Theoretical study of the valence-level photoemission spectrum of $C_6H_6$ adsorbed on Ni, Pd, and Pt metal surfaces

M. Ohno
Center for Atomic, Molecular and Surface Physics, School of Physical Sciences, Engineering and Technology, Murdoch University, South Street, Murdoch, Perth, WA6150, Australia

W. von Niessen
Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig, Federal Republic of Germany
(Received 16 August 1996)

The valence hole spectral functions of the Ni$C_6H_6$, Pd$C_6H_6$, and Pt$C_6H_6$ model molecules are calculated by the ab initio third-order algebraic-diagrammatic-construction [ADC(3)] Green-function method using an extended basis set. The calculation was performed assuming top-site adsorption. The theoretical predictions are compared with the experimental angle-resolved valence-level photoemission spectra of $C_6H_6$ adsorbed on Ni(110) Pd(110), Pd(111), and Pt(111) surfaces. The calculations provide an overall good agreement with experiment, and confirm the previous experimentally determined assignment of the spectra. A comparison with the results for the free $C_6H_6$ molecule shows that the many-body effects are considerably enhanced by the presence of the metal atom. There is a strong splitting of the lines and a concomitant intensity redistribution caused by the metal-ligand $\pi$-$\pi^*$ charge-transfer excitations. The ordering of the ionization levels of the adsorbate is the same as the one of the free molecule. For $C_6H_6$ on a Ni(110) surface the presence of the metal-ligand $\pi$-$\pi^*$ charge-transfer satellite of non-negligible spectral intensity accompanying the $1b_2$ ionization process is predicted about 10 eV below the Fermi level, which has not been observed so far. The influence of the bending of the H atoms out of the hexagonal ring plane on the photoemission spectrum is small.

I. INTRODUCTION

The chemisorption of aromatic molecules such as benzene and phenol on metal surfaces has become of great interest because of the growing technological importance of a microscopic understanding of the interactions and bonding mechanisms in organic film-metal interfaces. The electronic structure, orientation, and symmetry of pure benzene and benzene coadsorbed with CO, NO, O, or alkalis have been studied for many metal surfaces. For the pure and coadsorbed layers there is a consensus that benzene is $\pi$ bonded to the surface with the molecular plane oriented parallel to the substrate. Benzene adsorption on Ni(110) has been experimentally and theoretically studied by several groups.\textsuperscript{2,3,5} The adsorption geometry of benzene was obtained from theoretical calculations,\textsuperscript{2,3} near edge x-ray-adsorption fine-structure spectroscopy (NEXAFS) studies\textsuperscript{4} and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements.\textsuperscript{4,5}

The recent analysis of the ARUPS spectra of the dilute benzene layer on Ni(110) suggests an orientation of the molecular plane parallel to the surface with $C_2v$ symmetry of the adsorption complex and the molecules azimuthally oriented with their corners along the [001] direction.\textsuperscript{4,5} The analysis of the spectra of the saturated layer suggests that the molecular plane is still parallel to the surface, but the symmetry of the adsorption complex is lowered to $C_1$ symmetry due to an azimuthal rotation of the benzene molecules induced by strong lateral interactions in the densely packed saturated layer.\textsuperscript{4,5} The conclusion deduced for the geometric structure of benzene on the Ni(110) surface differs from the one obtained for the Pd(110) surface, with both systems exhibiting a C(4×2) structure at saturation coverage. The latter one is the only example where a nonplanar adsorption geometry of benzene has been proposed. First, no tilting of benzene molecules is observed for benzene on Ni(110). Second, on Ni(110) the molecules are azimuthally rotated in a way that the mirror planes of molecules do not coincide with the high-symmetry directions of the substrate, whereas for Pd(110) an azimuthal orientation of benzene molecules with its corners along [110] was proposed.\textsuperscript{14} For the reconstructed Pt(110)(1×2) surface, Surman et al.\textsuperscript{15} also proposed a parallel orientation from their high-resolution electron-energy loss spectroscopy data.

The comparison of the ultraviolet photoemission spectroscopy (UPS) spectrum for the dilute benzene layer on a Ni(110) surface to the gas phase spectrum shows that the $\pi$ levels 1$e_{1g}$ and 1$a_{2u}$ are shifted to higher binding energy by 1.4 and 1.2 eV, respectively.\textsuperscript{4,5} A comparison of the UPS spectrum of benzene on Pd(110) or Pd(111) to the gas phase spectrum shows that the 1$e_{1g}$ and 1$a_{2u}$ levels are shifted to higher binding energy by 1.7 and 1.3 eV, respectively.\textsuperscript{14,16–18} In the case of a Pt(111) surface, they are shifted by 2.1 and 1.7 eV, respectively.\textsuperscript{18} It would be beneficial to study such a spectral behavior of the adsorbate spectra theoretically, because to our knowledge there has not been any theoretical study of the UPS spectra of benzene adsorbed on a Ni, Pd, or Pt metal surface using an ab initio many-body technique.
Recently we calculated the valence-level photoemission spectra (more exactly the valence hole spectral functions) of NiC\(_2\)H\(_2\)(C\(_2\)H\(_4\)) and Pd(Pt)C\(_2\)H\(_2\)(C\(_2\)H\(_4\)) by the \textit{ab initio} third-order algebraic-diagrammatic-construction [ADC(3)] Green-function method using an extended basis set.\(^{20}\) Our calculations provide reasonably good descriptions of the valence-level photoemission spectra of C\(_2\)H\(_2\)(C\(_2\)H\(_4\)) adsorbed on Ni, Pd, and Pt metal surfaces. The use of the single-metal-atom model made it possible to treat quite accurately the many-body interactions in both ground and ionized states, and provided excellent reproductions of the valence- and core-level photoemission spectra and core-level resonant excitation spectra of adsorbates, including newly observed spectral details.\(^{21-26}\) The calculations emphasize the importance of a consistent treatment of many-body effects, such as correlations (fluctuations) and relaxations associated with the ionization (excitation) and the inadequacy of a simple mean-field approach. The success of the single-metal-atom models, together with \textit{ab initio} many-body calculations is ascribed to the accurate description of many-body effects associated with the dominant nature of the \(M\text{-metal}-L\text{(ligand)}\) interaction on a metal surface. In the case of Co or Ni adsorption on Ni (or Pd, Pt) the dominant nature of the \(M\text{-L}\) interaction, involving metal 3\(d(4d)\) and 4\(s(5s)\) orbitals, but with little contribution from 4\(p\) orbitals seems to be well described with the use of the minimal cluster model. The contribution from 4\(p\) becomes much more important when the \(d\) shell becomes nearly filled, as in Cu metal. Indeed in a preliminary study of the valence and core photoemission spectra of the CO/Cu system, it has been found that there is an indication of the inadequacy of the single-metal-atom cluster model, which is tied to the lack of occupation of the 4\(p\) level in the \(2\Sigma^+\) ground state of CuCO,\(^{27}\) a problem that may be alleviated by the use of an excited \(2\Pi\) initial state.\(^{28}\) Also, this model leads only to partially satisfactory results, indicating thus the real need for a large metal cluster to properly describe the adsorption on the Cu metal surface. From a recent investigation by Roszak and Balasubramanian,\(^{29}\) one can also derive strong arguments for the validity and usefulness of the single-metal-atom model to describe the photoemission of adsorbates on Ni, Pd, and Pt surfaces. These authors studied low-lying electronic states of the Pt\(_2\)CO complex using second-order perturbation theory and the complete-active-space multiconfiguration self-consistent-field method. The Mulliken population analysis shows that in the bridged Pt\(_2\)CO structure the \(s\) population on the Pt atom is considerably decreased compared to the dissociated fragments, whereas the \(d\) population is increased. This is consistent with the \(s\)-\(d\) promotion mechanism for the bonding picture.\(^{30,31}\) In the linear Pt\(_2\)CO structure there occurs a loss of electronic charge on the Pt atom participating in the bonding with CO, whereas there is hardly any change on the other Pt atom. This can be interpreted to reflect the fact that the role of the second Pt atom is small. In other words, a single-metal-atom model molecule is a reasonably good model for the top-site adsorption of CO on Pt. Thus for some cases there appears to be a sufficient understanding of the physical situation to justify the use of the single-metal-atom model.\(^{21-26}\)

In the present work, in order to study the valence-level photoemission spectrum of benzene adsorbed on Ni, Pd, and Pt surfaces, we shall calculate the valence-level photoemission spectra (the valence hole spectral functions) of C\(_6\)H\(_6\), NiC\(_2\)H\(_2\), PdC\(_2\)H\(_2\), and PtC\(_2\)H\(_2\) by the ADC(3) method. We assume the top site adsorption of C\(_6\)H\(_6\) on a metal surface. We compare the present theoretical predictions of the Ni(Pd,Pt)C\(_2\)H\(_4\) spectral features with the ARUPS spectra of C\(_6\)H\(_6\) adsorbed on a Ni(110), Pd(110), Pd(111), and Pt(111) surface. We show that the present single-metal-atom models can provide a reasonably good description of the UPS spectra of the adsorbates. We confirm the assignment of the spectra made by ARUPS studies, and make a comparison between the free-molecule spectrum and the adsorbate spectra from the viewpoint of the energy positions and spectral intensities.\(^{55}\)

II. NUMERICAL PROCEDURE

The Green-function formalism [the ADC(3) approach] is employed to calculate the ionization potentials (IP’s) and their spectral intensities (I) directly. In the ADC(3) method introduced by Schirmer and co-workers\(^{32-34}\) one renormalizes the three different types of basic diagrams, namely, the non-hole-hopping relaxation, hole-hopping relaxation, and ground-state correlation (fluctuation) diagrams. The first step of the renormalization procedure is the third-order self-energy diagram, describing repulsion between the holes and attraction between the electron and the holes. In the ADC(3) method one treats the 2\(h\)-1\(p\) (two hole-one particle) interaction by the sum of the 1\(h\)-1\(h\) and 1\(h\)-1\(p\) interactions within the framework of the random-phase approximation (RPA) and the diagrams appearing up to third order are summed to infinity. The appearance of 1\(p\) and 2\(p\)-1\(h\) configurations and their coupling with the 1\(h\) and 2\(h\)-1\(p\) configurations in the Dyson equation introduces the effects of ground-state correlation, and leads to the global inclusion of the effects of higher-order excitations (3\(h\)-2\(p\) configurations, etc.) on the ionic states.

The ADC(3) method is accurate to third order in the electron-electron interaction, and should thus yield reliable ionization energies provided the basis set is of sufficient quality.\(^{33,34}\) In the inner valence region, main line energies and intensities are calculated accurately to third order in the electron-electron interaction, but satellite lines only accurately to first order. This yields a semiquantitative reproduction of the spectrum if this is dominated by an extensive satellite structure. The lowest satellite lines are, however, in general reliably obtained in this approach. We refer to Refs. 32–34 for further details of the method and a detailed analysis of the many-body effects. The accuracy and reliability of the ADC(3) method has been tested not only for free molecules\(^{33,34}\) but also for several model molecules (adsorbates) and related charge-transfer systems.\(^{20,21,25,26,35,36}\)

\(XC\(_6\)H\(_6\) (X = Ni, Pd, Pt) represents the \(\pi\)-bonded geometry. The distance of the C\(_6\)H\(_6\) molecule above the metal atom was set at 3.31 a.u. for the top-site adsorption. The distance is obtained for the top site of C\(_6\)H\(_6\) on a Ni metal surface by the atomic superposition and electron delocalization molecular-orbital calculations.\(^{5}\) The geometry of C\(_6\)H\(_6\) is taken as that of the free molecule. We use basis sets of Cartesian Gaussian functions on the atoms to expand the molecular orbitals. For Ni the [14s9p5d] basis set of Wachters
for Ni (Ref. 37) is enlarged by two \( p \)-type functions with exponential parameters \( \alpha_p = 0.24 \) and 0.08 to describe the \( 4p \) orbital of Ni and the diffuse \( 3d \) function of Hay (\( \alpha_d = 0.1316 \)) and Chong et al.\(^{38} \) The two \( s \)-type functions with smallest exponential parameters are replaced by functions with \( \alpha_s = 0.32 \) and 0.08 to take into account the orbital contraction upon molecular bonding. The final basis set is [\( 14s11p6d \)] contracted to \( \{7s5p3d\} \) (contraction number 3 of Wachters). For Pt the \( \{17s14p9d\} \) basis set of Huzinaga\(^{40} \) is contracted in a general fashion to \( \{9s7p4d\} \). For Pt the \( \{20s16p11d6f\} \) basis set of Groppen\(^{41} \) is contracted in a general fashion to \( \{12s11p6d3f\} \).

The C basis set is taken from Widmark, Malmqvist, and Roos,\(^{42} \) [\( 14s9p4d \)] contracted to \( \{4s2p1d\} \). The H basis set is taken also from Ref. 42, [\( 8s4p \)] contracted to \( \{2s1p\} \).

The calculation of the self-consistent-field wave function and two-electron integral matrix elements has been performed with a standard program package MOLCAS-2 for calculation of Hartree-Fock and correlated wave functions using basis set expansion techniques.\(^{43} \) In the ADC(3) Green-function calculations for \( \text{C}_6\text{H}_6 \), Ni\( \text{C}_6\text{H}_6 \), Pd\( \text{C}_6\text{H}_6 \), and Pt\( \text{C}_6\text{H}_6 \), the lowest 84, 62, 60, and 53 virtual orbitals, respectively, and all occupied orbitals, except for the core orbitals, were taken into account. This leads to matrices of dimension of around 17,000, 26,000, 25,000, and 20,000, respectively. The basis set for benzene is nearly fully exhausted. The eigenvalues and eigenfunctions were extracted with a block Davidson method.\(^{44} \) For each symmetry, about 150 eigenvalues and eigenvectors were calculated.

We also performed ADC(3) calculations of Ni\( _2\text{C}_6\text{H}_6 \) with the short-bridge site (S1 according to the notation used by the authors of Ref. 2) and the short-bridge rotated site (S2). However, we found that because of a large number of near degeneracies of the \( 2h1p \) configurations with \( 1h \) configurations, the spectral intensities (pole strengths) are split into many lines. We consider that this is unphysical, and that the model is not appropriate for a description of the valence-level ionization.

### III. RESULTS AND DISCUSSION

In Table I we list the valence-level hole spectral functions for \( \text{C}_6\text{H}_6 \) obtained by the ADC(3) method. In Table II we list the valence-level hole spectral functions for Ni\( \text{C}_6\text{H}_6 \) obtained by the ADC(3) method with the ligand-metal distance of 3.31 a.u. and without the tilt of the C-H bond. The tilting of the C-H bond influences the spectrum little (at most a difference of 0.2 eV in the ionization energies was calculated). Therefore we present only the results obtained without the tilt of the C-H bond. In Tables III and IV we list the valence-level hole spectral functions for Pd\( \text{C}_6\text{H}_6 \) and Pt\( \text{C}_6\text{H}_6 \) calculated by the ADC(3) method. We list the Koopmans’ theorem (KT) energies, the ionization energies (IP’s), the relative spectral intensities (I), and the experimental ionization energies. The experimental ionization energies of the adsorbate listed in Table II are obtained by ARUPS for the dilute benzene layer (0.10 ML) on a Ni(110) surface.\(^{5} \) They are listed together with the ionization energies obtained for the saturated layer (0.23 ML) given inside brackets. To avoid the effects of the strong lateral interactions in the densely packed saturated layer, we compare the present theoretical predictions with the data from the dilute layer. The \( C_1 \) symmetry of the adsorption complex of benzene in the saturated layer could indicate a tilting of the benzene molecule. However, the authors of Ref. 4 concluded a parallel orientation of the benzene molecules with an uncertainty of \( \pm 5^\circ \) because they did not observe any emission from the \( 2a_{1g} \) state at normal incidence in either the saturated or dilute layers. The experimental ionization energies of the adsorbate listed in Tables III and IV are obtained by ARUPS measurements on a Pd(110) surface,\(^{14} \) on a Pd(111) surface,\(^{16-18} \) and on a Pt(111) surface.\(^{15} \)

#### A. \( \text{C}_6\text{H}_6 \)

A comprehensive investigation concerning the assignment of the outer-valence main ionic states is given in Ref. 45. Recently, Weikert and Cederbaum\(^{46} \) studied in detail the satellite lines accompanying the valence shell ionization of benzene by using the ADC(3) method and made a detailed comparison with experiment (see references to experiment cited in this paper). For an earlier investigation on the satellite line structure using the ADC(2) method, see Ref. 47. Weikert and Cederbaum used a procedure for the efficient numerical computation of the one-particle Green function. It makes use of the block-Lanczos method, which allows the effective reduction of the size of the secular matrices which are to be di-

---

**Table I. Calculated ionization energies and pole strengths \( (\geq 0.02) \) of \( \text{C}_6\text{H}_6 \) and the experimental ionization energies (all energies are in eV).**

<table>
<thead>
<tr>
<th>Level</th>
<th>KT</th>
<th>IP</th>
<th>I</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1e_{1g} )</td>
<td>19.85</td>
<td>21.34</td>
<td>0.80</td>
<td>17.0 a</td>
</tr>
<tr>
<td>( 2e_{2g} )</td>
<td>19.10</td>
<td>14.48</td>
<td>0.87</td>
<td>14.1 a</td>
</tr>
<tr>
<td>( 1a_{5u} )</td>
<td>16.82</td>
<td>20.89</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>( 2e_{1u} )</td>
<td>15.10</td>
<td>14.10</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>( 2a_{1g} )</td>
<td>17.35</td>
<td>17.60</td>
<td>0.84</td>
<td>15.5 a</td>
</tr>
<tr>
<td>( 1e_{2g} )</td>
<td>17.17</td>
<td>17.60</td>
<td>0.44</td>
<td>19.3 a</td>
</tr>
</tbody>
</table>

\( a \)Reference 48.

\( b \)Reference 49.

\( c \)Reference 50.
TABLE II. Calculated ionization energies and pole strengths (≥0.02) of NiC₆H₆ (on-top site with metal-ligand distance of 3.31 a.u. without the tilt of the H atoms) and the experimentally observed values for C₆H₆ adsorbed on a Ni(110) surface (all energies in eV). The experimental ionization energies are shifted by 6.0 eV. The levels inside the brackets are the corresponding levels of the free molecule, C, M, and H in the character column denote carbon, metal, and hydrogen, respectively. The experimental energies with a * are the mean experimental energies. The experimental energies in brackets are those from the saturated layer.

<table>
<thead>
<tr>
<th>Level</th>
<th>Character</th>
<th>KT</th>
<th>IP</th>
<th>I</th>
<th>Expt. (Ref. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2e₁</td>
<td>C-M</td>
<td>7.79</td>
<td>7.26</td>
<td>0.90</td>
<td>10.6*</td>
</tr>
<tr>
<td>3e₁</td>
<td>C-M</td>
<td>7.59</td>
<td>7.43</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>3a₁</td>
<td>M</td>
<td>8.39</td>
<td>7.94</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>2e₁(1e₁g)</td>
<td>C-M</td>
<td>10.78</td>
<td>10.09</td>
<td>0.82</td>
<td>10.6*</td>
</tr>
<tr>
<td>1e₂(2e₂g)</td>
<td>C-H</td>
<td>13.70</td>
<td>11.96</td>
<td>0.86</td>
<td>12.1*</td>
</tr>
<tr>
<td>2a₁(1a₂u)</td>
<td>C-C</td>
<td>14.29</td>
<td>11.88</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>1e₁(2e₁u)</td>
<td>C-H</td>
<td>16.38</td>
<td>14.37</td>
<td>0.56</td>
<td>14.0*</td>
</tr>
<tr>
<td>1b₁(1b₂u)</td>
<td>C-C</td>
<td>17.05</td>
<td>14.63</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>1b₂(1b₁u)</td>
<td>C-H</td>
<td>17.64</td>
<td>15.35</td>
<td>0.45</td>
<td>15.7</td>
</tr>
<tr>
<td>1a₁(2a₁g)</td>
<td>C-H</td>
<td>19.64</td>
<td>17.00</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

agonalized. They employed a contracted double-ζ plus polarization basis set and in addition a triple-ζ plus polarization basis set. The present results are in qualitatively good agreement with their results including the satellite line positions and intensities. The agreement of the results with experiment is also good. The ordering of the ionization levels is the same one as the KT energy levels. As the main aim of the present work is the theoretical study of the ionization spectrum of C₆H₆ adsorbed on a Ni metal surface, we refer to Ref. 46 for a detailed discussion of the satellite lines. We thus limit our discussion to the major spectral features.

The ordering of the ionization levels is the same as the one of the KT energy levels. Except for the 1e₂g level (and the higher-energy levels which are omitted from the table because no corresponding information is available for the chemisorbed system), the one-electron (quasiparticle) picture is valid. For the 1e₂g level, the one-electron picture begins to break down due to the strong configuration interaction between the single hole and the two-hole–one-particle configurations. But it should be mentioned that already the relatively low energy 1a₂u ionization level shows a satellite line of appreciable intensity (0.16) about 4.3 eV above the position of the main line. This feature is explained in Ref. 47. The energy difference between the KT energy and the ionization energy obtained by the ADC(3) method is the sum of the correlation energy shift and the relaxation energy shift. For the sake of simplicity we call this energy difference a final-state energy shift. Strictly speaking, the Hartree-Fock orbital energies have no physical relevance because the Hartree-Fock (mean-field) method neglects the electron correlation in the ground state. Thus the initial- and final-state energy shifts also have no physical relevance. However, these quantities can be interpreted to represent the magnitude of the energy shifts of the correlated systems. The final-state energy shifts for the 1e₁g, 2e₂g, 1a₂u, 2e₁u, 1b₁u, 2a₁u, 2e₂g, and 1e₂g levels are 0.02, 1.33, 1.33, 1.60, 1.80, 1.82, 2.0, and 2.87 eV, respectively. Except for the 1e₂g level, where the one-electron picture breaks down (in other words, the definition of the final-state energy shift becomes ambiguous) and the 1e₁g level, the final-state energy shifts are rather constant. Thus the ordering of the KT energy levels is valid for the ionization energy levels of benzene.

B. NiC₆H₆

The present results refer to an isolated molecule, and we do not take into account the photoionization cross sections of each symmetry species, so a direct comparison with the experimental photoemission spectrum cannot be made except for the ionization energies. A comparison with the experimental valence-level spectrum of the adsorbate is made simply by shifting the theoretical spectrum to the adsorbate spectrum by the following procedure. The ligand levels are not too strongly influenced by the presence of a metal surface. To obtain the matching between the free molecule ligand levels and the XC₆H₆, X=Ni,Pd,Pt ligand levels, the symmetries (D₆h) and the orbital characters (C-C or C-H bonds) of the ionization levels of free C₆H₆ were compared with those (C₆v symmetry) of the ionization levels of XC₆H₆. In this way we found the ionization level correspondences listed in Tables II, III, and IV. We optimized the energy shift between the experimental ionization energies and the present predictions by comparing these two sets of data and obtained 6.0, 6.5, 6.0, and 6.4 eV for Ni(110), Pd(110), Pd(111), and Pt(111) metal surfaces, respectively. They are close to the estimated work functions of the metal surfaces. The consistency of the present assignment of the peaks is reflected in the fact that the ionization levels which are assigned to the e₁ (or e₂) levels, are observed by ARUPS to be split5,5 (for a comparison with the theoretical predictions for these levels, the mean experimental ionization energies are listed in Table II).

The first three ionization levels (2e₂, 3e₁, and 3a₁ levels) may correspond to the structure observed about 2 eV below the Fermi level (see the spectrum in Fig. 3 of Ref. 5, and the one in Fig. 1(b) of Ref. 11). The structure is most likely due to the ionization from the metal substrate band. A description of the metal ionization levels by the present model is ex-
TABLE III. Calculated ionization energies and pole strengths ($>0.02$) of PdC$_6$H$_6$ (top-site adsorption with a metal-ligand distance of 3.31 a.u.) and the experimentally determined values for C$_6$H$_6$ adsorbed on a Pd(110) (Ref. 14) and on a Pd(111) surface (Refs. 16–18) (all energies are in eV). The experimental ionization energies are shifted by 6.5 and 6.0 eV, respectively. The levels inside the brackets are the corresponding levels of the free molecule. C, M, and H in the character column denote carbon, metal, and hydrogen, respectively.

<table>
<thead>
<tr>
<th>Level</th>
<th>Character</th>
<th>KT</th>
<th>IP</th>
<th>$I$</th>
<th>Expt. (Ref. 14)</th>
<th>Expt. (Refs. 16–18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3e_1$</td>
<td>C-M</td>
<td>7.44</td>
<td>7.04</td>
<td>0.90</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>$3e_2$</td>
<td>C-M</td>
<td>9.64</td>
<td>8.69</td>
<td>0.90</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>$3a_1$</td>
<td>C-M</td>
<td>9.79</td>
<td>8.86</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2e_1(1e_{1g})$</td>
<td>C-M</td>
<td>11.89</td>
<td>11.01</td>
<td>0.85</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>$2e_2(2e_{2g})$</td>
<td>C-H</td>
<td>13.91</td>
<td>12.36</td>
<td>0.22</td>
<td>12.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.0 - 12.8</td>
<td>12.0 - 12.5</td>
</tr>
<tr>
<td>$2a_1(1a_{2u})$</td>
<td>C-C</td>
<td>14.45</td>
<td>13.82</td>
<td>0.63</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>$1e_1(2e_{1u})$</td>
<td>C-H</td>
<td>16.75</td>
<td>14.94</td>
<td>0.36</td>
<td>14.3 - 14.7</td>
<td>14.0 - 14.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.98</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.25</td>
<td></td>
</tr>
<tr>
<td>$1b_1(1b_{2u})$</td>
<td>C-C</td>
<td>17.26</td>
<td>15.14</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.10</td>
<td></td>
</tr>
<tr>
<td>$1b_2(1b_{1u})$</td>
<td>C-H</td>
<td>17.76</td>
<td>15.72</td>
<td>0.52</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.60</td>
<td></td>
</tr>
<tr>
<td>$1a_1(2a_{1g})$</td>
<td>C-H</td>
<td>19.91</td>
<td>16.91</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.03</td>
<td></td>
</tr>
<tr>
<td>$1e_2(1e_{2g})$</td>
<td>C-H</td>
<td>22.88</td>
<td>19.23</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.97</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.98</td>
<td></td>
</tr>
</tbody>
</table>

expected to be rather poor because of the use of a single-metal atom in the present model. However, the first three ionization levels seem to agree well with the 2-eV structure. For the rest of the ionization levels which originate from the ligand levels, we obtain an overall good agreement with experiment. The present calculation confirms that the ordering of the ionization levels of the adsorbate is the same as that of the free molecule. The KT energy (initial state or chemical) shifts
TABLE IV. Calculated ionization energies and pole strengths (≥0.02) of PtC6H6 (top-site adsorption with a metal-ligand distance of 3.31 a.u.) and experimentally determined values for C6H6 adsorbed on Pt(111) (all energies in eV). The experimental ionization energies are shifted by 6.4 eV. The levels inside the brackets are the corresponding levels of the free molecule. C, M, and H in the character column denote carbon, metal, and hydrogen, respectively.

<table>
<thead>
<tr>
<th>Level</th>
<th>Character</th>
<th>KT</th>
<th>IP</th>
<th>I</th>
<th>Expt. (Ref. 19)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3e1</td>
<td>C-M</td>
<td>7.25</td>
<td>6.95</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>3e2</td>
<td>C-M</td>
<td>10.14</td>
<td>9.29</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>3a1</td>
<td>C-M</td>
<td>10.18</td>
<td>9.33</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>2e1(1e1g)</td>
<td>C-M</td>
<td>12.34</td>
<td>11.41</td>
<td>0.85</td>
<td>11.4</td>
</tr>
<tr>
<td>2e2(2e2g)</td>
<td>C-H</td>
<td>14.04</td>
<td>12.50</td>
<td>0.89</td>
<td>12.0</td>
</tr>
<tr>
<td>2a1(1a2u)</td>
<td>C-C</td>
<td>14.59</td>
<td>11.89</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>1e1(2e1u)</td>
<td>C-H</td>
<td>16.98</td>
<td>14.98</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>1b1(1b2u)</td>
<td>C-C</td>
<td>17.38</td>
<td>14.74</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>1b2(1b1u)</td>
<td>C-H</td>
<td>17.83</td>
<td>15.76</td>
<td>0.46</td>
<td>16.0</td>
</tr>
<tr>
<td>1a1(2a1g)</td>
<td>C-H</td>
<td>20.08</td>
<td>17.13</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>1e2(1e2g)</td>
<td>C-H</td>
<td>23.02</td>
<td>19.40</td>
<td>0.04</td>
<td></td>
</tr>
</tbody>
</table>

from the free molecule to NiC6H6 for the 1e1g, 2e2g, 1a2u, 2e1u, 1b2u, 1b1u, and 2a1g levels, are −1.59, −0.15, −0.62, −0.30, −0.15, −0.04, and −0.29 eV, respectively. Except for the first ligand ionization level, the KT energy shifts are rather small. Thus the KT energy ordering of NiC6H6 is the same as the one of the free molecule. The final-state energy shifts for the 1e1g, 2e2g, 1a2u, 2e1u, 1b2u, 1b1u, and 2a1g levels of the free molecule are 0.02, 1.33, 1.33, 1.60, 1.80, 1.82, and 2.0 eV, respectively, while those for the same levels of NiC6H6 are 0.69, 1.74, 1.07, 2.01, 2.12, 2.29, and 2.60 eV, respectively. The changes of the final-state energy shifts for these levels are 0.67, 0.41, −0.26, 0.41, 0.32, 0.47, and 0.6 eV respectively. These shifts are rather small. The effect of the metal-ligand charge-transfer screening channels on the relaxation energy shifts is thus rather small. The sum of the initial-state energy shifts and the changes in the final-state energy shifts for these levels are −0.92, 0.26, −0.88, 0.11, 0.17, 0.43, and 0.31 eV, respectively. Except for the 1a2u and 1e1g levels, the initial-state energy shift and the change of the final-state energy shift tend to cancel out. In other words, for most of the ionization levels, the energy-level separations do not change significantly from the free molecule to the adsorbate. This explains why the comparison of the data for the dilute benzene layer on Ni(110) to the gas phase data shows that the 1a2u and 1e1g levels are differently shifted to higher binding energies by 1.2 and 1.4 eV, respectively (when the 2a1g ionization levels are aligned). The present predictions are 1.2 in both cases, in excellent agreement with the experimentally determined shifts. These changes of the energy-level separations are due to both the initial-state energy shifts and the changes in the final-state energy shifts. From the spectrum of benzene adsorbed on a Ni(111) surface, it is concluded that the relative σ-orbital ionization energies and intensities of gaseous and chemisorbed benzene are essentially identical, except for the shift of 1.2 eV upon adsorption of the benzene 1e1g(σ) level. The claim that only the 1e1g level of the adsorbate on a Ni(111) surface is shifted substantially from the free molecule originates from an incorrect assignment of the 1a2u level [which is indeed shifted by as much as 1 eV in the case of chemisorption on a Ni(111) surface].

It is informative to make a comparison between the free molecule spectrum and the NiC6H6 spectrum both obtained by the ADC(3) method. In contrast to the case of the free molecule, where the one-electron picture of ionization is valid up to 1e2g ionization, the one-electron (quasiparticle) picture for NiC6H6 begins to break down for the 1b1u and 2a1g levels. Except for the first three ligand levels, one finds a splitting of the ionization levels into a few, in general, closely spaced lines. The many-body effects are thus strongly enhanced by the presence of the metal atom. These effects are dominantly due to the metal-ligand charge-transfer excitations and the intrametal excitations. The 2h1p configurations which mainly contribute to the wave function of the satellite lines of appreciable intensity are i−13e1−13e2 (i = 1e1, 1e2, and 2e1). We note that configurations which involve charge-transfer excitations such as 3e1 (metal-ligand bonding character) to 3e2 (ligand character) are the dominating ones. Moreover, the configurations...
are of the type of the hole-hopping relaxation process. In the free molecule it is also the π–π* excitation processes which dominate the character of the satellite lines. But there is a major difference. For NiC₆H₆ the π–π* excitations are of metal-ligand charge-transfer type.

C. PdC₆H₆

The first three ionization levels (3e₁, 3e₂, and 3a₁), which are of metal-ligand bonding character, may correspond to the structure observed about 2 eV below the Fermi level.¹⁴,¹⁶–¹⁸ The structure is most likely due to the ionization from the metal substrate band. For the rest of the ionization levels, which originate from the ligand levels, we obtain an overall good agreement with experiment. The present calculation confirms that the ordering of the ionization levels of the adsorbate is the same as that of the free molecule.¹⁴

The present assignment of the spectrum agrees well with the previous assignment made by ARUPS studies.¹⁴,¹⁶–¹⁸ Referring to Fig. 1 of Ref. 14 [C₆H₆ on Pd(110)], band A corresponds to the 1e₁g level, band B to the 2e₂g level, the broad-band C to the 1a₂u, 2e₁u, 1b₂g, and 1b₇u levels, band D to the 2a₁g level, and band E to the 1e₂g level.

The KT energy (initial state or chemical) shifts from the free molecule to PdC₆H₆ for the 1e₁g, 2e₂g, 1a₂u, 2e₁u, 1b₂g, 1b₇u, 2a₁g, and 1e₂g levels are −2.70, −0.36, −0.78, −0.67, −0.36, −0.16, −0.56, and −0.41 eV, respectively. Except for the first ligand ionization level, the KT energy shifts are relatively small. Thus the KT energy ordering of PdC₆H₆ is the same as the one of the free molecule. In comparison to the case of NiC₆H₆, the initial-state energy shifts are larger, particularly for the first ligand ionization level (1e₁g). The final-state energy shifts for the 1e₁g, 2e₂g, 1a₂u, 2e₁u, 1b₂g, 1b₇u, 2a₁g, and 1e₂g levels of the free molecule are 0.02, 1.33, 1.33, 1.60, 1.80, 1.82, 2.0, and 2.87 eV, respectively, whereas those for the same levels of PdC₆H₆ are 0.88, 1.50, 0.63, 1.77, 2.06, 2.04, 2.44, and 2.71 eV. The changes in the final-state energy shifts for these levels are 0.86, 0.17, −0.70, 0.17, 0.26, 0.22, 0.44, and −0.16 eV. Except for the first and third ligand levels, the changes are small. In comparison to the case of NiC₆H₆, the changes in the final-state energy shifts are smaller except for the first and third ligand levels. The sums of the initial-state energy shifts and the changes in the final-state energy shifts for these levels are −1.84, −0.19, −1.48, −0.50, −0.10, 0.06, −0.12, and −0.57 eV, respectively. In other words, except for the first and third ligand ionization levels, the energy-level separations do not change from the free molecule to the adsorbate. In comparison to NiC₆H₆, the sums of the initial-state energy shifts and the changes in the final-state energy shifts are much larger for the first and third ligand levels. The energy-level separation changes are due to both the initial-state energy shifts and the changes in the final-state energy shifts.

A comparison of the spectrum for benzene on Pd(110) [Pd(111)] to the gas phase spectrum shows that the 1e₁g and 1a₂u levels are differently shifted to higher binding energy by 1.4 (1.4) and 1.0 (1.8) eV, respectively, when the 2a₁g levels are aligned.¹⁴,¹⁶–¹⁸ The present predictions are 1.7 and 1.4 eV. The predictions thus agree well with the experimental findings, showing that the model is realistic.

It is informative to make a comparison between the free molecule spectrum and the PdC₆H₆ spectrum both obtained by the ADC(3) method. In contrast to the case of the free molecule, the main line spectral intensity in the adsorbate spectrum tends to be split into two lines of comparable spectral intensity. For the 1a₁g (2a₁g) and 1e₂g (1e₂g) levels, the one-electron picture breaks down. Thus the general spectral behavior is similar to the case of NiC₆H₆. As in the case for NiC₆H₆ the shake-up (down) satellite lines are dominated in their wave functions by the metal-ligand charge-transfer π→π* configurations. In the case of the free molecule the most dominant many-body processes are π→π* intraligand excitations. The metal-ligand π→π* charge-transfer excitations appear at lower energies; i.e., they dominate the spectrum and tend to suppress the intraligand π→π* excitations.

D. PtC₆H₆

The first three ionization levels (3e₁, 3e₂, and 3a₁ levels) may correspond to the ionization from the metal substrate band which is expected to be observed about 1–3 eV below the Fermi level. For the ligand ionization levels we obtain an overall good agreement with experiment. It appears that the peak which is expected to correspond to the 1b₁u level is obscured in the spectrum.¹⁹ The present calculation confirms that the ordering of the ionization levels of the adsorbate is the same as the one of the free molecule. The present assignment agrees with the experimental one.¹⁹ The KT energy ordering of PtC₆H₆ is the same as the one of the free molecule.

The initial-state energy shifts from the free molecule to PtC₆H₆ for the 1e₁g, 2e₂g, 1a₂u, 2e₁u, 1b₂g, 1b₇u, 2a₁g, and 1e₂g levels are −3.15, −0.49, −0.92, −0.90, −0.48, −0.23, −0.73, and −0.55 eV, respectively. The final-state energy shifts for these levels of PtC₆H₆ are 0.93, 1.54, 0.71, 1.82, 2.04, 2.07, 1.78, and 2.41 eV, respectively, compared to the corresponding values for the free C₆H₆ molecule of 0.02, 1.33, 1.33, 1.60, 1.80, 1.82, 2.0, and 2.87 eV. The changes in the final-state energy shifts for these levels are 0.91, 0.21, −0.62, 0.22, 0.24, 0.25, −0.22, and −0.46 eV, respectively. Except for the first and third ligand ionization levels the changes in the final-state energy shifts are rather small. The magnitude of the initial-state energy shifts and the final state energy shifts are similar for both PdC₆H₆ and PtC₆H₆. The sum of the initial-state energy shift and the change in the final-state energy shift for these levels of PtC₆H₆ are −2.24, −0.28, −1.54, −0.68, −0.24, 0.02, −0.95, and −1.01 eV, respectively. Except for the 1e₁g, 1a₂u, 2a₁g, and 1e₂g levels, the energy level separations do not change strongly from the free molecule to the adsorbate. Note that in the case of the 2a₁g and 1e₂g levels, as the one-electron picture of ionization breaks down, the definition of the final-state energy shift becomes ambiguous. Thus it becomes rather meaningless to talk about the changes in separation energies for these levels. The energy-level separation changes are similar between PdC₆H₆ and PtC₆H₆. As in the case of NiC₆H₆ and PdC₆H₆, the energy-level separation changes from the free molecule to the adsorbate are due to both the initial-state energy shifts and the changes in the final-state energy shifts.

A comparison of the spectrum of C₆H₆ on Pt(111) to the gas phase spectrum shows that again the 1e₁g and 1a₂u levels are differently shifted to higher binding energy by 1.7 and 1.3 eV, respectively, when the 2a₁g levels are aligned.¹⁹
present predictions from our model are 2.0 and 1.3 eV, respectively, which agree well with experiment. The larger energy shift for the $1e_g$ level, in comparison to the case of the Ni and Pd metal surfaces, is due to the larger initial-state energy shifts. As found in the case of NiC$_6$H$_6$ and PdC$_6$H$_6$, the satellite lines arise from the metal-ligand charge-transfer excitations. The metal-ligand charge-transfer $\pi \rightarrow \pi^*$ shake-up–shake-down processes dominate the satellite lines, in contrast to the case of the free molecule, where the $\pi \rightarrow \pi^*$ configurations, which dominate the satellite line structure, are of intraligand type. There is no significant difference in the spectral behavior among NiC$_6$H$_6$, PdC$_6$H$_6$, and PtC$_6$H$_6$.

As is generally the case, the valence-level ionization spectra of molecules adsorbed on transition-metal surfaces are dominated by the charge-transfer screening process rather than the intraligand excitations. It has been discussed in detail for the case of CO on a Ni metal surface$^{21}$ that the 1$h$-2$h1p$ energy separations for the intraligand excitations do not change significantly from the free molecule to the adsorbate because the free molecule to adsorbate KT energy shifts are small. The magnitude of the 1$h$-2$h1p$ coupling matrix elements, on the other hand, becomes smaller. This results in a suppression of the intraligand shake-up excitations in the higher-energy regions (about 5 eV above the main line).

For the CO adsorption systems and the related charge-transfer systems, recent extensive many-body calculations have shown that the main line spectral intensity of the free molecule spectrum is redistributed over a few lines of the adsorbate spectrum in the energy range where the metal-ligand charge-transfer excitations (and the intrametal excitations) are dominant.$^{20–26,35,36}$ In the NiC$_6$H$_6$ spectrum the main line spectral intensities of the inner valence levels of the free molecule tend to be split by the metal-ligand charge-transfer excitations into two relatively closely lying levels. The sum rule holds also in the present case. In our model the metal levels are treated as discrete levels, and band effects such as the broadening of the spectrum are neglected. The introduction of the adsorbate band broadening may significantly influence the imaginary part of the self-energy and thus the line profile function, which is not calculated in the present work. The substrate band broadening will smooth out mainly the singularities of the real part of the self-energy, which result from the metal-ligand charge-transfer excitations, and will not significantly modify the energetics of the hole excitations (in the case the poles of the excitations are well separated), the main line to satellite line energy separations and their intensities. However, when the split levels are located closely together, they may converge to a single peak with the spectral intensity equal to the sum of the spectral intensities of the split lines. As a result the main line spectral intensities of the ligand ionization levels of the adsorbate become approximately equal to those of the free molecule. In the discrete molecular orbital level picture employed in the present work, for NiC$_6$H$_6$ the main line spectral intensity tends to be distributed over a few closely spaced spectral lines, except for the first three ligand levels. However, when we take into account the band broadening effect, we expect broad peaks of large spectral intensities (about 0.8) for the ionization peaks, as in fact observed experimentally. For the 2$a_{1g}$ level of PdC$_6$H$_6$, from the two lines of comparable spectral intensity separated by less than 1 eV, we may obtain a single peak because of the line profile broadening due to the substrate band. For the 1$e_{2g}$ level of PdC$_6$H$_6$ we may obtain a single broad line profile of substantial spectral intensity (about 0.6). In the case of the other levels the one-electron picture applies, or the splitting of the lines is less severe than in the cases discussed above. For the 2$e_{1u}$, 1$b_{1u}$, 2$d_{1u}$, and 1$e_{2g}$ levels of PtC$_6$H$_6$, for which formally the one-electron picture of ionization breaks down, we may obtain prominent broadbands as observed experimentally. As a result the main line spectral intensities of the ligand ionization levels of the adsorbate become approximately equal to those of the free molecule. Concerning the 1$b_2$ satellite line structure predicted about 10 eV below the Fermi level by the present calculations for the case of a Ni metal surface, the experimental observation$^{45}$ does not reveal the existence of such a satellite line structure of a significant spectral intensity. The presence of the satellite line may be obscured by the width of the band which is estimated to be about 2-eV full width at half maximum. We note that the first effect of the relaxation (screening) in the ionic excited 2$h1p$ states [particularly, in the present case, the screening of the intraligand or metal-ligand Coulomb hole-hole (particle) interaction by the metal-ligand charge-transfer mechanism and the relaxation of the ligand holes by the same mechanism], which is totally neglected in the ADC(3) scheme, enter in the fourth order, i.e., they would only be taken into account in the ADC(4) method. The spectral features, such as the satellite line energies and intensities, are governed by the 1$h$-2$h1p$ energy separations and coupling strengths. The screening effects in the 2$h1p$ ionic state may shift the 2$h1p$ energy. As a result the satellite line positions are expected to move closer to the main line positions.$^{21}$

The present minimal cluster with a single-metal atom which models the top adsorption provides a reasonably good description of the valence photoemission spectrum of benzene adsorbed on a Ni(Pd,Pt) surface, although the adsorption geometry is considered to be quite complicated. It has also emerged from investigations similar to the present ones, and from other types of calculations discussed in Sec. I that also in the case of the top site adsorption of CO on a Ni(Pd,Pt) metal surface, the single-metal atom model provides a reasonably good model for both ground and ionic states. In spite of the much more complicated adsorption geometries of hydrocarbon molecules (such as C$_2$H$_2$, C$_2$H$_4$, and C$_6$H$_6$) on a Ni(Pd, Pt) metal surface, the success of the single-metal atom cluster models for the ionized hydrocarbon adsorbates demonstrated by the ADC(3) calculations,$^{20}$ is due to the localized polarisation of the metal surface in response to the ionized adsorbate.

Recently Weinelt et al.$^{51}$ studied experimentally and theoretically the ground-state electronic structure of ethylene on a Ni(110) surface. They calculated the electronic structure, with a local density functional method of the model clusters Ni$_5$(C$_2$H$_4$)$_2$ and Ni$_5$(C$_2$H$_4$)$_3$ for the di-$\sigma$ and -$\pi$ geometries, respectively. Very similar spectral structures were found for both chemisorption geometries, di-$\sigma$ and -$\pi$. In order to make an approximate comparison (by which it is possible to save the computational effort such as the self-consistent-field calculation for each ionic state) they compared the ground-state level energies for both geometries to their ARUPS data. Naturally this procedure is only valid when the final-state
energy shifts are rather uniform. Weinelt et al. claimed that 
this requirement is fulfilled satisfactorily because of the simi-
larly in the spatial characteristics of the orbitals. Then they 
concluded that it is not possible to determine the adsorption 
geometry by such a comparison. As the character of the or-
bital which are involved in the metal-ligand bonding is of-
ten quite different from the one in the free molecule, one can 
expect a substantial change in the relaxation energy shift. 
This is indeed the case, as shown in the present study. Thus, 
from this viewpoint, their conclusion indicates only that the 
initial-state energy shifts are rather independent of the geo-
metry of the adsorbate. Weinelt et al. commented critically on 
Demuth’s approach by which the geometrical and electronic 
structure of hydrocarbon molecules adsorbed on metal sur-
faces were determined by comparing the UPS binding ener-
gies of the various valence levels to theoretical ground-state 
energies of distorted structures of the free molecule.11–13 Most of the UPS studies were performed us-
ing saturated layers, neglecting the fact that molecular levels 
in densely packed layers can show significant dispersion. Re-
cently we examined also Demuth’s theoretical approach (free 
molecule approximation) and showed that the approach fails 
to describe the UPS spectra of the hydrocarbon adsorbates,20 
because of the neglect of the metal-ligand charge-transfer 
screening. Moreover, we show that the geometrical distortion 
of the molecule upon chemisorption does not influence sig-
ificantly the valence-level photoemission spectrum of the 
adsorbate. In other words the initial-state energy shifts due to 
the distortion of the molecule do not explain the changes in 
the ionization energy separations which are observed in go-
ing from the free molecule to the adsorbate. It appears that it 
is not possible to determine the geometry of the adsorption 
complex simply by using the UPS data. The angle-resolved 
UPS study is absolutely needed for this purpose.

IV. CONCLUSIONS

The valence hole spectral functions of the 
NiC_{6}H_{6}, PdC_{6}H_{6}, and PtC_{6}H_{6} model molecules are calcu-
lated by the ab initio third-order algebraic-diagrammatic-
construction [ADC(3)] Green-function method using an 
extended basis set. The top-site adsorption of C_{6}H_{6} on 
the metal surface was assumed. The theoretical spectra are com-
pared with the experimental valence-level photoemission 
spectra of C_{6}H_{6} adsorbed on Ni(110), Pd(110), Pd(111), and 
Pt(111) surfaces. The calculation provides an overall good 
agreement with experiment. The present calculation confirms 
that the ordering of the ionization levels of the adsorbate is 
the same as the one of the free molecule and also the same as 
the KT level ordering. The calculations also confirm the pre-
vious experimentally derived assignment of the spectra. The 
shifts of the 1e_{1g} and 1a_{2g} ionization levels from the free 
molecule to the adsorbate is due to both initial- and final-
state energy shifts, which almost cancel out for the rest of 
the ionization levels. The calculated shifts agree well with the 
experimentally determined values. This gives credence to the 
model with a single-metal atom for describing the adsorbate 
spectra of hydrocarbons adsorbed on transition-metal sur-
faces such as Ni, Pd, and Pt. It is also shown that in the 
adsorbate spectrum the main line spectral intensity of the 
valence levels of the free molecule will be redistributed over 
a few closely spaced lines. The metal-ligand π→π* charge-
transfer excitations are responsible for these many-body ef-
effects. Thus the presence of the metal atom strongly enhances 
the many-body effects. For the free molecule the one-
electron picture of ionization is valid up to the 1e_{2g} level, 
but in the adsorbate model cluster it begins to break down for 
the 1b_{1u}, 2a_{1g}, and 1e_{2g} levels. This splitting of the va-
ence levels is experimentally not observed for C_{6}H_{6} on 
a metal surface because of the band effect. If we take into 
account the band effect of the metal substrate, a single main 
line whose spectral intensity becomes approximately equal 
to the one of the free molecule will be observed in the adso-
bate spectrum. This explains the similarity in the spectral 
intensity distribution between the free molecule and the adso-
bate spectrum. For C_{6}H_{6} adsorbed on a Ni metal surface 
the present theory predicts the presence of the metal-ligand 
charge-transfer (π→σ) shake-up satellite of non-negligible 
intensity around 10 eV below the Fermi level. However, ex-
periments have not revealed the presence of such a satellite 
line. There is the possibility that the satellite line is obscured 
by the broadening of the main line by the substrate metal 
band, or it may be that this satellite is calculated at too high 
energies in the ADC(3) method. The bending of the H atoms 
out of the hexagonal ring plane hardly influences the spec-
trum. The present study shows that the single-metal-atom 
model can provide a reasonably good description of the UPS 
spectra of C_{6}H_{6} adsorbed on Ni, Pd, and Pt metal surfaces 
because of the local character of the metal-ligand charge-
transfer screening at the adsorption site.

ACKNOWLEDGMENTS

This work was supported by the Australian National Re-
search Council and in part by the Fonds der Chemischen 
Industrie.

1W. Huber, H.-P. Steinrück, T. Pach, and D. Menzel, Surf. Sci. 217, 103 (1989), and references therein
15 J. E. Demuth, Surf. Sci. 84, 315 (1979), and references therein.