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

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(Received 16 August 1996)

The valence hole spectral functions of the NiC_6H_6, PdC_6H_6, and PtC_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 π-π^* 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 π-π^* 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. [S0163-1829(97)09707-5]

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.[1] For the pure and coadsorbed layers there is a consensus that benzene is π 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.[2–13] The adsorption geometry of benzene was obtained from theoretical calculations,[2,3] near edge x-ray-adsorption fine-structure spectroscopy (NEXAFS) studies[4] and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements.[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.[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.[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 [1$\bar{1}$0] was proposed.[14] For the reconstructed Pt(110)(1×2) surface, Surman *et al.*[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 π levels $1e_{1g}$ and $1a_{2u}$ are shifted to higher binding energy by 1.4 and 1.2 eV, respectively.[4,5] A comparison of the UPS spectrum of benzene on Pd(110) or Pd(111) to the gas phase spectrum shows that the $1e_{1g}$ and $1a_{2u}$ levels are shifted to higher binding energy by 1.7 and 1.3 eV, respectively.[14,16–18] In the case of a Pt(111) surface, they are shifted by 2.1 and 1.7 eV, respectively.[19] 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 $NiC_2H_2(C_2H_4)$ and $Pd(Pt)C_2H_2(C_2H_4)$ by the *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_2H_2 (C_2H_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 *ab initio* many-body calculations is ascribed to the accurate description of many-body effects associated with the dominant nature of the M(metal)-L(ligand) interaction on a metal surface. In the case of CO or N_2 adsorption on Ni (or Pd, Pt) the dominant nature of the M-L interaction, involving metal $3d(4d)$ and $4s(5s)$ orbitals, but with little contribution from $4(5)p\pi$ seems to be well described with the use of the minimal cluster model. The contribution from $4p\pi$ 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 $4p\pi$ 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_2CO 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_2CO 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_2CO 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 photoemis-

sion spectra (the valence hole spectral functions) of C_6H_6, NiC_6H_6, PdC_6H_6, and PtC_6H_6 by the ADC(3) method. We assume the top site adsorption of C_6H_6 on a metal surface. We compare the present theoretical predictions of the $Ni(Pd,Pt)C_6H_6$ spectral features with the ARUPS spectra of C_6H_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.

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 $2h$-$1p$ (two hole-one particle) interaction by the sum of the $1h$-$1h$ and $1h$-$1p$ 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 $1p$ and $2p$-$1h$ configurations and their coupling with the $1h$ and $2h$-$1p$ 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 ($3h$-$2p$ 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 sattelite 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_6H_6 ($X=$Ni, Pd, Pt) represents the π-bonded geometry. The distance of the C_6H_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_6H_6 on a Ni metal surface by the atomic superposition and electron delocalization molecular-orbital calculations.[2] The geometry of C_6H_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[38] ($\alpha_d = 0.1316$) and Chong et al.[39] 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 Pd the $[17s14p9d]$ basis set of Huzinaga[40] is contracted in a general fashion to $(9s7p4d)$. For Pt the $[20s16p11d6f]$ basis set of Gropen[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 C_6H_6, NiC_6H_6, PdC_6H_6, and PtC_6H_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 $Ni_2C_6H_6$, 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 C_6H_6 obtained by the ADC(3) method. In Table II we list the valence-level hole spectral functions for NiC_6H_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 PdC_6H_6 and PtC_6H_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.[4] 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 predic-

TABLE I. Calculated ionization energies and pole strengths (≥ 0.02) of C_6H_6 and the experimental ionization energies (all energies are in eV).

Level	KT	IP	I	Expt.
$1e_{1g}$	9.19	9.17	0.88	9.3 [a]
		19.10	0.02	
$2e_{2g}$	13.55	12.22	0.90	11.7 [a]
$1a_{2u}$	13.67	12.34	0.74	12.2, [a] 12.44 [b]
		16.68	0.16	16.2 [c]
$2e_{1u}$	16.08	14.48	0.87	14.1 [a]
		20.89	0.02	
$1b_{2u}$	16.90	15.10	0.86	14.7 [a]
		20.78	0.02	
$1b_{1u}$	17.60	15.78	0.84	15.5 [a]
		21.10	0.04	
$2a_{1g}$	19.35	17.35	0.80	17.0 [a]
		19.99	0.02	
		21.85	0.03	
		25.81	0.02	
$1e_{2g}$	22.47	19.04	0.06	
		19.17	0.10	
		19.60	0.44	19.3 [a]
		20.58	0.02	
		20.67	0.03	
		21.00	0.04	
		21.25	0.07	
		21.85	0.04	
		25.73	0.02	

[a]Reference 48.
[b]Reference 49.
[c]Reference 50.

tions 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 $\pm 5°$ 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.[19]

A. C_6H_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 II. Calculated ionization energies and pole strengths (≥ 0.02) of NiC_6H_6 (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 C_6H_6 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.

Level	Character	KT	IP	I	Expt. (Ref. 4)
$2e_2$	C-M	7.79	7.26	0.90	
$3e_1$	C-M	7.59	7.43	0.91	
$3a_1$	M	8.39	7.94	0.92	
$2e_1(1e_{1g})$	C-M	10.78	10.09	0.82	10.6*
			11.26	0.04	(10.5*)
$1e_2(2e_{2g})$	C-H	13.70	11.96	0.86	12.1*
			12.08	0.03	(11.8*)
$2a_1(1a_{2u})$	C-C	14.29	11.88	0.17	
			13.22	0.64	13.3
			18.61	0.04	(13.3)
$1e_1(2e_{1u})$	C-H	16.38	14.37	0.56	(14.0*)
			14.42	0.26	(13.7*)
			15.36	0.02	
$1b_1(1b_{2u})$	C-C	17.05	14.63	0.29	
			14.93	0.51	14.7
			15.60	0.05	(14.7)
			16.08	0.02	
$1b_2(1b_{1u})$	C-H	17.64	15.35	0.45	15.7
			15.36	0.02	(15.8)
			15.66	0.15	
			15.78	0.08	
			16.22	0.13	
$1a_1(2a_{1g})$	C-H	19.64	17.00	0.03	
			17.04	0.32	16.9
			17.74	0.31	(17.3)
			17.91	0.04	
			18.07	0.03	
			18.27	0.06	
			18.51	0.02	

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 quantitatively 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 C_6H_6 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 $1e_{2g}$ 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 $1e_{2g}$ 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 $1a_{2u}$ 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 $1e_{1g}$, $2e_{2g}$, $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, $1b_{1u}$, $2a_{1g}$, and $1e_{2g}$ levels are 0.02, 1.33, 1.33, 1.60, 1.80, 1.82, 2.0, and 2.87 eV, respectively. Except for the $1e_{2g}$ level, where the one-electron picture breaks down (in other words, the definition of the final-state energy shift becomes ambiguous) and the $1e_{1g}$ 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. NiC_6H_6

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 XC_6H_6, X=Ni,Pd,Pt ligand levels, the symmetries (D_{6h}) and the orbital characters (C-C or C-H bonds) of the ionization levels of free C_6H_6 were compared with those (C_{6v} symmetry) of the ionization levels of XC_6H_6. 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 e_1 (or e_2) levels, are observed by ARUPS to be split[4,5] (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 ($2e_2$, $3e_1$, and $3a_1$ 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_6H_6 (top-site adsorption with a metal-ligand distance of 3.31 a.u.) and the experimentally determined values for C_6H_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.

Level	Character	KT	IP	I	Expt. (Ref. 14)	Expt. (Refs. 16–18)
$3e_1$	C-M	7.44	7.04	0.90		7.0
$3e_2$	C-M	9.64	8.69	0.90	8.5	9.0
$3a_1$	C-M	9.79	8.86	0.91		
$2e_1(1e_{1g})$	C-M	11.89	11.01	0.85	11.0	11.0
$2e_2(2e_{2g})$	C-H	13.91	12.36	0.22		
			12.41	0.67	12.0 - 12.8	12.0 - 12.5
$2a_1(1a_{2u})$	C-C	14.45	12.10	0.21		
			13.82	0.63	13.5	14.0 - 14.6
$1e_1(2e_{1u})$	C-H	16.75	14.77	0.05		
			14.94	0.36	14.3 - 14.7	14.0 - 14.6
			14.98	0.38		
			16.97	0.02		
			17.25	0.02		
$1b_1(1b_{2u})$	C-C	17.26	15.14	0.03		
			15.20	0.71	15.3	15.5 - 16.0
			15.38	0.05		
			16.58	0.04		
			17.10	0.03		
$1b_2(1b_{1u})$	C-H	17.76	15.72	0.52	16.0	15.5 - 16.0
			16.00	0.19		
			16.65	0.06		
			16.99	0.04		
			17.60	0.05		
$1a_1(2a_{1g})$	C-H	19.91	16.91	0.03		
			17.47	0.35	17.3	17.3
			17.74	0.03		
			18.15	0.03		
			18.38	0.21		
			18.53	0.02		
			18.56	0.03		
			19.28	0.03		
			19.32	0.02		
			19.50	0.02		
			20.03	0.02		
$1e_2(1e_{2g})$	C-H	22.88	19.23	0.02		
			20.00	0.04		
			20.17	0.16	19.5	19.4
			20.22	0.03		
			20.39	0.09		
			20.46	0.07		
			20.52	0.10		
			20.66	0.02		
			20.89	0.03		
			20.97	0.04		
			20.98	0.02		

pected 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 lev-els, 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.[4,5] The KT energy (inital state or chemical) shifts

TABLE IV. Calculated ionization energies and pole strengths (≥ 0.02) of PtC$_6$H$_6$ (top-site adsorption with a metal-ligand distance of 3.31 a.u.) and experimentally determined values for C$_6$H$_6$ 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.

Level	Character	KT	IP	I	Expt. (Ref. 19)
$3e_1$	C-M	7.25	6.95	0.91	
$3e_2$	C-M	10.14	9.29	0.09	
$3a_1$	C-M	10.18	9.33	0.92	
$2e_1(1e_{1g})$	C-M	12.34	11.41	0.85	11.4
$2e_2(2e_{2g})$	C-H	14.04	12.50	0.89	12.0
$2a_1(1a_{2u})$	C-C	14.59	11.89	0.14	
			13.88	0.70	13.9
$1e_1(2e_{1u})$	C-H	16.98	14.98	0.22	
			15.09	0.05	
			15.16	0.40	14.4
			15.25	0.07	
			16.12	0.02	
			17.10	0.03	
			17.51	0.02	
$1b_1(1b_{2u})$	C-C	17.38	14.74	0.03	
			15.25	0.06	
			15.34	0.66	15.2
			15.67	0.03	
			16.73	0.02	
			17.14	0.05	
$1b_2(1b_{1u})$	C-H	17.83	15.76	0.46	16.0
			15.87	0.15	
			16.24	0.09	
			16.72	0.06	
			17.12	0.06	
			17.85	0.04	
$1a_1(2a_{1g})$	C-H	20.08	17.13	0.06	
			17.46	0.12	
			17.59	0.15	17.4
			18.30	0.28	
			18.50	0.02	
			18.77	0.07	
			19.53	0.02	
			19.72	0.03	
			20.12	0.02	
$1e_2(1e_{2g})$	C-H	23.02	19.40	0.04	
			20.04	0.02	
			20.31	0.05	
			20.37	0.05	
			20.47	0.02	
			20.51	0.02	
			20.61	0.27	19.7
			20.87	0.02	
			20.94	0.04	
			21.12	0.04	
			21.13	0.02	
			21.19	0.03	
			21.60	0.02	

from the free molecule to NiC$_6$H$_6$ for the $1e_{1g}$, $2e_{2g}$, $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, $1b_{1u}$ and $2a_{1g}$ 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 NiC$_6$H$_6$ is the same as the one of the free molecule. The final-state energy shifts for the $1e_{1g}$, $2e_{2g}$, $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, $1b_{1u}$, and $2a_{1g}$ 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 NiC$_6$H$_6$ 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 $1a_{2u}$ and $1e_{1g}$ 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 $1a_{2u}$ and $1e_{1g}$ levels are differently shifted to higher binding energies by 1.2 and 1.4 eV, respectively (when the $2a_{1g}$ ionization levels are aligned).[4,5] 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 $1e_{1g}(\pi)$ level.[11,12] The claim that only the $1e_{1g}$ level of the adsorbate on a Ni(111) surface is shifted substantially from the free molecule originates from an incorrect assignment of the $1a_{2u}$ 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 NiC$_6$H$_6$ 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 $1e_{2g}$ ionization, the one-electron (quasiparticle) picture for NiC$_6$H$_6$ begins to break down for the $1b_{1u}$ and $2a_{1g}$ 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 $i^{-1}3e_1^{-1}3e_2$ ($i=1e_1$, $1e_2$, and $2e_1$). We note that configurations which involve charge-transfer excitations such as $3e_1$ (metal-ligand bonding character) to $3e_2$ (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 NiC_6H_6 the π-π^* excitations are of metal-ligand charge-transfer type.

C. PdC_6H_6

The first three ionization levels ($3e_1$, $3e_2$, and $3a_1$), 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.[14,16–18] 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 [C_6H_6 on Pd(110)], band A corresponds to the $1e_{1g}$ level, band B to the $2e_{2g}$ level, the broad-band C to the $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, and $1b_{1u}$ levels, band D to the $2a_{1g}$ level, and band E to the $1e_{2g}$ level.

The KT energy (inital state or chemical) shifts from the free molecule to PdC_6H_6 for the $1e_{1g}$, $2e_{2g}$, $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, $1b_{1u}$, $2a_{1g}$, and $1e_{2g}$ 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 PdC_6H_6 is the same as the one of the free molecule. In comparison to the case of NiC_6H_6, the initial-state energy shifts are larger, particularly for the first ligand ionization level ($1e_{1g}$). The final-state energy shifts for the $1e_{1g}$, $2e_{2g}$, $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, $1b_{1u}$, $2a_{1g}$, and $1e_{2g}$ 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 PdC_6H_6 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 NiC_6H_6, 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 NiC_6H_6, 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 $1e_{1g}$ and $1a_{2u}$ levels are differently shifted to higher binding energy by 1.4 (1.4) and 1.0 (1.8) eV, respectively, when the $2a_{1g}$ 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 PdC_6H_6 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 $1a_1(2a_{1g})$ and $1e_2(1e_{2g})$ levels, the one-electron picture breaks down. Thus the general spectral behavior is similar to the case of NiC_6H_6. As in the case for NiC_6H_6 the shake-up (-down) satellite lines are dominated in their wave functions by the metal-ligand charge-transfer $\pi \rightarrow \pi^*$ configurations. In the case of the free molecule the dominant many-body processes are $\pi \rightarrow \pi^*$ intraligand excitations. The metal-ligand $\pi \rightarrow \pi^*$ charge-transfer excitations appear at lower energies; i.e., they dominate the spectrum and tend to suppress the intraligand $\pi \rightarrow \pi^*$ excitations.

D. PtC_6H_6

The first three ionization levels ($3e_1$, $3e_2$, and $3a_1$ 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 $1b_{1u}$ 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 PtC_6H_6 is the same as the one of the free molecule.

The initial-state energy shifts from the free molecule to PtC_6H_6 for the $1e_{1g}$, $2e_{2g}$, $1a_{2u}$, $2e_{1u}$, $1b_{2u}$, $1b_{1u}$, $2a_{1g}$, and $1e_{2g}$ 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 PtC_6H_6 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 C_6H_6 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 PdC_6H_6 and PtC_6H_6. The sum of the initial-state energy shift and the change in the final-state energy shift for these levels of PtC_6H_6 are -2.24, -0.28, -1.54, -0.68, -0.24, 0.02, -0.95, and -1.01 eV, respectively. Except for the $1e_{1g}$, $1a_{2u}$, $2a_{1g}$, and $1e_{2g}$ levels, the energy level separations do not change strongly from the free molecule to the adsorbate. Note that in the case of the $2a_{1g}$ and $1e_{2g}$ 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 PdC_6H_6 and PtC_6H_6. As in the case of NiC_6H_6 and PdC_6H_6, 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 C_6H_6 on Pt(111) to the gas phase spectrum shows that again the $1e_{1g}$ and $1a_{2u}$ levels are differently shifted to higher binding energy by 1.7 and 1.3 eV, respectively, when the $2a_{1g}$ levels are aligned.[19] The

present predictions from our model are 2.0 and 1.3 eV, respectively, which agree well with experiment. The larger energy shift for the $1e_{1g}$ 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_6H_6 and PdC_6H_6, the satellite lines arise from the metal-ligand charge-transfer excitations. The metal-ligand charge-transfer $\pi \to \pi^*$ shakeup–shake-down processes dominate the satellite lines, in contrast to the case of the free molecule, where the $\pi \to \pi^*$ configurations, which dominate the satellite line structure, are of intraligand type. There is no significant difference in the spectral behavior among NiC_6H_6, PdC_6H_6, and PtC_6H_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 $1h$-$2h1p$ 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 $1h$-$2h1p$ 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_6H_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_6H_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 $2a_{1g}$ level of PdC_6H_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 $1e_{2g}$ level of PdC_6H_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 $2e_{1u}$, $1b_{1u}$, $2a_{1g}$, and $1e_{2g}$ levels of PtC_6H_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 $1b_2$ 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[4,5] 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 $2h1p$ 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 $1h$-$2h1p$ energy separations and coupling strengths. The screening effects in the $2h1p$ ionic state may shift the $2h1p$ 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_2H_2, C_2H_4, and C_6H_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 $Ni_{24}(C_2H_4)$ and $Ni_{25}(C_2H_4)_2$ for the di-σ and -π geometries, respectively. Very similar spectral structures were found for both chemisorption geometries, di-σ and -π. 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 similarity 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 orbitals which are involved in the metal-ligand bonding is often 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 geometry 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 surfaces were determined by comparing the UPS binding energies of the various valence levels to theoretical ground-state level energies of distorted structures of the free molecule.[11–13] Most of the UPS studies were performed using saturated layers, neglecting the fact that molecular levels in densely packed layers can show significant dispersion. Recently 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 significantly the valence-level photoemission spectrum of the adsorbate. In other words the initial-state energy shifts due to the distortion of the moelcule do not explain the changes in the ionization energy separations which are observed in going 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_6H_6, PdC_6H_6, and PtC_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 top-site adsorption of C_6H_6 on the metal surface was assumed. The theoretical spectra are compared with the experimental valence-level photoemission spectra of C_6H_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 previous experimentally derived assignment of the spectra. The shifts of the $1e_{1g}$ and $1a_{2u}$ 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 surfaces 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 $\pi \to \pi^*$ charge-transfer excitations are responsible for these many-body 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 valence levels is experimentally not observed for C_6H_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 adsorbate spectrum. This explains the similarity in the spectral intensity distribution between the free molecule and the adsorbate spectrum. For C_6H_6 adsorbed on a Ni metal surface the present theory predicts the presence of the metal-ligand charge-transfer (π-π^*) shake-up satellite of non-negligible intensity around 10 eV below the Fermi level. However, experiments 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 spectrum. The present study shows that the single-metal-atom model can provide a reasonably good description of the UPS spectra of C_6H_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

[1] W. Huber, H.-P. Steinrück, T. Pach, and D. Menzel, Surf. Sci. **217**, 103 (1989), and references therein

[2] D. R. Huntley, S. L. Jordan, and F. A. Grimm, J. Phys. Chem. **96**, 1409 (1992).

[3] T. Fox and N. Rösch, Surf. Sci. **256**, 159 (1991).

[4] W. Huber, M. Weinelt, P. Zebisch, and H. P. Steinrück, Surf. Sci. **253**, 72 (1991).

[5] M. G. Ramsey, D. Steinmüller, F. P. Netzer, T. Schedel, A. Santaniello, and D. R. Lloyd, Surf. Sci. **251/252**, 979 (1991).

[6] H. Bu, P. Bertrand, and J. W. Rabalais, J. Chem. Phys. **98**, 5855 (1993).

[7] A. B. Anderson, M. R. McDevitt, and F. L. Urbach, Surf. Sci. **146**, 80 (1984).

[8] E. L. Garfunkel, C. Minot, A. Gavezzotti, and M. Simonetta, Surf. Sci. **250**, 147 (1991).

[9] Z. Jing and J. L. Whitten, Surf. Sci. **250**, 147 (1991).

[10] M. A. Gallop, M. P. Gomez-Sal, C. E. Housecroft, B. F. G. Johnson, J. Lewis, S. M. Owen, P. R. Raithby, and A. H.

Wright, J. Am. Chem. Soc. **114**, 2505 (1992).

[11] J. E. Demuth and D. E. Eastman, Phys. Rev. Lett. **32**, 1123 (1974).

[12] J. E. Demuth and D. E. Eastman, Phys. Rev. B **13**, 1523 (1976).

[13] J. E. Demuth, Surf. Sci. **84**, 315 (1979), and references therein.

[14] F. P. Netzer, G. Rangelov, G. Rosina, H. B. Saalfeld, M. Neumann, and D. R. Lloyd, Phys. Rev. B **37**, 10 399 (1988).

[15] M. Surman, S. R. Bare, P. Hofmann, and D. A. King, Surf. Sci. **179**, 243 (1987).

[16] F. P. Netzer and J. U. Mack, J. Chem. Phys. **79**, 1017 (1983).

[17] G. L. Nyberg and N. V. Richardson, Surf. Sci. **85**, 335 (1979).

[18] P. Hofmann, K. Horn, and A. M. Bradshaw, Surf. Sci. **105**, 260 (1981).

[19] J. Somers, M. E. Bridge, D. R. Lloyd, and T. McCabe, Surf. Sci. **181**, L167 (1987).

[20] M. Ohno and W. von Niessen Surf. Sci. **366**, 209 (1996); Phys. Rev. B (to be published); and (unpublished).

[21] M. Ohno and W. von Niessen, Phys. Rev. B **42**, 7370 (1990); **44**, 1896 (1991); Surf. Sci. **269**, 258 (1992); Phys. Rev. B **45**, 9382 (1992); **51**, 13 547 (1995).

[22] M. Ohno and P. Decleva, Surf. Sci. **258**, 91 (1991); **269/270**, 264 (1992); Chem. Phys. **156**, 309 (1991); **169**, 173 (1993); J. Chem. Phys. **98**, 8070 (1993); Surf. Sci. **284**, 372 (1993); **296**, 87 (1993); Chem. Phys. **171**, 9 (1993).

[23] P. Decleva and M. Ohno, Chem. Phys. **160**, 341 (1992); **160**, 353 (1992); **164**, 73 (1992); J. Chem. Phys. **96**, 8120 (1992).

[24] M. Ohno, J. Electron Spectrosc. Relat. Phenom. **69**, 225 (1994); Mol. Eng. **4**, 61 (1994).

[25] M. Ohno, P. Decleva, and W. von Niessen, J. Chem. Phys. **97**, 2767 (1992).

[26] M. Ohno, W. von Niessen, and V. Zakrzewski, J. Chem. Phys. **97**, 6953 (1992).

[27] M. Ohno and P. Decleva (unpublished).

[28] K. Broomfield and R. M. Lambert, Chem. Phys. Lett. **139**, 167 (1987).

[29] S. Roszak and K. Balasubramanian, J. Chem. Phys. **103**, 1043 (1995).

[30] M. R. A. Blomberg, U. Brandemark, P. E. M. Siegbahn, K. Broch-Mathisen, and G. Karlström, J. Phys. Chem. **89**, 2171 (1985).

[31] C. W. Bauschlicher, Jr., P. S. Bagus, C. J. Nelin, and B. O. Roos, J. Chem. Phys. **85**, 354 (1986), and references therein.

[32] J. Schirmer, L. S. Cederbaum, and O. Walter, Phys. Rev. A **28**, 1237 (1983).

[33] W. von Niessen, J. Schirmer, and L. S. Cederbaum, Comput. Phys. Rep. **1**, 57 (1984), and references therein.

[34] L. S. Cederbaum, W. Domcke, J. Schirmer, and W. von Niessen, Adv. Chem. Phys. **65**, 115 (1986), and references therein.

[35] M. Ohno, W. von Niessen, and F. Tarantelli, Phys. Rev. B **45**, 1851 (1992).

[36] M. Ohno and W. von Niessen, J. Chem. Phys. **95**, 373 (1991); J. Electron Spectrosc. Relat. Phenom. **58**, 219 (1992); Chem. Phys. **158**, 1 (1991); Phys. Rev. A **51**, 1052 (1995).

[37] A. I. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[38] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[39] D. P. Chong, S. R. Langhoff, C. W. Bauschlicher, Jr., S. P. Walch, and H. Partridge, J. Chem. Phys. **85**, 2850 (1986).

[40] S. Huzinaga, J. Chem. Phys. **66**, 4245 (1977).

[41] O. Gropen, J. Comput. Chem. **8**, 982 (1987).

[42] P. O. Widmark, P.-Å. Malmqvist, and B. O. Roos, Theor. Chim. Acta **79**, 290 (1990).

[43] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, V. Kellö, R. Lindh, P.-Å. Malmquist, J. Noga, J. Olsen, B. O. Roos, A. J. Sadley, P. E. M. Siegbahn, M. Urban, and P.-O. Widmark, MOLCAS, Version 2, University of Lund, Sweden, 1991.

[44] E. R. Davidson, J. Comput. Phys. **17**, 87 (1975); B. Liu (unpublished); F. Tarantelli (unpublished).

[45] W. von Niessen, L. S. Cederbaum, and W. P. Kraemer, J. Chem. Phys. **65**, 1378 (1976), and references therein.

[46] H.-G. Weikert and L. S. Cederbaum, Chem. Phys. Lett. **237**, 1 (1995).

[47] L. S. Cederbaum, W. Domcke, J. Schirmer, W. von Niessen, and G. H. F. Diercksen, J. Chem. Phys. **69**, 1591 (1978).

[48] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, *Molecular Photoelectron Spectroscopy* (Wiley, London, 1970).

[49] H. Köppel, L. S. Cederbaum, and W. Domcke, J. Chem. Phys. **89**, 2023 (1988).

[50] S. Masuda, M. Aoyama, K. Ohno, and Y. Harada, Phys. Rev. Lett. **65**, 3257 (1990).

[51] M. Weinelt, W. Huber, P. Zebisch, H.-P. Steinrück, M. Pabst, and N. Rösch, Surf. Sci. **271**, 539 (1992)