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Green's-function calculations of valence photoemission spectra of Pd_2CO and Pt_2CO

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The ligand valence hole spectral functions of Pd_2CO and Pt_2CO are calculated by the *ab initio* third-order algebraic-diagrammatic-construction Green's-function method using an extended basis set. A comparison with the experimental valence-level ionization spectra of the CO bridge site adsorbed on a Pd(100) and a Pt(111) metal surface is made. In the CO/Pd system, the agreement with experiment is better for PdCO than Pd_2CO. Pd_2CO is not an adequate model for bridge bonding on an infinite surface. In the CO/Pt system, the agreement with experiment is better for Pt_2CO than PtCO. With an increase of the number of metal atoms (from the top-site bonding to the bridge-site bonding), the binding energy shifts towards smaller binding energy, in accord with experiment. The present study shows that the energy shift is mainly due to the initial-state energy shift, which is fairly independent of the substrate. The final-state (relaxation and correlation) energy shift is fairly independent of the number of metal atoms and the substrate. The major spectral features, such as the main line spectral intensity, remain independent of the increase of the number of metal atoms.

I. INTRODUCTION

A lower coordination of the surface atoms compared to the bulk atoms of a solid leads to the surface core-level shift, i.e., the substrate core-level peaks due to emission from bulk and surface atoms appear at different energies.[1] The chemisorption on the metal surface induces local changes in the properties of the surface atoms. This results in adsorption-induced binding energy shifts of the substrate surface. The adsorbate core-level binding energies depend also on the character of the adsorption sites.[2,3] Thus by using the sensitivity of the adsorbate and substrate surface core-level binding energies to the adsorption sites, it is possible to obtain qualitative and quantitative information about the overlayer structure.[4]

CO/Pt(111) is one of the most frequently studied absorbate systems and has served as a model system for catalytic reactions.[5] The overlayer structure formed by the CO molecules on the Pt(111) surface has been controversial. The adsorption sites for the CO molecule in a local $(\sqrt{3}\times\sqrt{3})R30^\circ$ formation with a long-range ordering of (4×4) and (8×8) symmetry, are suggested to be the on-top sites for low coverages,[6–9] although the onset coverage of bridge population has been discussed.[2,7,8] As proposed by Froitzheim *et al.*,[10] the $c(4\times2)$ structure involves equal population of on-top and bridge sites.[6–9] According to model calculations for the $c(5\times\sqrt{3})$ rectangular structure, $\frac{1}{3}$ of the molecules occupy the bridge sites and $\frac{2}{3}$ the on-top sites.[11] For the $c(7\times\sqrt{3})$ rectangular phase, the values are $\frac{1}{5}$ and $\frac{4}{5}$ for bridge and on top, respectively.[11]

Recently the Uppsala group measured the adsorbate and substrate core hole x-ray photoemission spectroscopy (XPS) spectra of the (4×4), $c(4\times2)$, and $c(5\times\sqrt{3})$ rectangular overlayers of CO/Pt(111).[12] For the (4×4) phase, there is only one peak in each C 1*s* and O 1*s* spectrum. The peak can be assigned to CO molecules in the top adsorption sites. This agrees well with previous XPS studies.[2,13,14] For the $c(4\times2)$ phase a second peak due to the bridge sites appears in each spectrum while the higher binding energy peaks remain at the same binding energies as for the (4×4) phase. The shifts between two components are 0.7 (C 1*s*) and 1.7 (O 1*s*) eV. This agrees also with previous XPS results.[2,13,14] For the $c(5\times\sqrt{3})$ rectangular phase, the two peaks appear at the same energies in each core-level spectrum, but the peak due to the on-top-site bonded molecules is more intense in each spectrum. As the CO molecule binds to the substrate with the carbon end, the diffraction effects are only present for the C 1*s* photoelectrons. For the outermost oxygen, there are no scattering atoms between the emitter and the detector. Thus they used the total O 1*s* spectral intensity from the three overlayer structures to estimate the coverages and the ratio of the on-top-site and the bridge-site bonding. Their results show that only the on-top adsorption sites are populated in the (4×4) phase. The $c(4\times2)$ and $c(5\times\sqrt{3})$ rectangular overlayers involve both on-top and bridge occupation. In the $c(4\times2)$ phase, there are equal amounts of on-top and bridge-bonded CO. For the $c(5\times\sqrt{3})$ phase, the ratio is about 2:1. Their results are in good agreement with the proposed structure models.[6,11] They measured also the Pt 4*f* XPS spectra of the same three overlayers of CO/Pt(111).[15] The relative Pt 4*f* component intensities for the different adsorption phases are also in good agreement with the proposed structure models.[6,11] The authors of Ref. 14 stated that the x-ray absorption spectrum of CO/Pt(111) can be fitted with two peaks spaced 0.2 eV apart with the peak corresponding to a bridge-bonded CO to a higher transition energy. The deexcitation electron spectroscopy (DES) spectrum of CO/Pt(111) shows the final states resulting from the decay of the bridge-bonded CO state. The final "two-hole" states for the bridge-bonded CO are 0.5 eV higher in binding energy than those for the top-bonded CO.[14]

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The XPS and UPS valence-level ionization spectra of CO/Pt(111) show that the sequence of CO levels in the adsorbate system is 1π, 5σ, and 4σ in order of increasing binding energy and that the 1π-4σ splitting is smaller (by 0.5 eV) in bridge-bonded than in linear-bonded CO.[2] In our previous work we calculated the hole spectral functions of the ligand valence levels of the linear model molecule PtCO by using an *ab initio* molecular orbital (MO) many-body technique such as the third-order algebraic-diagrammatic-construction [ADC(3)] method.[16] Our cluster many-body calculation confirms the ordering of the ligand valence-level ionization peaks, although it overestimates the $1\pi(5\sigma)$-4σ splitting by about 1 eV, compared to the metal surface. The results were obtained by high quality *ab initio* calculations on the minimal cluster model, *M-L* (here *M* and *L* denote the metal atom and the ligand molecule, respectively) of the adsorption site. The use of the minimal cluster model made it possible to treat quite accurately the many-body interactions in both ground and ionized states. However, the use of a minimal cluster requires justification. In the case of CO/Ni and N_2/Ni the electronic structure of the closed shell ${}^1\Sigma^+$ ground state of the minimal cluster model (NiCO, NiN_2) resembles quite well the structure of the adsorption site, and has often been employed to model on-top adsorption, giving satisfactory results for ground-state properties like equilibrium geometries, bonding energies, and stretching constants.[17–19] Moreover, excellent reproductions of the valence- and core-level photoemission spectra and core-level resonant excitation spectra, including recently observed spectral details, have been achieved by high quality *ab initio* many-body calculations by the authors.[20–29] The calculations emphasize the importance of 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 (which neglects the fluctuations). The success of the use of the minimal cluster models, together with many-body calculations, is ascribed to the accurate description of many-body effects associated with the dominant nature of the *M-L* interaction in a metal surface, involving metal 3*d* and 4*s* orbitals, but with little contribution from $4p\pi$. The latter becomes much more important when the *d* shell becomes nearly filled, like in the Cu atom. Indeed in a preliminary study of the valence and core photoemission spectra of the CO/Cu system,[30] an indication of the inadequacy of the single metal atom cluster model was found, tied to the lack of population of the $4p\pi$ levels in the ${}^2\Sigma^+$ ground state of CuCO. The problem may be alleviated by the use of an excited ${}^2\Pi$ initial state.[31] Also the latter gives, however, only partly satisfactory results, indicating the real need of a large metal cluster to properly describe the adsorption on the Cu metal surface. Thus there appears to be sufficient understanding of the physical situation to justify the use of the minimal cluster model employed. It is essential to be able to perform high quality *ab initio* many-body calculations on minimal cluster models to test the validity of the use of minimal cluster models. However, particularly in the case of ionization (excitation), until quite recently there does not seem to have been any high quality *ab initio* many-body calculation. From this point of view, the minimal cluster models do not appear to have been fully tested.

In the case of CO adsorption on Pd metal surface, CO is normally adsorbed in twofold bridge sites, the addition of NO onto the surface causes the CO to transfer to an on-top site, which it does not normally occupy.[32] The linear model molecule PdCO is a reasonably good model for descriptions of both core- (valence-) level ionized state and ground-state properties.[16,22,33] Our many-body calculation of the ligand valence-level ionization spectrum of PdCO confirms the ordering of the ligand valence-level ionization peaks, although it overestimates the $1\pi(5\sigma)-4\sigma$ level splitting by about 1 eV, compared to the metal surface.[16] The many-body calculation of the core-level ionized state predicted successfully the absence of the "giant satellite" line in the ionization spectra.[22] Moreover, in the case of the core-level ionization, both PdCO (on-top adsorption) and Pd_2CO (bridge bond) models do not make any significant differences.[22] In the case of CO/Pt, with an increase of the number of metal atoms bonding to the molecule (from the top-site bonding to the bridge-site bonding) the valence-level binding energy shifts towards smaller binding energy (0.7 eV for the 1π and 5σ levels and 0.4 eV for the 4σ level, according to our interpretation of the experimental data by the authors of Ref. 2). We investigate whether the minimal cluster model for the bridge-site bonding, namely, Pt_2CO, could provide an essential description of valence-level ionization in the bridge-bond CO on a Pt metal surface. A comparison with PtCO gives the binding energy shifts from the top-site to the bridge-site bonding. In the present work we calculate the hole spectral functions of the ligand valence levels of Pt_2CO by using the ADC(3) method. We analyze the spectra to see whether the binding-energy shift is mainly due to the initial-state energy shift (geometrical configuration change) or due to the final-state energy shift (relaxation and correlation). We consider also the case of Pd_2CO because the authors of Ref. 33 pointed out that Pd_2CO is not an adequate model for bridge bonding on an infinite surface. In the present work we calculate also the hole spectral functions of the ligand valence levels of Pd_2CO by using the ADC(3) method.

II. NUMERICAL PROCEDURE

We use the Green's-function formalism [in the ADC(3) approach] to calculate the ionization potentials (IP) and their spectral intensities directly. 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.[34–36] 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. The accuracy and reliability of the ADC(3) method has been tested not only for free molecules[35,36] but also for several model molecules (adsorbates) and related charge-transfer systems.[26–29,37,38]

We start with the renormalization of the three different types of basic diagrams, namely, 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. We approximate the $2h$-$1p$ 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 by the ADC(3) method. 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. We refer to Refs. 34–36 for further details of the method.

The calculation is performed for Pd_2CO keeping the CO distance at 2.2 a.u. and the Pd-C distance at 3.65 a.u. The Pd-C distance of 3.65 a.u. is the experimental distance of CO adsorbed on a Pd(100) surface (bridge bonding[39]). The Pd-Pd distance is 5.25 a.u. which is the Pd-Pd distance of bulk Pd metal. The calculation is performed for Pt_2CO keeping the CO distance at 2.2 a.u. and the Pt-C distance at 3.75 a.u. The Pt-C distance of 3.75 a.u. is the geometrically optimized distance obtained for the linear PtCO molecule.[40] The Pt-Pt distance is 5.25 a.u. which is the Pt-Pt distance of bulk Pt metal. We use basis sets of Cartesian Gaussian functions on the atoms to expand the MO's. For PdCO the $[17s,11p,8d]$ basis set of Huzinaga optimized for the $^3F(4d^85s^2)$ state of Pd (Ref. 41) is enlarged by an additional $3d$ function [optimized for the $^1S(4d^{10})$ state ($\alpha_d=0.0838$)] and two p-type functions with exponential parameter $\alpha_p=0.1586, 0.05122$ to describe the $5p$ orbital of Pd. The final basis is $[17s,13p,9d]$ contracted to $(9s7p5d)$. For PtCO the $[19s,14p,10d,5f]$ basis set of Gropen optimized for the $5d^{10}$ state of Pt (Ref. 42) is enlarged by an additional $4f$ function ($\alpha_f=0.7$), an additional $5d$ function ($\alpha_d=0.1$), two additional p-type functions with exponential parameter $\alpha_p=0.22, 0.07$ to describe the $6p$ orbital of the Pt atom, and one additional s-type function with $\alpha_s=0.027$, which is used in order to achieve a better description of the bonding. The final basis set is $[20s,16p,11d,6f]$ contracted to $(12s11p6d3f)$. The C and O basis sets are taken from Salez and Veillard, $[11s,7p,1d]$ contracted to $(5s3p1d)$.[43] The exponential parameters of the d-type functions are $\alpha_d(\mathrm{C})=0.6$ and $\alpha_d(\mathrm{O})=0.8$. The calculation of the self-consistent field (SCF) wave functions 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.[44] In the ADC(3) Green's-function calculations for Pd_2CO (Pt_2CO) the lowest 63 (62) virtual orbitals and all occupied orbitals, except for the core orbitals, were taken into account. This leads to matrices of dimension of around 20 000. The eigenvalues and eigenfunctions were extracted with a block Davidson method.[45] For each symmetry about 100 eigenvalues and eigenvectors were calculated.

III. RESULTS AND DISCUSSIONS

In Tables I and II, we summarize the present results for the ligand valence-level ionization energies for Pd_2CO and Pt_2CO, together with the previous results for PdCO and PtCO which are obtained by the same method.[16] We list the Koopmans theorem (KT) energies, the ionization energies (IP), the relative spectral intensities (I), and the experimental ionization energies. For $2a_1(4\sigma)$ ionization of Pd_2CO, the spectral function calculated by the ADC(3) shows a complete breakdown of the one-electron picture in the energy range from about 18 to 19.3 eV. We consider that this is unphysical and must be due to an effect introduced by increasing the number of the metal atoms from 1 to 2 and the lowering of the symmetry from $C_{\infty v}$ to C_{2v}. In the reduced symmetry the π orbitals on the metal can mix with the CO σ orbitals leading to an apparent stronger many-body effect. The increase of the number of metal atoms and the symmetry reduction introduces the splitting of ligand and metal levels. This results in the increase of the number of the $2h1p$ configurations and also in small energy separations between the $2h1p$ configurations. As a result, the real part of the self-energy shows a larger number of singularities. The pole strength obtained for a certain eigenstate of the Dyson equation for the single-metal-atom model will be approximately distributed over a larger number of eigenstates of the Dyson equation for the two-metal-atom model. The latter eigenstates lie in the energy region of about 1 eV. This explains why the increase of the number of metal atoms from 1 to 2 leads to an unphysical many-body effect, such as the complete breakdown of the one-electron picture for the ionization process. The distribution of the pole strength over many eigenstates can be understood as a consequence of the sum rule for the spectral function (which is valid within the Hartree-Fock scheme). This is also reflected in the fact that the relaxation and correlation energy shifts obtained as the difference between the ionization energies ("renormalized" ionization energies in the case of the two-metal-atom model) and the KT energies by both single-metal-atom and two-metal-atom models are approximately the same. Thus we consider that for the $2a_1$ level ionization, it is more appropriate to determine the center of gravity for the spectral intensity in the energy region from 18.0 to 19.3 eV. The "renormalized" ionization energy (18.84 eV) and "renormalized" spectral intensity (0.54) presented in Table I for the $2a_1$ level ionization of Pd_2CO is determined in this manner. This is also the case with the $3a_1(5\sigma)$ level (15 to 17 eV) and the $1b_1(1\pi)$ level (14 to 15.5 eV) ionization of Pd_2CO and the $2a_1(4\sigma)$ level (18 to 19.5 eV), the $3a_1(5\sigma)$ level (15 to 16 eV), and the $1b_1(1\pi)$ level (14 to 15.3 eV) ionization of Pt_2CO.

Strictly speaking, the Hartree-Fock (HF) eigenvalues have no physical relevance because of the neglect of ground-state and final-state correlation (fluctuation) and

TABLE I. Theoretical valence IP of PdCO and Pd_2CO and experimental values for CO on Pd metal surfaces (eV). For experimental data, only the main line energy observed is listed. The estimated work function of 6.0 eV is added to the experimental data. (KT= Koopmans' theorem energies; IP=ionization energies; I =relative spectral intensities.)

	PdCO					Pd_2CO		
Level	KT	IP	I	Level	KT	IP	I	Expt.[a]
1π	16.83	14.94	0.62	$1b_1$	16.65	14.62	0.74	13.3
		15.59	0.05			16.95	0.01	
		16.49	0.06	$1b_2$	16.10	14.13	0.60	
		17.38	0.03					
		20.24	0.11					
5σ	17.25	14.87	0.14	$3a_1$	17.39	13.66	0.01	13.6
		15.21	0.67			15.39	0.76	
		18.57	0.04					
		20.39	0.03					
4σ	21.58	18.57	0.09	$2a_1$	21.38	16.81	0.02	16.5
		18.97	0.65			18.84	0.54	
		20.39	0.02			19.57	0.10	
						20.31	0.04	

[a]Reference 46.

relaxation in the final state. However, the eigenvalue shift due to a change of environment (such as the change of a bond length or the removal of the metal atom to infinity) should indicate the initial-state (chemical) shift (neglecting the ground-state correlation energy shift). For both the single-metal-atom model and the two-metal-atom model of Pd and Pt, the ordering of the 5σ and 1π levels (eigenvalues) is reversed compared to that of a free CO molecule (the eigenvalues of the 5σ, 1π, and 4σ levels for free CO are 15.11, 17.49, and 21.89 eV, respectively).[26] In comparison to free CO, in PdCO and Pd_2CO the 5σ orbital, which is directed towards the metal atom(s), is shifted to larger binding energy by as much as 2.1 and 2.3 eV, respectively, whereas the $4\sigma(1\pi)$ level,

TABLE I. Theoretical valence IP of PdCO and Pd_2CO and experimental values for CO on Pd metal surfaces (eV). For experimental data, only the main line energy observed is listed. The estimated work function of 6.0 eV is added to the experimental data. (KT= Koopmans' theorem energies; IP=ionization energies; I =relative spectral intensities.)

	PdCO					Pd_2CO		
Level	KT	IP	I	Level	KT	IP	I	Expt.[a]
1π	16.93	14.98	0.40	$1b_1$	16.80	14.52	0.38	14.1[a]
		15.37	0.28	$1b_2$	16.22	13.95	0.16	14.4[b]
		16.71	0.05			14.12	0.48	14.3[c]
		17.64	0.02			14.19	0.01	13.8[d]
		20.30	0.09			14.58	0.04	13.4[e]
		20.55	0.03					
5σ	17.52	14.90	0.03	$3a_1$	17.81	13.63	0.02	15.0[a]
		15.48	0.74			15.45	0.73	14.4[b]
		15.70	0.03					14.3[c]
		18.46	0.04					15.0[d]
		19.99	0.02					14.3[e]
		20.08	0.01					14.3[f]
4σ	21.69	18.46	0.06	$2a_1$	21.60	16.77	0.02	17.6[a]
		19.13	0.65			18.78	0.61	17.3[b]
		20.08	0.03			20.22	0.02	17.4[c]
								17.5[d]
								17.2[e]
								17.3[f]

On-top-site adsorption (a) Ref. 2, (b) Ref. 47, (c) Ref. 14, (d) Ref. 48. Bridge-site adsorption (e) Ref. 2, (f) Ref. 48.

which is predominantly localized on the oxygen, is shifted to smaller binding energy by about 0.3 (0.7) and 0.5 (0.84 for the $1b_1$ level and 1.4 for the $1b_2$ level) eV, respectively. In comparison to free CO, in PtCO and Pt_2CO the 5σ level is shifted by as much as 2.4 and 2.7 eV, respectively, whereas the $4\sigma(1\pi)$ level is shifted to smaller binding energy by about 0.2 (0.6) and 0.3 (0.7 for $1b_1$ and 1.3 for $1b_2$) eV, respectively. The initial-state energy shift is fairly independent of the substrate. At a fixed metal-carbon bond length, the initial-state shift for the 5σ level of XCO (X = Ni, Pd, and Pt) increases in the sequence of Ni, Pd, and Pt, thus indicating that the ligand 5σ orbital is oriented toward the metal (the adsorption geometry), whereas for the 1π and 4σ levels, the shifts at a fixed metal-carbon bond length are fairly independent of the substrate.[16] With an increase of the number of metal atoms, except for the 5σ level, the KT eigenvalues become smaller for both Pd_2CO and Pt_2CO.

The final-state shifts (sum of the correlation and relaxation energy shift) of the main line states of the largest spectral intensity for 1π levels of PdCO (Pd_2CO) and PtCO (Pt_2CO) are 1.9 (2.0 for both the $1b_1$ and $1b_2$ levels) and 2.0 (2.3 for the $1b_1$ level and 2.1 for the $1b_2$ level) eV, respectively, while the energy shift for free CO is 0.5 eV. For the 5σ level, they are 2.0 (2.0) and 2.0 (2.4) eV, respectively, while the one for free CO is 1.2 eV. For the 4σ level, they are 2.6 (2.5) and 2.6 (2.8) eV, respectively, while the one for free CO is 1.8 eV. Thus the final-state energy shift is fairly independent of the number of metal atoms (geometrical configuration change) and the substrates. For XCO (X = Ni, Pd, and Pt) the final-state shift is fairly independent both of the metal-carbon bond length and of the substrates.[16] This shows that the hole screening which determines the final-state energy shifts and spectral intensities are localized processes, whose major effects could be essentially described by the minimal cluster models. We note that not only the metal-ligand charge transfer but also the intraligand relaxation (screening) play an important role in the screening process, although in the literature the former is emphasized and the latter is almost ignored.[26] Except for the 5σ level of PdCO, the energies shift towards smaller binding energies with an increase of the number of metal atoms. The binding-energy shift is mainly due to the initial-state shift (from the top-site to the bridge-site adsorption). Thus the valence-level ionization energy shift provides information about the initial-state energy shift due to different geometrical configurations. It appears that in the experimental study of the ligand level binding-energy shifts, the dependence of the final-state energy shift on the geometrical changes has not been considered. Fortunately the final-state energy shift is fairly independent of the geometrical configuration changes. The initial-state energy shifts of C 1s and O 1s from PdCO to Pd_2CO are 0.68 and 1.1 eV, respectively, while the ones from PtCO to Pt_2CO are 0.63 and 1.1 eV, respectively. For CO/Pt the experimental binding-energy shifts for C 1s and O 1s from the top-site to the bridge-site bonding are 0.7 and 1.7 eV, respectively.[2,12–14] It appears that also in the case of the ligand core-level ionization the initial-state energy shift governs the binding-energy shift.

In general the major spectral features such as the appearance of the shakedown satellite states of small intensities below the main lines states for the 5σ and 4σ level ionization and the tendency towards the breakdown of the one-electron picture for the 1π level ionization still remains, with an increase of the number of metal atoms. With an appreciable increase of the number of metal atoms (approaching to real metal surface), the self-energy's singularity becomes smeared out because of the broadening of the levels by hybridization between the metal band and ligand orbitals. However, the major structure of the self-energy obtained by the single-metal-atom model remains so that the major spectral feature is rather independent of the number of metal atoms.

The total spectral intensities of the lower-energy shakeup region up to about 21 eV [where the metal-ligand charge transfer (CT) and local metal excitations dominate rather than the intraligand excitations] are about 0.9 for the ligand levels of Pd_2CO and Pt_2CO. The values are also fairly independent of the number of metal atoms and the substrate. As already pointed out in previous work,[16] these values are almost the same as the main line intensities of free CO calculated by using the same method. This shows that in the coordinated molecule the main line intensity of free CO is distributed over several spectral lines by the metal-ligand CT and local metal excitations, and the intraligand excitations appear in the higher-energy region, although it should be noted that the intraligand excitations mix very much with the metal-ligand CT excitations and their shakeup spectral intensities becomes much less pronounced than for a free molecule. This is also the case with metal carbonyls and the core hole spectra of the adsorbates (see Refs. 16, 20–29, and 37).

The present results refer to an isolated molecule. In the present work a comparison with the experimental results for the adsorbate system is made simply by adding the work function to the binding energy of the adsorbed molecule measured relative to the Fermi level of the substrate to bring the data to a common reference level. In the present work 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. As the relative separation of the 5σ and 4σ levels to the lowest 1π level are independent of the work function, we compare also these quantities with experiment.

A. CO/Pd case

The 1π-5σ and 1π-4σ splittings observed for CO/Pd are 0.3 and 3.2 eV, respectively,[46] while the present theoretical prediction for PdCO is 0.3 and 4.0 eV, respectively. The prediction by the Pd_2CO model is 1.0 and 4.5 eV, respectively. It appears that the prediction by Pd_2CO is less accurate than that by PdCO. Recent accurate *ab initio* calculation of Pd_2CO shows the binding of CO to Pd_2 (55 kcal/mol) is much larger than the carbon chemisorption energy on a palladium surface of 37 kcal/mol.[33] The authors of Ref. 33 concluded that Pd_2CO is not an adequate model for bridge bonding on an infinite surface.

It appears that PdCO which provides 33 kcal/mol (Ref. 33) is more suitable for a description of the bonding of CO on a Pd metal surface. With a larger binding energy of CO to the dimer than to the surface, the effect which will be emphasized in the surface case is the breaking of bonds between palladium atoms. The bonds between palladium atoms are much stronger in a surface than for the dimer, which has to do with the dominance of the d^9s state for the surface in contrast to the dominance of the d^{10} state for the dimer. The d^9s state can form strong s bonds, whereas the d^{10} state is quite ineffective at forming bonds since a natural covalency is lacking.[33] The calculation on bridge-bonded CO to the palladium dimer shows that the bond between the metal atoms is effectively broken when CO is bridge bonded.[33]

B. CO/Pt case

The 1π-5σ and 1π-4σ splittings observed for the top-site chemisorbed CO/Pt by the authors of Ref. 2 are 0.9 and 3.5 eV, respectively, and the ones by the author of Ref. 48 are 1.2 and 3.7 eV, respectively. The present theoretical prediction by PtCO is 0.5 and 4.2 eV, respectively. The agreement is reasonably good. The 1π-5σ and 1π-4σ splittings observed for the bridge-site chemisorbed CO/Pt by Norton *et al.*[2] are 0.8 and 2.9 eV, respectively, because they interpreted the peak at 8.6 eV as the 1π level and the one at 9.4 eV as the 5σ level. However, the difference spectrum obtained between 1.5 and 4 L by Schneider[48] shows peaks at 8.6 and 11.56 eV, while the spectrum obtained at 1.5 L shows peaks at 9.3 and 11.8 eV. The peaks at 8.6 and 11.56 eV should be interpreted as the 5σ and 4σ peaks for the bridge bonding, respectively, while the peaks at 9.3 and 11.8 eV should be interpreted as the 5σ and 4σ peaks for the top-site bonding, respectively. Norton *et al.*[2] observed the peak at 7.7 eV (at CO coverage $=0.54$). If we interprete the peak as the 1π level for the bridge bonding, the 1π-5σ and 1π-4σ splittings for the bridge bonding are 0.9 and 3.86 eV, respectively. The prediction by the Pt_2CO model is 1.1 and 4.5 eV, respectively. The agreement is good. The binding energy shifts of 1π, 5σ, and 4σ peaks from the top-site bonding to the bridge bonding are 0.7 (0.4), 0.7, and (0.24) eV, respectively (towards smaller binding energy), while the present theoretical predictions are 0.66, 0.03, and 0.35 eV, respectively. The agreement is good, except for the 5σ level.

IV. CONCLUSION

In the present work we calculated the hole spectral functions of the ligand valence levels of bridge-bonded Pd_2CO and Pt_2CO by using a high quality *ab initio* many-body approach. The major spectral features such as the main line spectral intensity remain unchanged, irrespective of the increase of the number of metal atoms. For the bridge-bonding CO/Pd system, Pd_2CO seems to be an inadequate model for both ground and valence-level ionized states. For the bridge-bonding CO/Pt, it appears that Pt_2CO provides a reasonably good description of the valence ionization of the bridge-bonded CO on a Pt metal surface. For both Pd_2CO and Pt_2CO, except for the 5σ level, the increase in the number of metal atoms shows the binding energy shift towards smaller binding energy, while for CO/Pt all ligand valence ionization energies are shifted towards smaller binding energies from the top-site to the bridge-site chemisorption. The binding-energy shift is interpreted mainly as being due to the initial-state energy shift. The initial-state energy shifts are fairly independent of the substrate, while the final-state energy shifts are fairly independent of both the substrate and the number of metal atoms. The final-state many-body effects associated with the valence- (core-) level ionization can be correctly described by the minimal cluster model. Thus the binding energy shift due to different geometrical adsorption sites should provide information about the initial-state energy shift. This supports the experimental studies of the adsorbate binding energy shifts to determine the geometrical change of the adsorption site.

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