^+)$, $E(I^-)$, and $E(Pt_{31}I)$ are the calculated SCF energies and EA and ϕ are taken from experiment. Overall, there is considerable evidence from previous cluster model studies, for example Refs. [10,11,27,28,37], that the HF SCF WFs we have used give reliable descriptions of many properties of chemisorbed species.

3. Properties of $I/Pt(111)$

Our main concern in this section is to establish the electronic character of the interaction of $I/Pt(111)$ and to examine the site dependence of this interaction. We show, through detailed analyses of the $Pt_{31}I$ cluster wavefunctions, that the bond is dominantly ionic at both 3-fold and on-top adsorption sites; other properties are shown to be different for these two sites.

3.1. General considerations

In Table 1, we present the equilibrium distance of I above the surface plane of $Pt(111)$, denoted z_e , the change in the surface dipole, $\Delta\mu_z$, along the surface normal, and the adsorption bond strength or the depth of the potential well at z_e , denoted D_e . We also give the harmonic vibrational frequency, ω_e , for motion of I normal to the surface; ω_e is determined from a least square fit of a cubic polynomial to the five points nearest the minimum on the computed potential energy curve, $V(Z)$. These properties are given for both 3-fold and on-top adsorption sites. For z_e , ω_e , and $\Delta\mu$, the properties are given for neutral and negatively charged clusters, denoted with $Q=0$ and $Q=-1$, respectively. We note the z_e for $Q=0$ and $Q=-1$ cluster charges are quite similar for each site although they differ considerably between the two sites. For the 3-fold site, $z_e \sim 4.7$ bohr, or ~ 2.5 Å, above the surface while for

Table 1

Properties of $Pt_{31}I$ for I at 3-fold and on-top sites of $Pt(111)$ are given for two charge states of the cluster, $Q=0$ for $Pt_{31}I^0$ and $Q=-1$ for $Pt_{31}I^-$. The properties are z_e , the distance of the adsorbate above the surface, ω_e , the harmonic vibrational frequency for translation of I normal to the surface, D_e , the chemisorption bond energy, and $\Delta\mu(z_e)$, the dipole moment change induced by the adsorbed I at z_e . More detailed definitions of these quantities are given in the text.

Site	3-Fold		On-top	
	$Q=0$	$Q=-1$	$Q=0$	$Q=-1$
Charge	$Q=0$	$Q=-1$	$Q=0$	$Q=-1$
z_e (bohr)	4.7	4.8	5.3	5.3
ω_e (cm^{-1})	101	89	114	102
D_e (eV)	3.75	–	3.39	–
$\Delta\mu(z_e)$ (D)	8.13	7.87	4.95	4.57

the on-top site, $z_e \sim 5.3$ bohr and I is 0.3 Å further away from the surface. The Pt– I bond distance at the 3-fold site is ~ 3.0 Å, slightly longer than the Pt– I distance of ~ 2.8 Å at the on-top site. However, as we show later, the changes in adsorption properties correlate more closely with z , the distance of I above the surface, than with the Pt– I distance. Our immediate concern is to establish the ionic character of the Pt– I interaction, then we will consider other properties.

In order to characterize the effective charge state of the adsorbed I , we use a projection operator method [30,43], where the orbitals of an isolated I anion are projected on the cluster WFs; the choice of orbitals of I^- rather than of neutral I will become clear shortly. The projection avoids artifacts arising with population analysis methods for counting effective charges. [31,46] In Table 2, we give the projections for clusters with charge $Q=0$ for values of $z(I)$ within 0.5 bohr of z_e , and for $z(I)$ near z_e , we compare the projections for $Q=0$ and $Q=-1$. Since the core orbitals of I are not involved in the chemistry, we give the projections, $n(i\lambda)$, for the $5s$, $5p\sigma$, and $5p\pi$ shells of I and we give their sum, $n(\text{Total})$. For ideal anionic I , $n(\text{Total})=8$. The data in Table 2 shows that the projections are weak functions of $z(I)$ and of Q and that $n(\text{Total})$ is close to the ideal value of 8 in all cases. For the 3-fold site with $z(I)=4.80$ bohr, $n(5s)=2.00$ for both $Q=0$ and $Q=-1$ showing that the I $5s$ orbital is fully occupied and is not involved in covalent bonds with Pt. The $n(5p\sigma)$ and $n(5p\pi)$ are slightly, ~ 0.1 electron, less than their values for perfect I^- . For $I/Cu(111)$ [9], small decreases from perfect ionicity of I are due to a small donation from I^- to Cu; i.e., to covalent bonding between I^- and the substrate. We shall see that this weak covalent bonding is also present for $I/Pt(111)$.

The $n(i\lambda)$ change very slightly as $I(z)$ is varied. In particular, $n(5p\pi)$ becomes smaller by 0.05 electrons as $z(I)$ is reduced and increases by a similarly small amount when $z(I)$ becomes larger. This is fully consistent with small changes in the donation and covalent bonding as the bond distance, and hence the substrate–adsorbate

Table 2

Projections of the I orbitals on the WFs for the $Pt_{31}I^Q$ cluster with I at 3-fold and on-top sites; the projections, $n(i\lambda)$, are given for the $5s$, $5p\sigma$, and $5p\pi$ I orbitals as well as for the sum over these orbital, labeled total. The projections are given for a position of I above the surface, $z(I)$ in bohrs, near z_e and for a shorter and a larger distance. For the distance near z_e , projections for clusters with charges $Q=0$ and $Q=-1$ are both given; for the other distances, projections are given only for $Q=0$.

Site	3-Fold				On-top			
	4.20	4.80	5.20	5.70	4.90	5.30	5.70	6.10
$z(I)$	4.20	4.80	5.20	5.70	4.90	5.30	5.70	6.10
Q	0	0	–1	0	0	0	–1	0
$n(5s)$	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
$n(5p\sigma)$	1.88	1.88	1.89	1.88	1.82	1.84	1.86	1.86
$n(5p\pi)$	3.88	3.93	3.94	3.95	3.98	3.98	3.99	3.99
Total	7.75	7.80	7.83	7.82	7.79	7.82	7.84	7.84

overlap changes. Furthermore, the projections for 3-fold and on-top site show the dominant ionic character of I at both of these sites. Since the effective charge on I is almost -1 , it is appropriate to project the I^- rather than neutral I orbitals from the Pt_{31} WFs [43]. The projections give strong support that the $Q=0$ clusters are $Pt_{31}[+]$ interacting with I^- and the $Q=-1$ clusters are $Pt_{31}[0]$ interacting with I^- . They also show that this ionic view needs to be slightly modified by a small covalent bonding and donation from I^- to the substrate. The properties of $I/Pt(111)$ obtained with the $Q=0$ and $Q=-1$ clusters must converge in the limit of large clusters. For finite Pt clusters, the differences show the limitations of the cluster response to the charged adsorbate due to the finite size of the cluster. The projections indicate that the bonding and electronic structure are similar for the charged and neutral Pt_{31} clusters. Further evidence for this similar behavior, discussed below, is obtained from other properties of the $Q=0$ and $Q=-1$ clusters.

The high ionicity of chemisorbed $I/Pt(111)$ is also shown by the dipole moment curves of the $Pt_{31}I$ clusters as a function of $z(I)$. In particular, we are concerned with the change in the dipole between $I/Pt(111)$ as represented by $\mu(Pt_{31}I)$ and the dipole of the bare $Pt(111)$ surface represented by $\mu(Pt_{31})$. The change in the dipole moment induced by a single adsorbate, $\Delta\mu = \mu(Pt_{31}I) - \mu(Pt_{31})$, can be related to the $\Delta\phi$ induced by the adsorption of I [9,34,47]. The relationship between $\Delta\mu$ and $\Delta\phi$ is discussed in more detail in Section 4. The specific definitions that we use for $\Delta\mu$ are discussed below.

With the C_{3v} symmetry of I at a 3-fold site, the only non-zero component of μ is along the surface normal, μ_z . For I at an on-top site, where the cluster symmetry is only C_s , μ_x is also non-zero. However, since only μ_z is relevant for surface properties, we consider only μ_z and denote it simply as μ . Furthermore, we consider the quantity $\Delta\mu$ as the difference between the μ for Pt_{31} and for $Pt_{31}I$, where $\Delta\mu(Q=0) = \mu(Pt_{31}I[0]) - \mu(Pt_{31}[+])$ and $\Delta\mu(Q=-1) = \mu(Pt_{31}I[-1]) - \mu(Pt_{31}[0])$. For the charged species, the origin for the calculation of μ is fixed as $z=0$. Defined in this way, $\Delta\mu$, can be directly related to the $\Delta\phi$ induced by the adsorption of I [9,34,47]. The calculated $\Delta\mu(z)$ are least square fit to quadratic polynomials with

$$\Delta\mu(z) = M_0 + M_1(z - z_0) + M_2(z - z_0)^2, \quad (2)$$

where the origin for the expansion, z_0 , was taken as $z_0 = 5.0$ bohr, roughly centered between z_e for the 3-fold and the on-top sites. Values of the M_i are given in Table 3. The choice of $\Delta\mu$ rather than μ affects only M_0 , the absolute value of the dipole moment curve; it does not affect the slope, M_1 , or the curvature, M_2 . The slope and curvature provide measures of the ionic contrasted to covalent character of a bond [27,30,43,48]. A small slope indicates a dominantly covalent bond where the center of charge remains roughly fixed in space between the surface and the adsorbate. A slope with a large magnitude indicates an adsorbate with a large effective charge so that the center of charge moves as the adsorbate moves. While, it is an oversimplification to relate the effective charge to the

slope since this neglects the responses of the substrate and adsorbate charges as the distance changes, a dominantly ionic interaction should have a small curvature. In particular, $M_2/M_1 \ll 1$ shows that the bond has considerable ionic character [49,50].

For all the $\mu(z)$ in Table 3, both M_1 and M_2/M_1 satisfy the conditions for an ionic bond. Note, however, that the magnitudes of the slopes are considerably greater than the unit charge expected for an ideal anionic adsorbate; in fact, they are between 50% and 90% larger than one. These large values of M_1 arise from changes in the polarization of the metal substrate [49,50] and of the adsorbate with bond distance; such large values of M_1 have also been found for halogens on $Ag(111)$ [10]. While the values of M_1 and M_2 give clear proof that the $I/Pt(111)$ bond is dominantly ionic, the projections provide quantitative indications of the small departures from pure ionic character. The values of the M_i are similar for the $Q=0$ and $Q=-1$ clusters for both sites consistent with the similar values for the z_e , in Table 1, and the projections in Table 2. Given this similarity, our focus will be on the $Q=0$ clusters, especially for the detailed decomposition of the bonding presented in the following sub-section. The magnitude of the slope, M_1 , at the 3-fold site is $\sim 20\%$ larger than at the on-top site because the polarizability of $Pt(111)$ is greater at the 3-fold site than at the on-top site, see Section 3.3. The magnitudes of $\Delta\mu$ at $z = 5.00$ bohr, M_0 in Table 3, are large and positive at both sites. At first sight, this seems counterintuitive because an anionic adsorbate is expected to lead to $\Delta\mu < 0$ [9,13,21]; the origin of this counterintuitive $\Delta\mu$ is explained in the following sub-section. The large slope of the dipole moment curves show how strongly $\Delta\mu$ depends on the position of the adsorbate above the surface. This dependence means that $\Delta\mu$, and hence $\Delta\phi$, will be quite different for the 3-fold and on-top sites since z_e is quite different for these two sites see Table 1.

The distances determined for ionic adsorbates, I^- and Cs^+ , above $Cu(111)$ [9] are reviewed to help understand the z_e for $I/Pt(111)$; in particular, the site dependence of z_e . For $I/Cu(111)$ at an on-top site, $z_e = 2.74$ Å, which is significantly shorter than the $z_e = 3.31$ Å for $Cs/Cu(111)$. The much closer approach of I to the surface is due to a covalent bond present for I but not for Cs. The $z_e = 2.8$ Å for the on-top site for $I/Pt(111)$ is quite close to the z_e found for $I/Cu(111)$. The similar values of z_e for the on-top sites of the two metals are not surprising given the dominant ionic bonding complemented with an additional covalent donation from I^- to the substrate that is present for both Cu and Pt. However, the fact that I is 0.6 bohr or 0.3 Å closer to $Pt(111)$ at the 3-fold than at the on-top site is surprising. The chemical reasons for this difference are analyzed in the following sub-section and this will help us understand whether the site dependence of z_e may also hold for other metals besides Pt.

The values of $\Delta\mu(z_e)$ in Table 1 are obtained by evaluating the polynomial of Eq. (2) with the coefficients in Table 3 at z_e . As expected from the large magnitudes of slopes, M_1 , $\Delta\mu(z_e)$ is much larger for the 3-fold site than for the on-top site. This means that I adsorbed at a 3-fold site will lead to a larger lowering of the work function than I at an on-top site. As we discuss later, this difference is fully consistent with coverage dependent measurements of $\Delta\phi$ [6]. We turn finally to our estimates of the chemisorption bond energies for the on top and 3-fold sites. For the $Q=0$ clusters, it is possible to obtain a reliable estimate of the bond energy, or D_e , with our HF WFs [32,45] by combining our calculated SCF energies with values for the $Pt(111)$ ϕ , 5.85 eV [6], and the EA of I, 3.06 eV [7]; see Eq. (1). The bond energy is larger by ~ 0.4 eV for the 3-fold site and this is consistent with the determination [6] that on top sites fill only at higher coverages, while at low coverages, I bonds preferably at 3-fold sites. We recall that we have used C_{3v} symmetry for the 3-fold site WFs and there may be a symmetry broken solution [51] with a lower energy for this site. The main consequence, if such a symmetry broken solution exists, is that the sta-

Table 3

Least square fits of quadratic polynomials to the dipole moment curves of I as a function of distance above $Pt(111)$ at on-top and 3-fold sites with $z_0 = 5.00$ bohr; see Eq. (2). The units are atomic units.

Site/charge	M_0	M_1 (Slope)	M_2 (Curvature)
<i>On-top</i>			
$Q=0$	2.37	-1.56	-0.29
$Q=-1$	2.31	-1.50	-0.34
<i>3-Fold</i>			
$Q=0$	2.58	-1.88	-0.12
$Q=-1$	2.75	-1.69	-0.25

bility of the 3-fold site over the on-top site may be somewhat larger than our estimated 0.35 eV.

3.2. Decomposition of the contributions to the I/Pt(111) interaction

The constrained space orbital variation, CSOV, method [25,26] allows us to decompose an interaction into the individual contributions from the various chemical and physical mechanisms responsible for the interaction. Given the strong similarity of the results with the $Q=0$ and $Q=-1$ clusters, the CSOV decompositions are reported only for the $Q=0$ clusters. We give in Table 4, the CSOV analysis for $\Delta\mu$ and for the interaction energy, E_{INT} . For the 3-fold site, the CSOV analysis is made for two different $z(\text{I})$ with $z(\text{I}) = 4.60$ bohr, near z_e for this site, and with the longer $z(\text{I}) = 5.30$ bohr, near z_e for the on-top site; for the on-top site, only $z(\text{I}) = 5.30$ bohr is used. Given the dominant ionic character of the bond, we start the CSOV from the superposition of isolated I^- and $\text{Pt}_{31}[+]$ WFs. The E_{INT} tabulated at each CSOV step are:

$$E_{\text{INT}}(\text{CSOV Step } n) = E(\text{Pt}_{31}[+]) + E(\text{I}^-) - E(\text{Pt}_{31}\text{I}; \text{CSOV Step } n) - \phi[\text{Pt}(111)] + \text{EA}(\text{I})$$

$$\text{and } \delta E_{\text{INT}}(\text{CSOV Step } n) = E_{\text{INT}}(\text{CSOV Step } n) - E_{\text{INT}}(\text{CSOV Step } n-1), \quad (3)$$

where E_{INT} gives the cumulative interaction energy and δE_{INT} gives the energy increment from the current CSOV step. The E_{INT} 's are defined in the same way as the D_e in Table 1; see Eq. (1). The definitions of the CSOV dipole moments follow the usage in Tables 1 and 3 and are explained in Section 3.1 in the discussion around Eq. (2):

$$\Delta\mu(\text{CSOV Step } n) = \mu(\text{Pt}_{31}\text{I}[0]; \text{CSOV Step } n) - \mu(\text{Pt}_{31}[+]) \quad \text{and}$$

$$\delta\mu(\text{CSOV Step } n) = \Delta\mu(\text{CSOV Step } n) - \Delta\mu(\text{CSOV Step } n-1) \quad (4)$$

Where, as in Eq. (3), $\Delta\mu$ gives the cumulative change while $\delta\mu$ gives the change from the current step.

The steps of the CSOV decomposition follow the same logic as was used earlier for Cs, I, and Xe on Cu surfaces [9,52]. The CSOV steps considered and the physical effects treated at each step are the following: Step (0): A point charge, PC, with $\text{PC} = -1$ is placed at the position of the I atom and the charge distribution of the Pt_{31} cluster in the presence of this PC is fixed, or frozen, as variationally optimized for isolated $\text{Pt}_{31}[+]$. We use the notation FO to describe these frozen orbitals and this step is called Point Charge-FO. The only property considered at this step is $\Delta\mu$ and it is used to measure the changes that occur, in later CSOV steps, as the various physical and chemical degrees of freedom are tuned on. Step (1): Here the WFs of the separated $\text{Pt}_{31}[+]$ and I^- are superimposed but they are required to form an anti-symmetric to-

tal WF. This is done by forming a Slater determinant with the FO's of the separated ionic species. No Chemistry is allowed and only physical, Pauli exclusion, effects are possible; this step is called Pauli-FO. Because of the overlap of the adsorbate and substrate charge distributions, $\mu(\text{Pt}_{31}\text{I})$ is not equal to the sum of the dipole moments of $\text{Pt}_{31}[+]$ and I^- [9,34,52]. Our experience with adsorbed species is that the Pauli exclusion always increases μ over the value given by the sum of the separated dipole moments and $\Delta\mu > 0$. There are two contributions to E_{INT} at this step. The electrostatic interaction of $\text{Pt}_{31}[+]$ and I^- leads to an attraction with $E_{\text{INT}} > 0$ while the overlap of the charge distributions of these two units leads to a steric or Pauli repulsion [25,26]. Thus, for large distances of I^- from $\text{Pt}_{31}[+]$, $E_{\text{INT}} > 0$ while at shorter distances, the overlap, which grows exponentially, will dominate and the interaction will become repulsive, $E_{\text{INT}} < 0$. At CSOV Step (2), denoted V(Pt), the I orbitals are held fixed as variationally optimized for the isolated anion but the Pt cluster orbitals are variationally optimized to take into account the presence of I^- . This CSOV step includes polarization of the Pt surface charge distribution to reduce the steric or Pauli repulsion between the Pt and I charge distributions and, in principle, back-donation or dative covalent bonding between Pt and I. However, since the I has been fixed as an anion, back-donation into the unoccupied I 6s and 6p Rydberg levels is energetically unfavorable and will not occur. The changes at this step are due entirely to polarization of Pt(111). At CSOV Step (3), the polarized Pt_{31} charge distribution is held fixed and the I^- adsorbate is variationally optimized in response to the presence of the Pt(111) substrate. This step, denoted V(I), includes both polarization of the I charge away from being spherically symmetric and donation, covalent bonding, with the empty surface conduction band levels of Pt(111). We have not explicitly separated these two effects but rely on our earlier study of I/Cu(111) [9] where we found them to be of comparable magnitude. We found that there were large differences between the E_{INT} and $\Delta\mu$ from this CSOV step and from an unconstrained SCF calculation. This indicates that there is significant coupling between the V(Pt) and V(I) CSOV steps, not surprising given the large changes at each of these steps. In order to take this coupling into account, we carried out a second pass of constrained variations [31]. At CSOV Step (4), denoted V(Pt)-Pass 2; the I^- charge distribution after V(I), including the I polarization and donation, is frozen and another variation of the Pt orbitals is made to take into account the response of the Pt to the changes in the I^- charge distribution. At CSOV Step (5), denoted V(I)-Pass 2, the Pt orbitals are frozen and the I orbitals are re-optimized. Finally, at the final CSOV Step (6), all constraints are removed and a full, unconstrained SCF calculation, denoted Full SCF, is performed. It is expected that there will only be small changes from the results of the preceding CSOV step (5) since the second pass of CSOV steps has taken account of the coupling between the Pt and I variations.

Table 4
CSOV decomposition of the interaction energy, E_{INT} , and the dipole change, $\Delta\mu$, for a series of CSOV steps for I at 3-fold and on-top sites of Pt(111). The decompositions for the 3-fold and on-top sites are made for $z(\text{I})$ near z_e for the respective sites. For the 3-fold site, the decomposition is also made for $z(\text{I})$ at the longer, on-top site distance; this is done to separate effects of distance from those of adsorption site. The incremental changes at the current CSOV step, δE_{INT} and $\delta\mu$ are also given. Energies are in eV, dipoles in Debye, and $z(\text{I})$ in bohr.

Site/ $z(\text{I})$	3-Fold/ $z(\text{I}) = 4.60$				3-Fold/ $z(\text{I}) = 5.30$				On-top/ $z(\text{I}) = 5.30$			
	E_{INT}	δE_{INT}	$\Delta\mu$	$\delta\mu$	E_{INT}	δE_{INT}	$\Delta\mu$	$\delta\mu$	E_{INT}	δE_{INT}	$\Delta\mu$	$\delta\mu$
Point Charge-FO	–	–	–11.68	0	–	–	–13.47	0	–	–	–13.47	0
Pauli-FO	–0.66	0	–10.66	+1.02	+0.89	0	–12.90	+0.57	+0.60	0	–13.04	+0.43
V(Pt)	+1.35	+2.01	–0.16	+10.51	+2.12	+1.23	–2.40	+10.50	+1.81	+1.21	–2.76	+10.28
V(I)	+3.30	+1.94	+5.26	+5.42	+3.31	+1.19	+2.47	+4.87	+3.06	+1.25	+1.60	+4.36
V(Pt)-Pass 2	+3.62	+0.33	+6.57	+1.31	+3.50	+0.19	+3.64	+1.17	+3.30	+0.24	+2.82	+1.21
V(I)-Pass 2	+3.70	+0.08	+7.91	+1.35	+3.54	+0.04	+4.70	+1.06	+3.36	+0.07	+4.07	+1.25
Full SCF	+3.73	+0.03	+8.44	+0.53	+3.55	+0.01	+5.12	+0.41	+3.39	+0.03	+4.78	+0.71

We analyze first E_{INT} and $\Delta\mu$ for I at a 3-fold site with $z(\text{I}) = 4.60$ bohr, near z_e . At the FO-Pauli CSOV step, the interaction is repulsive by 0.7 eV. In other words the chemistry draws the I sufficiently close to the surface that the Pauli, or steric, repulsion dominates over the Coulomb attraction between $\text{Pt}_{31}[+]$ and I^- . Another indication of the overlap of the I and Pt charge distributions is the change in $\Delta\mu$ at the FO-Pauli charge superposition CSOV step is 1.0 Debye, D , to a interface μ larger than given by simply adding a point charge and neglecting the Pauli exclusion principle; see CSOV step (0). The polarization of the Pt induced by the presence of I is immense. At the first V(Pt) CSOV step, $\delta E_{\text{INT}} = 2.0$ eV and $\delta\mu = 10.5$ D. Thus, the polarization of the Pt surface charge dramatically increases the interface dipole induced by the presence of I^- . The Pt polarization is so large that it almost offsets the decrease in dipole caused by the point charge, $\text{PC} = -1$; in fact, the sum of the $\delta\mu$ for the FO-Pauli exclusion and the $\delta\mu$ for the Pt polarization leads to a total $\Delta\mu \approx 0$. For E_{INT} , the Pt polarization also more than offsets the steric repulsion leading to an interaction that is attractive by 1.4 eV. At the first V(I) CSOV step, the δE_{INT} due to the polarization and donation from I^- is almost as large as at the first V(Pt) step but $\delta\mu$ at this step, while rather large, is only half as large as at V(Pt). However, the contribution of the I polarization and donation is sufficiently large that the sign of $\Delta\mu$ changes from $\Delta\mu < 0$ to $\Delta\mu > 0$, which corresponds to $\Delta\phi < 0$. The values of ΔE_{INT} and $\Delta\mu$ at the Full SCF CSOV step, see Table 4, are modestly different from the values at the first V(I) step showing that there is some coupling of the V(Pt) and V(I) variations. However, after the second pass of CSOV variations, the non-additivity, as measured by the difference of the results at V(I)-Pass2 and the Full SCF results, see Table 4, is acceptably small.

The E_{INT} between I and Pt(111) near the z_e for the 3-fold site is reasonably strong, ~ 3.7 eV, due, in particular, to the electrostatic attraction of the anionic adsorbate with its “image” in the substrate and the donation from I^- to Pt. The dipole induced by a point charge placed at $z = 4.6$ bohr above a frozen Pt(111) surface is $\Delta\mu = -11.7$ D; this has the expected sign for the dipole induced by a negative adsorbate although this $\Delta\mu$ per adsorbate would correspond to a huge work function increase even for very low coverages [9,47]. However, all the physical and chemical effects arising from the interaction of I^- with Pt act to increase the interface dipole. The Pauli exclusion at the Pauli-FO CSOV step increases $\Delta\mu$ by 1 D. The Pt polarization, summing the contributions of the 2 passes, increases $\Delta\mu$ by 11.8 D. This large increase arises from a net polarization of the Pt electronic density down into the substrate and away from the I^- adsorbate. This charge motion serves two purposes: (1) it reduces the steric repulsion between the substrate surface charge and Iodine and (2) it increases the electrostatic interaction between the anionic adsorbate and the substrate. The $\delta\mu$ due to the Pt polarization is sufficient to lead to a $\Delta\mu > 0$ consistent with $\Delta\phi < 0$. The I polarization and donation increase $\Delta\mu$ by an additional 6.8 D. The Full SCF $\Delta\mu = +8.4$ D is very large. The Helmholtz formula relating $\Delta\phi$ to coverage and the induced dipole per adsorbate, $\Delta\mu$ [47,53], would give, for the Full SCF $\Delta\mu$, $\Delta\phi \sim 4$ eV even for a low coverage of $\theta \sim 0.1$ monolayer. This is an order of magnitude larger than the measured $\Delta\phi$ [6]. Clearly, the value of $\Delta\mu$ must be very strongly coverage dependent and, in the following section, we will discuss possible mechanisms for this coverage dependence.

We next consider how E_{INT} and $\Delta\mu$ change as the I adsorbate is moved out further from to surface to $z(\text{I}) = 5.30$ bohr, or close to z_e for I at an on-top site. While there are important similarities, the distance dependence of these properties gives useful insight into how observed properties [6] may provide information about the bond character and the bond distance. For the Pauli-FO charge superposition at $z(\text{I}) = 5.30$ bohr, the interaction is attractive with $E_{\text{INT}} = +0.9$ eV. Thus, the electrostatic attraction between the adsor-

bate and substrate ions is larger than the steric repulsion, yielding a net attractive interaction even before any chemistry is allowed to be included through orbital variations. This is different from the net repulsion at the Pauli-FO step at $z(\text{I}) = 4.6$ bohr where the larger overlap between the Pt and I charge distributions leads to a net repulsion at the shorter distance. The δE_{INT} for the chemical effects arising from the Pt polarization and the I polarization and donation at the first and second passes of the V(Pt) and V(I) CSOV steps are parallel to but smaller, $\sim 60\%$, of the values at $z(\text{I}) = 4.60$ bohr. The reduction in the polarizations are to be expected since the driving force for these polarizations is the overlap of the I and Pt charge distributions, which decreases exponentially with the separation of the two units. The I to Pt donation also depends on this overlap and is smaller at the larger $z(\text{I})$. The overall effect from these cancelling contributions is that E_{INT} is different by less than 0.2 eV, or 5%, between the two distances. In other words, the potential curve is rather flat. The ω_e for motion of the I normal to the surface at the 3-fold site is indeed small, $\omega_e = 101$ cm^{-1} ; it is also small at the on-top site where $\omega_e = 114$ cm^{-1} ; see Table 1. It is a general observation that the vibrations of adsorbed ions, either cations or anions, on metal surfaces are small with $\omega_e \sim 100$ cm^{-1} [10,18,54]. It is interesting that, for low coverages of Cs/Cu(100), the frequency for translation of the Cs normal to the surface is even smaller, $\omega = 52$ cm^{-1} [55], or about half of our calculated values of ω for I/Pt. Since the masses of Cs and I differ by only 5%, the different values of ω for Cs and I must reflect differences in the force constants for these two adsorbates. The somewhat larger values of ω for I/Pt are increases that would be expected from the, albeit small, covalent contribution to the bond in the case of I/Pt while, for Cs, the bonding is essentially purely ionic [9].

The situation is different for the changes in the surface dipole. A PC at a longer distance of $z(\text{I}) = 5.30$ bohr gives a Point Charge-FO value for $\Delta\mu$ that is more negative by 1.8 D than at the shorter $z(\text{I}) = 4.60$ bohr. The Pauli exclusion at the Pauli-FO CSOV step only increases $\Delta\mu$ by 0.6 D or 60% of the increase at the shorter $z(\text{I})$. This is consistent with the smaller overlap at the larger $z(\text{I})$. While the changes, $\delta\mu$, at the following CSOV steps for V(Pt) and V(I) are also smaller at $z(\text{I}) = 5.30$ bohr, they are closer to values of $\delta\mu$ for the shorter $z(\text{I}) = 4.60$ bohr than was the case for the Pauli-FO CSOV step. However, the consistently smaller values of $\delta\mu$ at the CSOV steps for $z(\text{I}) = 5.30$ bohr than for those at the shorter $z(\text{I}) = 4.60$ bohr are the reason that the magnitudes of the slopes of the $\Delta\mu$ curves are much larger than one; see Table 3. The result is that the interface dipole and, hence, the work function changes are strongly affected by the distance of anionic I from Pt(111), especially since Iodine has a covalent bond that supplements the dominant ionic bonding. Thus changes in the work function induced by adsorbed Iodine, and possibly other halogens [11], are very sensitive to the distance of the adsorbate from the substrate. We see that this also applies when the adsorbates are at different sites; see Table 1.

The CSOV decomposition of E_{INT} and μ for I at the on-top site with $z(\text{I}) = 5.30$ bohr are remarkably similar to those for I at the same distance from a 3-fold site. The largest difference in E_{INT} is for the Pauli-FO CSOV step, where, at the on-top site, the net attraction is 0.3 eV smaller than at the 3-fold site while the δE_{INT} at the other CSOV steps are the same for the two sites within 0.06 eV; see Table 4. It is likely that the difference at the Pauli-FO charge superposition CSOV step is due to a larger steric repulsion at the on-top site since, at this site, I is closer to the charge distribution of the more localized Pt 5d electrons. This larger steric repulsion may prevent I at the on-top site from approaching the surface as closely as I at the 3-fold site leading to I being more weakly bound at the on-top site. The CSOV contributions to $\Delta\mu$ are also quite similar for the 3-fold and on-top sites for the same $z(\text{I}) = 5.30$ bohr and the Full SCF total values of $\Delta\mu$ differ by only 0.3 D or 7%. This is

strong evidence that the 3D smaller value of $\Delta\mu$ at the on-top site than the 3-fold site when the equilibrium distances are used, see Table 1, is directly related to the much smaller value of z_e at the 3-fold site. The fact that $\Delta\mu$ is significantly smaller at the on-top site is consistent with the fact that $\Delta\phi$ increases, approaches closer to zero, when the on-top site is occupied [6]. This will be addressed further in Section 4.

3.3. Decomposition of changes in the I(3d) binding energies

Jo and White [6] observed two I(3d) XPS BE's for I/Pt(111) and they assigned the higher energy BE to I adsorbed at 3-fold sites and the lower energy BE to I at on-top sites. We provide an explanation for the I(3d) BE shift. ΔBE , between the two sites from a CSOV decomposition of the Koopmans' Theorem, KT, shifts, see Ref. [56] and references therein. Because they do not include final state relaxation, the KT BE will, for I(3d), be a few 10's of eV larger than observed. However, the KT BE will give information that relates the I(3d) ΔBE to the initial state chemical interaction of I with Pt. Furthermore, there is compelling evidence that the final state relaxation is only a weak function of the position of the core-ionized atom [56,57]. Especially, when the response and screening of a core-ionized atom is from a metal with diffuse and mobile conduction band electrons, the screening, or relaxation, energies will be approximately independent of the position of the atom with the core-hole. We give, in Table 5, the CSOV decomposition of the KT BE's for the same clusters and $z(I)$ as in Table 4.

Since our calculations are non-relativistic, the spin-orbit splitting of the 3d shell is neglected. However, we do not feel that this is significant since the chemistry of the I-Pt interaction should have comparable effects on the ΔBE of the spin-orbit split $3d_{3/2}$ and $3d_{5/2}$ shells [58]. There are also "crystal-field" splittings of the I(3d) shell due to the reduced point-group symmetry of I in these sites. Since these splittings are small, 0.05 eV, especially as compared to the changes in the BE(3d) between CSOV steps, we consider only the average KT BE's over the 5 components of the 3d shell. Finally, we report the BE's at the various CSOV steps as shifts, ΔBE , with respect to the BE's of the isolated I^- anion. These ΔBE show how the chemistry and physics of the interaction modifies the BE. While the individual KTBE's cannot be compared directly to experiment, the differences of the Full SCF values of the ΔBE 's at the different sites can be compared with experiment [56]. In Table 5, we report the quantities:

$$\begin{aligned} \Delta BE(\text{CSOV Step } n) &= BE(\text{KT}; \text{CSOV Step } n) - BE(\text{KT}; I^-) \text{ and} \\ \delta BE(\text{CSOV Step } n) &= \Delta BE(\text{CSOV Step } n) - \Delta BE(\text{CSOV Step } n-1), \end{aligned} \quad (5)$$

where the $BE(\text{KT}, \text{CSOV Step } n)$ are the average values of $-\varepsilon(3d)$, the I 3d orbital energies, in the Pt_{31} clusters and $BE(\text{KT}; I^-)$ is $-\varepsilon(3d)$ for isolated I^- . As before, the ΔBE values are cumulative including the effects of all CSOV steps considered so far and the δBE represent the contribution to ΔBE of the present CSOV step only.

We consider first the $\Delta BE(3d)$ for I at a 3-fold site with $z(I) = 4.6$ bohr near z_e for this site. At the first, FO-Pauli, CSOV step, the I(3d) BE is shifted to 0.9 eV higher BE. At this step, there are two mechanisms that contribute to the shift of the BE's. One is the electrostatic field of the Pt_{31} cluster model of the surface [56,59,60]; this acts to shift the I core level BE's to higher energies, $\Delta BE > 0$. The second is the environmental charge density around the adsorbed I from the conduction band electrons at the Pt(111) surface [56,57] which acts to lower the BE; i.e., it contributes to a $\Delta BE < 0$. Clearly the first term dominates. The polarization of the Pt moves electronic charge away from the I anion increasing the electrostatic field at I and raising the BE(3d); the sum of the BE increases for the two V(Pt) passes is 3.2 eV. The $\delta BE > 0$ at the V(Pt) CSOV steps can be understood in terms of the formation of a positive "image charge" in Pt in response to the presence of the adsorbed I anion. The positive image charge generates an electric field that raises the I^- core-level BE's [56]. The polarization and the donation of I at the two passes of the V(I) CSOV steps also contribute to an increase of BE(3d) by a total of 1.7 eV, or about half of the BE shift due to the Pt polarization. The way in which hybridization and covalent bonding contribute to ΔBE , as distinct from the contributions of polarization, has been discussed in detail elsewhere [37,58,61]. The overall shift of the I(3d) BE from the reference of the BE for isolated I^- is quite large, $\Delta BE = +6.0$ eV.

For I at a 3-fold site but further from the surface, $z(I) = 5.30$ bohr, the ΔBE at the Pauli-FO CSOV step is slightly, 0.1 eV, larger than at the shorter distance of $z(I) = 4.60$ bohr. This is because there is only a slightly different cancellation between the $\Delta BE > 0$ contribution from the positive charge on Pt_{31} and the $\Delta BE < 0$ contribution from the surface charge density. Both individual terms become smaller as the distance of I from the surface is increased but the net cancellation is similar. For the same reasons as for the shorter $z(I) = 4.60$ bohr, all the other CSOV terms act to make the ΔBE larger; however, they are smaller, $\sim 80\%$ of the values at the shorter $z(I)$. The net effect is that ΔBE at the 3-fold site is 0.8 eV smaller when the I adsorbate is moved from z_e to a position ~ 0.7 bohr or ~ 0.4 Å further away from the surface; differences in BE's of ~ 1 eV can be easily measured [6]. For I at the on-top site with $z(I) = 5.3$ bohr, near z_e for this site, $\Delta BE = 1.1$ eV at the Pauli-FO CSOV step is similar to the values for both distances of I at the 3-fold site. Thus, the electrostatic effect of the Pt_{31} charge, which contributes to $\Delta BE > 0$, dominates over the environmental charge contribution to $\Delta BE < 0$ at the on-top as well as at the 3-fold site. As for the 3-fold site, all the chemical terms, polarizations and donations, also contribute to further raising ΔBE at the on-top site. The contributions to ΔBE for the various CSOV steps at the on-top site are similar to, but slightly smaller than, at the 3-fold site with the same $z(I)$; the sum of the δBE for the on-top site is 3.8 eV compared to 4.2 eV for the 3-fold site. This roughly 10% difference is due to somewhat different chemistry and different environments at the two sites. However, the larger total ΔBE at the 3-fold site with $z(I) = z_e$ clearly reflects the much shorter adsorbate to surface distance at this site.

Table 5
CSOV decomposition of the shift of the I(3d) XPS BE, ΔBE , for I at 3-fold and on-top sites for a series of CSOV steps. The ΔBE and the incremental δBE are both given in eV. See the caption of Table 4 for further details.

Site/ $z(I)$	3-Fold/ $z(I) = 4.60$		3-Fold/ $z(I) = 5.30$		On-top/ $z(I) = 5.30$	
	ΔBE	δBE	ΔBE	δBE	ΔBE	δBE
Pauli-FO	+0.88	0	+1.00	0	+1.10	0
V(Pt)	+3.47	+2.57	+3.16	+2.16	+3.09	+1.99
V(I)	+4.95	+1.49	+4.43	+1.27	+4.07	+0.98
V(Pt)-Pass 2	+5.57	+0.62	+4.90	+0.47	+4.53	+0.47
V(I)-Pass 2	+5.77	+0.20	+5.05	+0.14	+4.69	+0.16
Full SCF	+5.97	+0.20	+5.19	+0.15	+4.90	+0.21

4. Comparison with experimental data for I/Pt(111)

Jo and White [6] reported a detailed study of the coverage dependence of I/Pt with coverages ranging from $\theta \approx 0.02$ to $\theta = 0.43$ which is monolayer coverage; their study included XPS of the I(3d) level and work function changes. Based on their data, they assign I adsorption at low coverages to 3-fold sites with on-top sites becoming occupied only for $\theta > 0.33$; they conclude that I is bound more strongly at the 3-fold site. They also argue, based in part on XPS data, that the adsorbed I is negatively charged. This is consistent with our analysis which shows that I adsorbed at both 3-fold and on-top sites is dominantly anionic, or I^- , with a donation or covalent bonding involving ~ 0.2 I(5p) electrons. We compare first our results for site preference and I(3d) BE shifts with their results because the agreement between theory and experiment provides further support for the accuracy of our cluster model results. We then discuss our results for the surface dipole induced by the adsorbed I, $\Delta\mu$, in terms of the measured $\Delta\phi$, which involves a refinement and an extension of the analysis of Jo and White [6]. In particular, Jo and White argued that adsorption at the different sites led to different shifts in the work function with adsorption at 3-fold sites leading to $\Delta\phi < 0$ while adsorption at on-top sites leads to $\Delta\phi > 0$. On the other hand, we argue that adsorption of isolated I atoms at both sites leads to $\Delta\phi < 0$, albeit with different magnitudes; the shift being larger for adsorption at the 3-fold site.

4.1. Site preference

Our theoretical results, see Table 1, show that I is bound 0.35 eV more strongly at a 3-fold than at an on-top site and that $D_e = 3.75$ eV for an isolated I adsorbate at a 3-fold site. Since the D_e is computed with respect to a neutral $Pt_{31}I$ cluster, see Eq. (1), the adsorbed I anion will have a large Coulomb attraction to the positively charged Pt_{31} cluster model of the Pt(111) surface. It is likely that the Coulomb attraction will become smaller when the size of the Pt cluster is increased since the positive charge on the larger cluster could be more delocalized. For this reason, the computed D_e is likely to be an over-estimate [10,27,28]. Despite the fact that the absolute value of the computed D_e may be somewhat too large, we expect the differences of the D_e calculated for the two sites to be reliable. The temperature programmed desorption, TPD, measurements of Jo and White are interpreted as showing that desorption from the on-top peak is centered at ~ 650 K and from the 3-fold site at ~ 900 K. Although, they do not attempt to determine binding energies from their TPD data, it is clear that I is more strongly bound at a 3-fold site and their TPD is consistent with our calculated difference in binding at the two sites of 0.35 eV. The relatively high desorption temperatures are consistent with strongly bound I/Pt(111).

4.2. I(3d) BE's

From the I(3d_{5/2}) XPS data as a function of θ , Jo and White [6] conclude that there are two I(3d_{5/2}) BE's of 619.3 eV for the 3-fold site and 618.2 eV for the on-top site. In other words, the BE at the on-top site is shifted to a 1.1 eV lower energy. From our calculations, see Table 5, we find also find a 1.1 eV shift to lower BE for the on-top site, in excellent agreement with experiment. At first sight, such a large BE difference is surprising, especially since our analysis shows large and comparable anionicities of I at both sites. However, our theoretical analysis permits the large ΔBE to be understood on the basis of the different z_e at the two sites. The BE is closely related to the distance of I above the Pt(111) surface where, in the range of distances we studied, the BE is larger at

smaller distances. Thus, the closer approach to the surface at the 3-fold site is the major reason for the larger I(3d_{5/2}) BE at this site. Our close agreement with experiment for the BE shifts serves to further support our cluster model description of the I adsorption on Pt(111) and to give confidence in our analysis.

4.3. Work function changes

With our cluster model, we calculate the dipole change, $\Delta\mu$, due to a single adsorbate when I is adsorbed on Pt(111). If we neglect the coupling, or interaction between adsorbates [9,13,34,47,62], then

$$\Delta\phi(\theta) \propto -N\Delta\mu, \quad (6)$$

where N is the adsorbate density or coverage. While this approximation holds for low θ , it does not hold as well at high coverage and needs to be corrected [53,63]. In the low coverage region, there is an initial linear behavior of $\Delta\phi$ as a function of θ which then develops curvature. For cationic adsorbates [9,13,62], where $\Delta\mu > 0$, there is an initial decrease of ϕ with a minimum around $\theta = 0.25$. The increase of ϕ past the minimum is ascribed to a reduction of the ionicity of the cationic adsorbate [12,13,62]. There are many textbook examples of this behavior [13].

For an anionic adsorbate, one would expect, strictly on the basis of the interface dipole due to a charged object on the surface, an initial work function increase with a maximum at some coverage [21,64]. By analogy with the coverage dependence of $\Delta\phi$ for cations, one might also expect a maximum followed by a decrease of ϕ as the coverage increases and the adsorbate loses its anionic character. However, the $\Delta\phi$ for anionic adsorbates is much more complicated and there are several instances where an anionic adsorbate leads to $\Delta\phi < 0$ rather than the expected $\Delta\phi > 0$ [9,23,24]. In order to have $\Delta\phi < 0$, then $\Delta\mu$ must be > 0 ; see Eq. (6). The response, or polarization, of the substrate greatly offsets and reduces the magnitude of $\Delta\mu$ due to an unscreened ionic adsorbate; see Table 4 and Refs. [9,11]. However, this offset is reasonably symmetric in the changes induced in $\Delta\mu$ for anions and cations [9]. On the other hand, an effect that is present for anionic but not cationic adsorbates is the formation of covalent bonds that lead to significant decreases in the distance of anionic adsorbates above the surface [9]. For ionic adsorbates, $\Delta\mu$ is a strong function of the distance of the adsorbate above the surface; see Tables 3 and 4 and Refs. [9,11]. For an anionic adsorbate, $\Delta\mu$ has a large magnitude and $\Delta\mu < 0$ when the adsorbate is at large distances from the surface; as the adsorbate approaches the surface, $\Delta\mu$ increases and, for I/Cu [9] and I/Pt, it changes sign and becomes $\Delta\mu > 0$. The large negative slope of $\Delta\mu(z)$, Table 3, shows this strong distance dependence and indicates that the sign changes from $\Delta\mu < 0$ for $z \gtrsim 3.5$ Å to $\Delta\mu > 0$ for $z \lesssim 3.5$ Å.

For I/Cu(111), a $\Delta\mu = +1.5$ D was predicted and found to be in good agreement with the low coverage measurements of $\Delta\phi$ extrapolated to $\theta = 0$ [9]. For I/Pt(111), $\Delta\phi$ has been studied as a function of coverage and $\Delta\phi < 0$ is found [6]. However, the data is too limited to allow an extrapolation to $\theta = 0$ and, hence, a direct comparison with our theoretical $\Delta\mu = +8.4$ D for z_e at a 3-fold site cannot be made. The curve of $\Delta\phi(\theta)$ for I/Pt(111) [6] shows a minimum at $\theta \sim 0.33$ and increases by 0.2 eV for monolayer coverage at $\theta \sim 0.43$. Clearly, there is considerable coupling between the adsorbed I anions and the $\Delta\mu$ per adsorbate is much smaller than we have determined for a single isolated adsorbate at a 3-fold site of Pt(111). It is tempting to argue, by analogy with cationic adsorbates [13], that the charge on the anion reduces with coverage until it reaches zero. However, while this must occur for sufficiently high coverage, it is not at all clear that the charge on adsorbed I^- is significantly reduced in the coverage range studied by Jo and White [6]. First, at least in the initial stages of reducing the charge

on anionic I adsorbates, the $\Delta\phi$ would become more negative rather than going toward a minimum. This is because the negative charge on I contributes a large $\Delta\mu < 0$. Table 4, and if this were removed, $\Delta\mu$ might become larger leading to a greater decrease in $\Delta\phi$ as coverage is increased, the opposite of what is observed. Furthermore, our calculated properties for the site dependence of the bond strength, the XPS BE for I(3d), and the $\Delta\mu$ are consistent with observations [6] which would not be the case if the I charge were considerably reduced from the value that we calculate for an isolated I adsorbate. An alternative reason for the coverage dependence of $\Delta\mu$ is that the substrate polarization induced by the presence of the Γ^- adsorbate, CSOV steps $V(I)$, becomes reduced with increasing coverage. Thus, reducing the extent that this polarization offsets the $\Delta\mu < 0$ due to the presence of the charged adsorbate. This behavior would also lead to a minimum in the curve of $\Delta\phi$ with coverage. A test of this hypothesis is that, if sufficiently high coverage could be obtained, then the $\Delta\phi$ would change sign and become positive indicating a $\Delta\mu < 0$. Such behavior would be consistent with the adsorbed I still being anionic but with the polarization no longer large enough to change the sign of $\Delta\mu$ and, hence, of $\Delta\phi$. In fact, precisely this behavior has been found for I/Cu(111) where $\Delta\phi(\theta)$ is initially negative at low θ and as the coverage increases goes through a minimum and becomes positive [65].

There is another effect that contributes to an increase in $\Delta\phi$ at $\theta \sim 0.33$; on-top sites begin to fill at this coverage. We find a $\Delta\mu = 5.0$ D for I at z_e on an on-top site, which still corresponds to $\Delta\phi < 0$ although to a decrease that is 40% less rapid than at the 3-fold site. If we neglect changes in $\Delta\mu$ due to coupling of the adsorbed I, then when I occupies on-top sites, the $\Delta\phi$ would still decrease, albeit with a smaller slope. However, that smaller slope may not be sufficient to off-set the decrease of the Pt polarization with coverage and the minimum in $\Delta\phi$ is reached when the adsorption site changes from 3-fold to on-top. It is not necessary that $\Delta\mu > 0$ at the on-top site as proposed by Jo and White [6]. It might be possible to resolve this difference in interpretation by measuring $\Delta\phi$ at a finer spacing of θ , especially in the region about the maximum coverage for adsorption at the 3-fold site, $\theta = 0.33$. It would also be useful to have a finer spacing of the experimental data at low θ , so that $\Delta\phi(\theta)$ could be extrapolated to $\theta = 0$ and a value obtained for $\Delta\mu$ at $\theta = 0$.

5. Conclusions

Our calculated properties for I/Pt(111) are consistent with the measurements of Jo and White [6], especially for site preferences, core level BE shifts and changes in ϕ with adsorption of I. This agreement gives considerable support for the adequacy of our cluster model and for the reliability of our Hartree–Fock theoretical methodology. However, we have gone beyond a simple comparison with already measured properties and we have predicted new properties of the interaction that have not yet been measured. In particular, we have determined the D_e at the 3-fold site to be 0.36 eV larger than at the on-top site; this difference could be estimated from an analysis of experimental TPD spectra. We have determined that I approaches closer to the surface by 0.6 bohr, ~ 0.3 Å, at the 3-fold site than at the on-top site and we have shown that this closer approach contributes, in large part, to the different properties of the two sites. The Pt–I bond distances in the 3-fold and on-top sites could be determined by extended X-ray adsorption fine structure [66] and our prediction could be validated. We have also determined the frustrated translation of the I normal to the surface to have a low energy, $\omega_e \approx 100$ cm $^{-1}$ at both sites; this prediction could also, in principle, be confirmed by measurements [54]. The low frequency is consistent with the ionic character of the

interaction that we predict on the basis of our analysis of our cluster model wavefunctions.

We have also analyzed the character of the interaction and decomposed different contributions to the interaction through a CSOV or constrained space orbital variation. This has been done in order to relate the features of the bonding to observable properties. The key results are summarized as follows:

1. The interaction is dominated by an anionic adsorbate although there is some donation from the filled $I^-(5p)$ shell into unoccupied Pt surface levels that adds some covalent character to the ionic bond. We argue that this allows the I to be drawn closer to the surface and that the shorter bond distance has important consequences for $\Delta\phi$ and ΔBE .
2. The different contributions to ΔBE for the I(3d) XPS have been considered for two distances of the I at a 3-fold site, one close to the equilibrium distance at the 3-fold site and the other close to the equilibrium for the on-top site, and compared with the contributions for I at an on-top site. It was shown that there is a strong correlation between the BE shift and the distance of the adsorbate from the surface with ΔBE being larger when the adsorbate is closer to the surface. Thus, for ionic adsorbates, relative values of the XPS core-level BE's are likely to provide information about the relative distances of the adsorbate from the surface.
3. We have also shown a strong correlation between $\Delta\mu$ and the distance of the adsorbate from the surface. For I/Pt, when the distance becomes smaller, $\Delta\mu$ becomes larger with a rate of increase much larger than expected for an unscreened negatively charged adsorbate. This correlation has been explained in terms of the magnitudes of the changes in the substrate and adsorbate charge distributions. The important role of adsorbate-substrate distance should be considered in order to interpret the sign and magnitude of work function changes.

Acknowledgements

This work was partially supported by the NSF under grant NSF CHE06-51083 and the German DFG through SFB 558. We acknowledge partial computer support from the National Center for Supercomputing Applications, Urbana-Champaign, Illinois. We wish to dedicate this paper to the memory of Mike White who held positions at the University of Texas at Austin and at the Pacific Northwest National Laboratory and who passed away in the Summer of 2007. His experimental work with Sam Jo on I/Pt(111) was a major motivation for our theoretical study.

References

- [1] A.T. Hubbard, *Heterogenous Chem. Rev.* 1 (1994) 3.
- [2] P. Broekmann, A. Spaenig, A. Hommes, K. Wandelt, *Surf. Sci.* 517 (2002) 123.
- [3] A. Hommes, A. Spaenig, P. Broekmann, K. Wandelt, *Surf. Sci.* 547 (2003) 239.
- [4] P. Broekmann, N.T.M. Hai, K. Wandelt, *J. Appl. Electrochem.* 36 (2006) 1241.
- [5] S. Huemann, N.T.M. Hai, P. Broekmann, K. Wandelt, H. Zajonz, et al., *J. Phys. Chem. B* 110 (2006) 24955.
- [6] S.K. Jo, J.M. White, *Surf. Sci.* 261 (1992) 111.
- [7] T. Andersen, H.K. Haugen, H. Hotop, *J. Phys. Chem. Ref. Data* 28 (1999) 1511.
- [8] A.T. Hubbard, *Chem. Rev.* 88 (1988) 633.
- [9] P.S. Bagus, D. Kafer, G. Witte, C. Woll, *Phys. Rev. Lett.* 100 (2008) 126101.
- [10] P.S. Bagus, G. Pacchioni, M.R. Philpott, *J. Chem. Phys.* 90 (1989) 4287.
- [11] L.G.M. Pettersson, P.S. Bagus, *Phys. Rev. Lett.* 56 (1986) 500.
- [12] I. Langmuir, K.H. Kingdon, *Phys. Rev.* 21 (1923) 381.
- [13] H.P. Bonzel, *Surf. Sci. Rep.* 8 (1987) 43.
- [14] H. Ishida, *Phys. Rev. B* 38 (1988) 8006.
- [15] H. Ishida, *Phys. Rev. B* 42 (1990) 10899.
- [16] B.N.J. Persson, H. Ishida, *Phys. Rev. B* 42 (1990) 3171.
- [17] D.M. Riffe, G.K. Wertheim, P.H. Citrin, *Phys. Rev. Lett.* 64 (1990) 571.
- [18] G. Pacchioni, P.S. Bagus, *Surf. Sci.* 286 (1993) 317.
- [19] P.S. Bagus, G. Pacchioni, *Phys. Rev. B* 48 (1993) 15262.

- [20] M. Scheffler, C. Droste, A. Fleszar, F. Maca, G. Wachutka, et al., *Physica B* 172 (1991) 143.
- [21] M.P. Kiskinova, *Surf. Sci. Rep.* 8 (1988) 359.
- [22] A. Migani, C. Sousa, F. Illas, *Surf. Sci.* 574 (2005) 297.
- [23] A. Michaelides, P. Hu, M.H. Lee, A. Alavi, D.A. King, *Phys. Rev. Lett.* 90 (2003) 246103.
- [24] Y. Yang, J.A. Yarmoff, *J. Vac. Sci. Technol.*, A 21 (2003) 1317.
- [25] P.S. Bagus, K. Hermann, C.W. Bauschlicher Jr, *J. Chem. Phys.* 80 (1984) 4378.
- [26] P.S. Bagus, F. Illas, *J. Chem. Phys.* 96 (1992) 8962.
- [27] P.S. Bagus, F. Illas, in: P.V.R. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer (Eds.), *Encyclopedia of Computational Chemistry*, vol. 4, Wiley, Chichester, United Kingdom, 1998, p. 2870.
- [28] P.S. Bagus, C.J. Nelin, G. Pacchioni, in: R. Carbo (Ed.), *Studies in Physical and Theoretical Chemistry*, vol. 62, Elsevier, Amsterdam, 1989, p. 475.
- [29] J.L. Whitten, H. Yang, *Surf. Sci. Rep.* 24 (1996) 55.
- [30] C.J. Nelin, P.S. Bagus, M.R. Philpott, *J. Chem. Phys.* 87 (1987) 2170.
- [31] C.W. Bauschlicher Jr., P.S. Bagus, *J. Chem. Phys.* 81 (1985) 5889.
- [32] P.S. Bagus, F. Illas, *Phys. Rev. B* 42 (1990) 10852.
- [33] M.G. Samant, R. Viswanathan, H. Seki, P.S. Bagus, C.J. Nelin, et al., *J. Chem. Phys.* 89 (1988) 583.
- [34] P.S. Bagus, K. Hermann, C. Wöll, *J. Chem. Phys.* 123 (2005) 184109.
- [35] K. Hermann, P.S. Bagus, C.J. Nelin, *Phys. Rev. B* 35 (1987) 9467.
- [36] P.S. Bagus, C.W. Bauschlicher Jr., C.J. Nelin, B.C. Laskowski, M. Seel, *J. Chem. Phys.* 81 (1984) 3594.
- [37] B. Richter, H. Kuhlenbeck, H.J. Freund, P.S. Bagus, *Phys. Rev. Lett.* 93 (2004) 026805.
- [38] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [39] S. Zurita, J. Rubio, F. Illas, J.C. Barthelat, *J. Chem. Phys.* 104 (1996) 8500.
- [40] T.A. Wesolowski, H. Chermette, J. Weber, *J. Chem. Phys.* 105 (1996) 9182.
- [41] T.A. Wesolowski, *J. Chem. Phys.* 106 (1997) 8516.
- [42] T.A. Wesolowski, Y. Ellinger, J. Weber, *J. Chem. Phys.* 108 (1998) 6078.
- [43] P.S. Bagus, C.J. Nelin, W. Muller, M.R. Philpott, H. Seki, *Phys. Rev. Lett.* 58 (1987) 559.
- [44] P.S. Bagus, G. Pacchioni, *J. Phys.: Conf. Ser.* 117 (2008) 012003.
- [45] P.S. Bagus, C.J. Nelin, C.W. Bauschlicher Jr., *J. Chem. Phys.* 79 (1983) 2975.
- [46] P.S. Bagus, in: R.T.H. Chang, B. Abeles (Eds.), *Mater. Res. Soc. Symp. Proc.*, vol. 38, Materials Research Society, Pittsburgh, 1985, p. 179.
- [47] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, NY, 1994.
- [48] P.S. Bagus, A. Clotet, D. Curulla, F. Illas, J.M. Ricart, *Journal of Molecular Catalysis A Chemical* 119 (1997) 3.
- [49] P.S. Bagus, M. Garcia-Hernandez, F. Illas, *Surf. Sci.* 429 (1999) 348.
- [50] M. Garcia-Hernandez, P.S. Bagus, F. Illas, *Surf. Sci.* 409 (1998) 69.
- [51] H.F. Schaefer, *The Electronic Structure of Atoms and Molecules*, Addison-Wesley, Reading, 1972.
- [52] P.S. Bagus, V. Staemmler, C. Wöll, *Phys. Rev. Lett.* 89 (2002) 096104.
- [53] J. Topping, *Proc. R. Soc. London*, A 114 (1927) 67.
- [54] H. Ibach, D.L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, New York, 1982.
- [55] P. Senet, J.P. Toennies, G. Witte, *Chem. Phys. Lett.* 299 (1999) 389.
- [56] P.S. Bagus, F. Illas, G. Pacchioni, F. Parmigiani, *J. Electron Spectrosc. Relat. Phenom.* 100 (1999) 215.
- [57] P.S. Bagus, C.R. Brundle, G. Pacchioni, F. Parmigiani, *Surf. Sci. Rep.* 19 (1993) 265.
- [58] P.S. Bagus, A. Wieckowski, H.J. Freund, *Chem. Phys. Lett.* 420 (2006) 42.
- [59] P.S. Bagus, F. Illas, C. Sousa, G. Pacchioni, in: T.A. Kaplan, S.D. Mahanti (Eds.), *Electronic Properties of Solids Using Cluster Methods*, Plenum, New York, 1995, p. 93.
- [60] G. Pacchioni, P.S. Bagus, *Phys. Rev. B* 50 (1994) 2576.
- [61] A. Lewera, W.P. Zhou, R. Hunger, W. Jaegermann, A. Wieckowski, et al., *Chem. Phys. Lett.* 447 (2007) 39.
- [62] T. Aruga, Y. Murata, *Prog. Surf. Sci.* 31 (1989) 61.
- [63] G. Witte, S. Lukas, P.S. Bagus, C. Wöll, *Appl. Phys. Lett.* 87 (2005) 263502.
- [64] N.W. Ashcroft, N.D. Mermin, *Solid State Physics*, Holt, Rinehart, and Winston, NY, 1976.
- [65] D. Käfer, G. Witte, in press.
- [66] J. Stöhr, *NEXAFS Spectroscopy*, Springer-Verlag, Berlin, 1992.