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Theoretical study of the valence-level photoemission spectrum of C_2H_4 adsorbed on a Ni metal surface

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In order to investigate the valence-level photoemission spectrum of C_2H_4 adsorbed on a Ni metal surface, we calculated the valence-hole spectral functions of NiC_2H_4 (π bonding) using the *ab initio* third-order algebraic-diagrammatic-construction (ADC(3)) Green-function method using an extended basis set. We obtained an overall good agreement with experiment. The changes in the spectral features such as the changes in the separations of the ionization energies from the gas phase to the chemisorbed phase are due to the metal ligand bonding exerted via the charge-transfer excitations and do not arise from the distortion of the molecule, which occurs upon chemisorption. [S0163-1829(97)01004-7]

I. INTRODUCTION

The adsorption of ethylene on Ni has been widely studied as one of the simplest hydrocarbon adsorptions on metal surfaces. Two possible bonding mechanisms have been proposed to describe the bonding of ethylene to metal surfaces.[1] The first one involves the formation of a π donor bond with a surface atom (or atoms), as in various organometallic complexes. The π orbital donates its electrons to vacant d orbitals of the metal while the π^* orbital accepts electrons from filled d orbitals (the Dewar-Chatt, Duncansen π-d bonding model[2]). The second one involves the rehybridization of the carbon atoms in ethylene (from sp^2) to sp^3 with the formation of two σ bonds to adjacent surface metal atoms. In the literature this is called the di-σ configuration. The geometry of the adsorption site of ethylene on metal surfaces such as Ni and Pt has been controversial. In order to distinguish between a di-σ configuration, a π adsorption or some intermediate species, the state of hybridization of carbon is considered to be determined. Demuth[3–5] has developed a method for predicting the geometry of adsorbed molecules from ultraviolet photoelectron spectroscopy (UPS). Provided that there is a uniform relaxation shift of the ionization energy levels of the molecule, the energy-level separation is reflected in the UPS peak separations. The changes in these separations, compared with the free molecule case, provide information on the distortion of the molecule, when it interacts with the surface. In order to determine this distortion, a free molecule approximation is made. The changes in the separations of the energy levels of the adsorbed molecule are assumed to arise from the same distortions that lead to identical changes in the separations of the energy levels of the free molecule.

The UPS spectrum of an ethylene molecule adsorbed on a Ni(111) surface shows that the relative σ-orbital ionization energies and intensities of gaseous and chemisorbed ethylene are essentially identical, except for an ethylene π-level bonding shift of 0.9 eV upon adsorption.[6,7] The analysis of the UPS spectra by Demuth leads to the conclusion that C_2H_4 chemisorbs on Ni(111) as a π-adsorbed species and significant rehybridization does not occur upon chemisorption.[3–5] The self-consistent-field (SCF) $X\alpha$ scattered-wave method calculations of the ionization spectra of NiC_2H_4 and $Ni_2C_2H_4$, simulating the π-bonded complex and the di-σ bonding, respectively, gave an ionization energy shift for the C_2H_4 $b_{2u}(\pi)$ orbital of 0.72 eV for the π bonded complex and 0.30 eV for di-σ bonding.[8] Comparison with the experimental shift of 0.9 eV strongly favors the π bonded configuration. Demuth's approach has been extended by Felter and Weinberg by relating linearly the shifts in the molecular energy levels with the distortions of the molecule.[9] The di-σ configuration (the distorted molecule) resembles the lowest-energy configuration of the first excited state of the free molecule. The distortions that resemble the first excited states might occur as a consequence of donation of bonding electrons from the normally filled π orbitals to the empty d-band states of the metal and backbonding to the empty π^* orbital from the filled d-band states. The net effect on the hydrocarbon to partially empty the π level and fill the π^* level is analogous to a low excitation of the free molecule, $\pi \rightarrow \pi^*$. For C_2H_4 (planar in the ground state), the lowest excitation is the triplet T state of minimal energy for a 90° twisted configuration with a lengthened C-C bond. A geometry in the chemisorbed state derived from this configuration was proposed by Felter and Weinberg[9] as a possibility for C_2H_4 on Ni(111), while the di-σ configuration was proposed for C_2H_4 on Pt(111), as proposed previously in the literature.[5]

Many predictions based on experiment have been made for the conformation of the chemisorbed species and a consensus on the major qualitative distortions has emerged.[5,10,11] Thus, it is generally believed that the C-C bond length increases and that the C-C-H angle and the H-C-H angle decreases due to the movement of the hydrogen atoms away from the surface. These conclusions have been drawn principally from electron-energy-loss spectroscopy (EELS) and photoelectron spectroscopy. An EELS study of ethylene chemisorbed on Pt(111) has been carried out and it was concluded that ethylene is sp^3 hybridized on the surface, namely it is bonded in the di-σ configuration.[12] The near edge x-ray-absorption fine-structure (NEXAFS) spectra of ethylene on Pt(111), when compared to the spectra calculated using the multiple-scattering $X\alpha$ method for a cluster model of adsorbed ethylene, indicate that ethylene is adsorbed on Pt(111) in the di-σ configuration.[13] A similar NEXAFS study of ethylene on Ni(111) (Ni(110)) indicates that ethylene is also adsorbed on Ni(111) (Ni(110)) in the di-σ configuration.[14,15] The adsorption and thermal decomposition of C_2H_4 on Ni(110) has been studied by Anson *et al.*[16] and Stroscio, Bare, and Ho[17] using high-resolution electron-energy-loss spectroscopy (HREELS), programmed desorption temperature (TPD), and low-energy electron diffraction (LEED). From HREELS Anson *et al.*[16] propose a di-σ-bonded C_2H_4 species with the C-C axis parallel to the surface, and Stroscio, Bare, and Ho determine the site symmetry of the adsorption complex for the saturated layer to be lower than C_{2v} symmetry.[17] Recently, Weinelt *et al.*[18,19] studied the electronic structure of C_2H_4 adsorbed on Ni(110) by angle-resolved ultraviolet photoemission spectroscopy (ARUPS), TPD, and LEED. The ARUPS measurements were performed for a dilute layer, where the lateral interactions are not important. From the ARUPS spectra, they deduced an orientation of the ethylene molecules with the molecular plane parallel to the surface and the C-C axis preferentially aligned along the $[1\underline{1}0]$ azimuth. The symmetry of the adsorption complex is determined as C_1. The ethylene π-orbital $1b_{2u}$ exhibits a shift of 1.1 eV to higher binding energy as compared to the free molecule.

Our many-body calculations of the valence-hole spectral functions for the model cluster of CO (N_2) adsorbed on metal surfaces, provide a reasonably good description of the valence-level photoemission spectra, confirming the ordering of the ligand valence-level ionization peaks.[20] The results were obtained by high-quality *ab initio* calculations on the single metal-atom model, M_x-L of the adsorption site (here M and L denote the metal atom and the ligand molecule, respectively, and $x=1$ or 2). 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. However, the use of a single metal-atom model 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 single metal-atom 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.[21–23] 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.[20,24–29] 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 (which neglects the fluctuations). The success of the single metal-atom 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 on a metal surface, involving metal $3d$ ($4d$) and $4s$ ($5s$) orbitals, but with little contribution from $4p\pi$ ($5p$). The latter becomes much more important when the d shell becomes nearly filled, as in the Cu atom. Thus, for certain cases there appears to be a sufficient understanding of the physical situation to justify the use of the single metal-atom model employed. Recently, Roszak and Balasubramanian[30] studied the 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.[21–23] 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 terminal Pt atom. This can be interpreted to reflect the fact that the role of the second Pt atom is small. Thus, a single metal-atom model is a reasonably good model for the top site adsorption of CO on Pt.

The authors of Refs. 18 and 19 concluded that the comparison of the ARUPS data to the corresponding cluster results does not allow any discrimination between the two main adsorption geometries, π or di-σ. Moreover, they critically commented on the fact that in Demuth's approach, most of UPS studies have been performed using saturated layers and the ethylene levels can show significant dispersion in densely packed layers. Thus any conclusions on the adsorbate geometry based on orbital energies of the molecule are not well founded. The authors of Refs. 18, 19 made linear combination Gaussian-type orbital–local-density functional (LCGTO-LDF) model cluster calculations and used the ground-state level spectrum for a comparison to ARUPS data, assuming that the relaxation energy shift is rather uniform. They ascribed the $1b_{2u}$ level shift to higher binding energy as due to the chemical (initial state) shift. Nowadays, it is quite well established that the approach of Demuth *et al.* is too simplified because of the dominant role of the metal-ligand interaction. The establishment of this fact relies on extensive experimental and theoretical work and the possibility to perform a calculation on models with the inclusion of a cluster model for the metal surface. The present work contributes here too. The main target of the investigation, however, is to study the many-body effects on the photoemission spectrum and their influence on various initial- and final-state energy shifts.

In the present work in order to study the valence-level photoemission spectrum of an ethylene molecule adsorbed on a Ni metal surface, we shall calculate the valence-level photoemission spectra (more exactly, the valence-hole spectral functions) of C_2H_4, ‘‘distorted C_2H_4’’ and NiC_2H_4 (π complex, ‘‘distorted’’ and ‘‘undistorted’’ ethylene) by the ADC(3) method. We shall show that the present single metal-atom model which represents the π-bonding complex, provides a reasonably good description of the ionization of the ligand levels and that a free molecule approximation (Demuth's approach) fails to describe the changes in the ionization energy separations from C_2H_4 to C_2H_4/Ni(110). It is the metal-ligand bonding not the distortion of the molecule which is the cause of the changes in the ionization energy separations from the free molecule to the adsorbate.

II. THEORY AND NUMERICAL PROCEDURE

The Green-function formalism, in particular, the ADC(3) approach of Ref. 31 is used in the present work to calculate the ionization potentials (IP) and their relative spectral intensities (the pole strengths) directly. We give a brief review of the one-particle Green-function formalism, and particularly of the ADC(n) approach introduced by Schirmer, Cederbaum, and Walter.[31]

We consider an N-electron system with a nondegenerate normalized ground state $|\Psi_0^N\rangle$ and energy E_0^N. In the case of a molecule a fixed nuclear geometry is assumed and rotation and vibration degrees of freedom are suppressed. The electronic Hamiltonian of the system consists of a one-particle part $\hat{T}$ and of the two-particle Coulomb interaction $\hat{V}$. In the second quantization we can write

$$\hat{H}=\hat{T}+\hat{V}=\sum T_{ij}c_i^\dagger c_j+\frac{1}{2}\sum V_{ijkl}c_i^\dagger c_j^\dagger c_l c_k, \tag{1}$$

where $c_i^\dagger(c_i)$ denote creation (annihilation) operators for the one-particle state $|\psi_i\rangle$ of a suitably chosen basis, in general, the Hartree-Fock (HF) basis of the ground state. The Coulomb matrix elements are given by

$$V_{ijkl}=\langle\psi_i(1)\psi_j(2)|V(1,2)|\psi_k(1)\psi_l(2)\rangle \tag{2}$$

and T_{ij} denote the matrix elements of the one-particle operator $\hat{T}$. The spectral representation of the one-particle Green function $G(\omega)$ is given by

$$G_{pq}(\omega)=\sum_n \frac{\langle\Psi_0^N|c_p|\Psi_n^{N+1}\rangle\langle\Psi_n^{N+1}|c_q^\dagger|\Psi_0^N\rangle}{\omega+E_0^N-E_n^{N+1}+i\eta}$$

$$+\sum_n \frac{\langle\Psi_0^N|c_q^\dagger|\Psi_n^{N-1}\rangle\langle\Psi_n^{N-1}|c_p|\Psi_0^N\rangle}{\omega+E_n^{N-1}-E_0^N-i\eta}. \tag{3}$$

Here $|\Psi_n^{N\pm1}\rangle$ are the complete set of eigenfunctions of the Hamiltonian for the $N\pm1$ electron system with eigenenergies $E_n^{N\pm1}$ and η is a positive infinitesimal. As is apparent from the spectral representation Eq. (3), the vertical electronic ionization energies

$$I_n=E_n^{N-1}-E_0^N \tag{4}$$

and electron affinities

$$A_N=E_0^N-E_n^{N+1} \tag{5}$$

are given by the negative pole positions of the Green function. The residue corresponding to a pole n

$$Q_{pq}^n=\chi_p^{(n)}\chi_q^{(n)*} \tag{6}$$

is given by the product of the two transition amplitudes

$$\chi_p^{(n)}=\begin{cases}\langle\psi_0^N|c_p|\psi_n^{N+1}\rangle & \text{for } n\varepsilon(N+1)\\ \langle\psi_n^{N-1}|c_p|\psi_0^N\rangle & \text{for } n\varepsilon(N-1).\end{cases} \tag{7}$$

Within the sudden approximation, partial-channel photoionization cross sections are given by

$$\sigma_n(\epsilon)=\frac{2}{3}\,\epsilon\left|\sum_p \tau_{\epsilon p}\chi_p^{(n)}\right|^2. \tag{8}$$

Here

$$\tau_{\epsilon p}=\langle\psi_\epsilon|\hat{d}|\psi_p\rangle \tag{9}$$

denotes the matrix element of the dipole operator $\hat{d}$ taken between the one-particle state $|\psi_p\rangle$ and the one-particle scattering state $|\psi_\epsilon\rangle$ with kinetic energy $\epsilon=\omega_0-I_n$, with ω_0 the photon energy. In general, the sum over orbitals p in Eq. (8) runs over all occupied and unoccupied orbitals. Often, however, to a good approximation only one term gives a nonvanishing contribution. Then Eq. (8) simplifies to

$$\sigma_n(\epsilon)=\frac{2}{3}\,\epsilon|\tau_{\epsilon p}|^2|\chi_p^{(n)}|^2. \tag{10}$$

The pole strength

$$P_n=|\chi_p^{(n)}|^2 \tag{11}$$

is called the relative intensity, since it provides a measure for the relative intensities of the states n which derive their intensity from the same orbital p ($|\tau_{\epsilon p}|^2$ is assumed to be only weakly energy dependent).

The perturbation expansion of the one-particle Green function $G(\omega)$ is based on the usual decomposition of the full Hamiltonian $\hat{H}$ into an unperturbed diagonal one-particle Hamiltonian $\hat{H}_0$ and a perturbation part $\hat{H}_1$:

$$\hat{H}=\hat{T}+\hat{V}=\hat{H}_0+\hat{H}_1, \tag{12}$$

$$\hat{H}_0=\sum \epsilon_i c_i^\dagger c_i, \tag{13}$$

$$\hat{H}_1=\hat{W}+\hat{V}=\sum W_{ij}c_i^\dagger c_j+\frac{1}{2}\sum V_{ijkl}c_i^\dagger c_j^\dagger c_l c_k. \tag{14}$$

Here, we use the second quantized representation based on ground-state HF one-particle states $|\psi_j\rangle$; ϵ_j denote the HF orbital energies, and W_{ij} denote matrix elements of the nondiagonal one-particle perturbation contribution $\hat{W}$. In the HF case they are given by

$$W_{ij}=-\sum_k V_{ik[jk]}n_k, \tag{15}$$

$$V_{ij[kl]}=V_{ijkl}-V_{ijlk}, \tag{16}$$

$$n_k=1-\overline{n_k}. \tag{17}$$

The n_k denote orbital occupation numbers in the N-electron HF ground state $|\Phi_0^N\rangle$. $G(\omega)$ is related to the self-energy $\Sigma(\omega)$ by the Dyson equation

$$G(\omega)=G^0(\omega)+G^0(\omega)\Sigma(\omega)G(\omega). \tag{18}$$

$G^0(\omega)$ is the free (or HF) Green function. The self-energy $\Sigma(\omega)$ can be written as a sum of a static (ω-independent) part $\Sigma(\infty)$ and a dynamic (ω-dependent) part $M(\omega)$. The dynamic self-energy part $M(\omega)$ consists of two parts which are analytic in the upper and lower complex ω plane, respectively. They are associated with excitations of $N+1$ and $N-1$ particles, respectively.

A general construction scheme, referred to as ADC(n) (algebraic diagrammatic construction accurate to the order n) of perturbation theory in the residual electron-electron interaction (residual beyond the HF approximation) has been developed by Schirmer, Cederbaum, and Walter.[31] This scheme is designed to derive systematically infinite partial summations for $M(\omega)$ complete through a finite order of perturbation theory. In the following we present the essential ingredients of the ADC(n) concept and refer for a more comprehensive discussion of this approach to Ref. 31. The basic point of the ADC method is that the exact self-energy part $M(\omega)$ can be given by the simple algebraic form

$$M_{pq}(\omega)=U_p^{\dagger}(\omega I-K-C)^{-1}U_q\,. \tag{19}$$

In Eq. (19), U_p denotes a constant vector of modified (effective) coupling amplitudes for the orbital p. I is a unit matrix and K and C are constant Hermitian matrices, the latter being referred to as the matrix of modified (effective) interaction. The configuration space for these matrices is given by the physical excitations of $N\pm1$ particles, excluding the 1 hole $(1h)$ and 1 particle $(1p)$ configurations. More precisely, the configuration space for the $(N+1)$ particle case of $M(\omega)$ is given by the $2p1h$, $3p2h$,... configurations (with respect to the HF ground-state configuration), whereas the $2h1p$, $3h2p$,... configurations are required for the $(N-1)$ particle case.

The effective quantities U_p and C are determined by perturbation expansions

$$U_p=U_p^{(1)}+U_p^{(2)}+\dots, \tag{20}$$

$$C=C^{(1)}+C^{(2)}+\dots, \tag{21}$$

each series starting with a first-order contribution. The matrix K is a diagonal matrix of zeroth-order (HF) excitation energies, e.g.,

$$K_{jkl,jkl}=-\epsilon_j+\epsilon_k+\epsilon_l \quad \text{with} \quad n_j\overline{n_k n_l}=1, \tag{22}$$

$$K_{ijklm,ijklm}=-\epsilon_i-\epsilon_j+\epsilon_k+\epsilon_l+\epsilon_m \quad \text{with} \quad n_i n_j\overline{n_k n_l n_m}=1, \tag{23}$$

for the $2p1h$ and $3p2h$ space, respectively.

A well-defined approximation $M(\omega;n)$ complete to the nth order of perturbation theory is obtained by comparing the ADC form

$$M_{pq}(\omega;n)=U_p^{\dagger}(n)[\omega I-K-C(n)]^{-1}U_q(n), \tag{24}$$

with the diagrammatic perturbation series up to the nth order

$$M_{pq}(\omega;n)=\sum_{\nu=2}^{n} M_{pq}^{(\nu)}(\omega)+O(n+1), \tag{25}$$

and by requiring that $M_{pq}(\omega;n)$ is exact up to the nth order. It is demonstrated in Ref. 31 that this requirement enables a unique construction of the quantities $U_p(n)$ and $C(n)$ in the nth order ADC form.

The static self-energy part can be obtained by a contour integration of the Green function in the upper half plane, which leads then to an equation containing the HF Green function, the dynamic self-energy, and the static self-energy which has to be solved self-consistently.[31] The following states the content of the ADC(3) approach in simple words: in the ADC(3) method one approximates the $2h$-$1p$ interaction of the second-order self-energy diagram by the sum of the $1h$-$1h$ and $1h$-$1p$ interactions within the framework of the random-phase approximation 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 should yield reliable ionization energies provided that the basis set is of sufficient quality.[32,33] In the inner valence region, main line energies and intensities are calculated accurately to the third order in the electron-electron interaction but satellite lines only accurately to the 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. 31–33 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[32,33] but also for several model molecules (adsorbates) and related charge-transfer systems.[20,34–39]

The ARUPS studies show that the molecules are adsorbed with their molecular plane essentially parallel to the surface and the C-C axis preferentially oriented along the rows ([110] direction) of the substrate [in the case of C_2H_4/Ni(110)].[18,19] Moreover, the symmetry of the adsorption complex C_2H_4/Ni(110) is only C_1, possibly due to a low-symmetry adsorption site and/or some twisting of the adsorbed molecule.[18,19] As stated already, the comparison of the ARUPS data to the corresponding cluster results does not allow any discrimination between the two main adsorption geometries, π or di-σ.[18,19] The calculated bonding energies favor the π coordination versus the di-σ coordination,[19] in contrast to the experimental determination stated in the Introduction. In the present work we take the minimal cluster model NiC_2H_4 which represents the π-bonded geometry. The distance of the C_2H_4 molecule above the Ni atom was set at 3.78 a.u. This value is very close to the one determined experimentally by Bao *et al.* from their studies on C_2H_2/Ni(111). They obtained a NiC distance of 3.74 a.u.[40] The geometry of C_2H_4 is taken to be the same one as that of the free molecule. We use basis sets of Cartesian Gaussian functions on the atoms to expand the MO's. For Ni the $[14s,9p,5d]$ basis set of Wachters for Ni (Ref. 41) is enlarged by two p-type functions with exponential parameters $\alpha_p=0.24$, 0.08 to describe the $4p$ orbital of Ni and the diffuse $3d$ function of Hay ($\alpha_d=0.1316$).[42,43] The two s-type functions with smallest exponential parameters are replaced by functions with $\alpha_s=0.32$, 0.08 to take into account the orbital contraction upon molecular bonding. The final basis set is $[14s,11p,6d]$ contracted to $(7s5p3d)$ (contraction number 3 of Wachters). The C basis set is taken from Salez and Veillard,[44] $[11s,7p,1d]$ contracted to $(5s3p1d)$. The exponential parameter of the d-type function is $\alpha_d(C)=0.6$.

TABLE I. Calculated and experimentally observed ionization energies and calculated pole strengths (⩾0.02) for C_2H_4 (all energies are in eV).

		OVGF		ADC(3)		
Level	KT	IP	I	IP	I	Exp.
$1b_{2u}$	10.20	10.39	0.92	10.46	0.91	10.51[a]
$1b_{2g}$	13.74	13.05	0.91	13.08	0.91	12.85[a]
				25.87	0.02	
$3a_g$	15.88	14.69	0.91	14.86	0.90	14.66[a]
$1b_{3u}$	17.45	16.12	0.87	16.14	0.79	15.87[a]
				17.75	0.06	
				22.59	0.07	
$2b_{1u}$	21.45	19.55	0.85	19.28	0.65	19.23[a]
				20.28	0.14	
				25.01	0.07	
$2a_g$	28.02			22.77	0.02	
				23.70	0.39	23.65[b]
				24.65	0.12	
				27.31	0.20	27.39[b]
				29.60	0.05	

[a] Reference 55.
[b] Reference 56.

The H basis set is taken also from Salez and Veillard,[44] $[6s,1p]$ contracted to $(3s1p)$. The calculation of the SCF wave functions and two-electron integral matrix elements has been performed with a standard program package MOLCAS-2 for the calculation of Hartree-Fock and correlated wave functions using basis set expansion techniques.[45] In the ADC(3) Green-function calculations for NiC_2H_4 the lowest 69 virtual orbitals and all occupied orbitals, except for the core orbitals, were taken into account. This leads to matrices of dimension of around 15 000. The eigenvalues and eigenfunctions were extracted with a block Davidson method.[46] For each symmetry about 60 eigenvalues and eigenvectors were calculated.

We performed also calculations on $Ni_2C_2H_4$. The $Ni_2C_2H_4$ cluster was taken to present the di-σ configuration and consisted of two Ni atoms separated by the bulk internuclear distance (4.71 a.u.) bonded symmetrically to an ethylene molecule with the C-C axis parallel to the Ni-Ni axis. The ethylene was distorted [see Sec. III B]. However, because of a large number of degeneracies of metal levels and two-hole-one-particle configurations, which leads to a physically unacceptable redistribution of spectral intensities over many lines already close to the ionization threshold, $Ni_2C_2H_4$ does not seem to be an appropriate model for the di-σ configuration.

III. RESULTS AND DISCUSSIONS

In Tables I–V we summarize the hole spectral functions of C_2H_4, distorted C_2H_4, NiC_2H_4 and NiC_2H_4 with distorted C_2H_4. We list the Koopmans' theorem (KT) energies, the ionization energies (IP), the relative spectral intensities (I) and the experimental ionization energies.[18,19] The ARUPS measurements were performed for two differently prepared dilute layers with a coverage of about one half of the saturation value (0.25 ML). This allows one to investigate the

TABLE II. Calculated ionization energies and pole strengths (⩾0.02) of the distorted C_2H_4 and the experimentally observed ionization energies of C_2H_4 adsorbed on a Ni(110) surface (all energies are in eV). 5.98 eV is added to the experimental ionization energies listed in Refs. 5, 18, 19 (see text). The levels inside brackets are the corresponding levels of free C_2H_4.

Level	KT	IP	I	Exp.
$4a_1$ $(1b_{2u})$	9.86	10.12	0.86	10.98[a]
$1a_2$ $(1b_{2g})$	13.11	12.23	0.90	12.18[a]
$3a_1$ $(3a_g)$	14.53	13.83	0.89	13.98[a]
$1b_2$ $(1b_{3u})$	17.65	13.64	0.03	
		16.02	0.67	15.18[a]
		17.85	0.13	
		19.15	0.02	
		20.65	0.07	
$2b_1$ $(2b_{1u})$	21.14	17.89	0.04	
		18.68	0.42	18.68[a]
		19.92	0.31	
		21.85	0.03	
		22.02	0.03	
$2a_1$ $(2a_g)$	28.49	22.21	0.10	
		23.42	0.07	
		24.67	0.06	
		25.64	0.26	23.33[b]
		26.20	0.10	
		27.23	0.03	
		27.65	0.03	
		28.01	0.02	
		30.98	0.02	

[a] References 18 and 19.
[b] Reference 5.

TABLE III. Calculated ionization energies and pole strengths ($\geqslant 0.02$) of NiC_2H_4 (without distortion of the molecule) and the experimentally observed ionization energies of C_2H_4 adsorbed on a Ni(110) surface (all energies are in eV). 7.93 eV is added to the experimental ionization energies listed in Refs. 18, 19 (see text).

Level	KT	IP	I	Exp
$5a_1$	5.13	5.55	0.88	
		11.37	0.02	
$4a_1$ ($1b_{2u}$)	13.50	12.76	0.02	
		12.93	0.77	12.93
		13.92	0.04	
$2a_2$ ($1b_{2g}$)	15.54	13.97	0.58	14.13
		14.38	0.03	
		14.58	0.25	
$3a_1$	16.81	12.93	0.05	
		13.92	0.62	
		14.14	0.10	
		15.73	0.02	
		16.04	0.06	
		16.35	0.02	
$2b_1$	17.49	14.00	0.36	
		14.13	0.22	
		14.41	0.15	
		14.53	0.02	
		17.50	0.02	
		18.20	0.05	
$1a_2$	17.88	13.97	0.22	
		14.58	0.43	
		14.88	0.04	
		15.77	0.05	
		16.51	0.02	
		16.94	0.02	
		17.18	0.02	
		18.25	0.05	
$2a_1$ ($3a_g$)	18.03	13.92	0.04	
		15.38	0.06	
		16.04	0.03	
		16.35	0.69	15.93
		16.82	0.03	
$1b_2$ ($1b_{3u}$)	19.57	17.27	0.07	
		17.32	0.07	
		17.61	0.02	
		17.83	0.08	
		17.90	0.51	17.13
		18.04	0.04	
$1a_1$	20.56	14.66	0.02	
		15.38	0.15	
		16.82	0.03	
		17.53	0.03	
		17.73	0.26	
		18.10	0.04	
		18.41	0.23	
		18.73	0.02	
		19.10	0.03	
$1b_1$ ($2b_{1u}$)	23.62	20.60	0.03	
		20.75	0.08	
		20.82	0.06	
		20.94	0.04	
		21.03	0.48	20.63
		22.05	0.03	
		22.84	0.02	

electronic structure of ethylene on Ni(110) at coverages where lateral interactions in the adsorbed layer are much reduced from those occurring in the saturated $c(2\times4)$ layer.[18,19] We use the data from the dilute layers. The Hartree-Fock (HF) eigenvalues have no physical relevance because of the neglect of ground-state and final-state correlation (fluctuation) and relaxation in the final state. However, the eigenvalue shift due to a change of environment (such as the removal of the metal atom to infinity) should indicate the initial-state (chemical) shift (neglecting the ground-state correlation energy shift). We begin with the valence-level ionization spectrum of the free C_2H_4 molecule.

A. C_2H_4

For C_2H_4, we present in addition to the other data also the hole spectral functions calculated by the outer valence Green function (OVGF) method which is simpler than the ADC(3) method from a computational point of view, but it is only suited for outer valence ionizations (with satellite structure absent or negligible). The method is correct to the third order in the perturbation expansion of the self-energy.[32,33] Both methods provide excellent agreement with the experimental data. The present results are in much better agreement with experimental data, in comparison to the results by Cederbaum *et al.*,[47] who calculated the spectrum by the method employed in the present work but used a smaller basis set. The interpretation of the spectrum by Rösch *et al.*,[48] who calculated the ionization energies by the SCF X-α scattered-wave method, was adapted by Demuth and Eastman[7] for an interpretation of the adsorbate spectrum. However, the assignment for the first two ionization levels by Rösch *et al.* differs from the present one. The assignment of the peaks by Rösch *et al.* is $1b_{2g}$, $1b_{2u}$, $3a_g$, $1b_{3u}$, $2b_{1u}$, and $2a_g$ in the order of the increasing binding energy, while the present one is $1b_{2u}$, $1b_{2g}$, $3a_g$, $1b_{3u}$, $2b_{1u}$, and $2a_g$ which agrees with experiment.

B. ''Distorted'' C_2H_4

In order to study the effects of the geometrical distortion of C_2H_4 due to the adsorption on a metal surface, we calculated also the hole spectral functions of the distorted C_2H_4, taking the geometrical configuration of the molecule adsorbed on a Ni metal surface.[49] The calculated IP's and the pole strengths are listed in Table II, together with the KT energies. First, we compare the KT energy separations with the experimentally observed ionization energy separations of the adsorbate, assuming that the ''free molecule approximation'' is valid, namely, the relaxation and correlation energies are independent of the environmental (or geometrical) changes. Aligning the $2a_g$ level KT energy of C_2H_4 to the $2a_1$ level KT energy of the distorted C_2H_4, we obtain the KT binding-energy shifts (distorted molecule - free molecule) of -0.78, -0.27, -1.82, -1.1, and -0.81 eV for the $2b_1$, $1b_2$, $3a_1$, $1a_2$, and $4a_1$ levels, respectively. Aligning the $2a_g$ level binding energy of C_2H_4 to the first a_1 valence-level binding energy of the adsorbed C_2H_4, we obtain the experimental binding-energy shifts (adsorbed molecule - free molecule) of -0.23, -0.37, -0.36, -0.35, and 0.81 eV for the $2b_1$, $1b_2$, $3a_1$, $1a_2$, and $4a_1$ levels, respectively. The KT energy of the $4a_1$ level becomes smaller with the distortion

TABLE IV. Calculated ionization energies and pole strengths (OVGF results) of NiC_2H_4 (without distortion of the molecule) and the experimentally observed ionization energies of C_2H_4 adsorbed on a Ni(110) surface (all energies are in eV). 8.31 eV is added to the experimental ionization energies listed in Refs. 18, 19 (see text).

Level	IP	I	Exp.
$1b_{2u}$	13.31	0.82	13.31
$1b_{2g}$	14.38	0.90	14.51
$3a_g$	16.31	0.89	16.31
$1b_{3u}$	17.81	0.84	17.51

of the molecule, while the binding energy of the adsorbed molecule becomes larger in comparison to the free molecule case. There is no obvious correlation between the chemical shifts and the observed binding energy shifts (binding-energy separation changes). This is also the case when we align the $1b_{3u}$ level KT energy of C_2H_4 to the $1b_2$ level KT energy of the distorted C_2H_4 (as Demuth and Eastman[6,7] did). We obtain 0.27, −0.51, −1.55, −0.83, and −0.54 eV for the $2a_1$, $2b_1$, $3a_1$, $1a_2$, and $4a_1$ levels, respectively, while the experimental energy shifts are 0.37, 0.14, 0.01, 0.02, and 1.16 eV, respectively. In the present work we took the experimentally determined geometry for the distorted molecule. It appears that the KT eigenvalue shifts due to the distortion, which are not negligible, do not provide any reasonable description of the changes in the ionization energy separations from the free molecule to the adsorbate.

To study the effects of the correlation and relaxation we compared the calculated spectral functions with the experimental valence photoemission spectrum of the adsorbate. 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 spectrum of the adsorbate is made simply by adding 5.98 eV to the adsorbate data, to align the $2b_{1u}$ peak of the adsorbate spectrum to the $2b_1$ level. The energy positions of the $4a_1$, $1b_2$, and $2a_1$ levels are not well described. The energy difference between the KT eigenvalue and the calculated ionization energy of the main line (the largest spectral intensity line) is a sum of the ground-state correlation and relaxation energy shifts. For the sake of simplicity, we call these energy shifts the final-state energy shifts. Strictly speaking the HF orbital (KT) energies have no physical relevance because the HF (mean field) method neglects the electron correlation in the ground state. Consequently, 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. These quantities are useful ones for the interpretation of experimental spectra. The final-state energy shifts for the $4a_1$, $1a_2$, $3a_1$, $1b_2$, $2b_1$, and $2a_1$ ionization levels of the ''distorted molecule'' are −0.26, 0.88, 0.7, 1.63, 2.46, and 2.85 eV, respectively. The energy shifts for the $1b_{2u}$, $1b_{2g}$, $3a_g$, $1b_{3u}$, $2b_{1u}$, and $2a_g$ ionization levels of C_2H_4 are, −0.26, 0.66, 1.02, 1.31, 2.17, and 4.32 eV, respectively. Except for the $2a_1$ ($2a_g$) level, the changes in the final-state energy shifts due to the geometrical distortion of the molecule are very small. In other words the magnitude of the intraligand relaxation energy shift is rather independent of the distortion. For the $2a_1$ ($2a_g$) level the one-electron (even quasiparticle) picture breaks down due to the intraligand excitations. Thus the meaning of the final-state energy shifts becomes ambiguous. The initial-state energy shifts from the free molecule to the distorted molecule for the $1b_{2u}$, $1b_{2g}$, $3a_g$, $1b_{3u}$, $2b_{1u}$, and $2a_g$ levels are 0.34, 0.63, 1.35, −0.2, 0.31, and −0.47 eV, respectively. The energy shift for the $3a_g$ level is much larger than the shifts for the other ionization levels. As the KT energy shifts are also rather small for these other levels we conclude that, in general, the $1h$-$2h1p$ energy separations and the magnitude of the coupling matrix elements do not change significantly from the free molecule to the distorted one. This explains the similarity in the spectral features (intensities, satellite line separations) between the spectrum of the free molecule and the one of the distorted molecule. Except for the $2a_g$ level, the energy shifts from the free to the distorted molecule are dominantly due to the initial-state energy shifts. However, as already pointed out, these energy shifts do not explain the energy shifts of the $1b_{2u}$ level upon chemisorption. Thus even when the final-state energy shifts are taken into account, the geometrical distortion of the molecule upon chemisorption does not explain the observed changes in the ionization energy separations which occur upon adsorption. It is necessary to examine the effects of the metal-ligand bonding (the presence of metal surface) on the spectrum of the chemisorbed molecule.

There is one more point we should mention here as it plays a role later on. If we compare the pole strengths of the main lines between the undistorted and the distorted C_2H_4 we note that the pole strengths decrease significantly for the fourth and fifth level in going from the undistorted molecule to the distorted one. Later on we shall find this effect also for NiC_2H_4 when we introduce the distortion of the C_2H_4 molecule. This effect is thus a local effect of the distortion of the ethylene allowing via the symmetry reduction in the free molecule the mixing of more configurations. For NiC_2H_4 we have to conclude that it is not an effect introduced by the addition of the metal atom, but also a local effect in the ethylene part of the complex. Here there is certainly no symmetry reduction if we compare the undistorted with the distorted case of NiC_2H_4. Thus the effect has to do with the local changes in the bonding.

C. NiC_2H_4

We begin with NiC_2H_4 where the geometry of C_2H_4 is the same as the one of the free molecule (see Table III). A comparison with the experimental valence spectrum of the adsorbate is made by adding 7.93 eV to the adsorbate data to align the $1b_{2u}$ peak (observed at 5.0 eV below the Fermi level[18,19]) to the $4a_1$ level. The calculated ionization energies of NiC_2H_4 are shifted by a fairly constant amount from the experimentally observed values for C_2H_4 on a Ni metal surface. This energy shift includes the work function, which is of the order of 6 eV for a Ni metal surface. The remainder of about 2 eV is due to the change of the environment from a single metal atom to a metal surface. This change induces the extra initial-state energy shift of the ligand levels. As stated below, the initial-state energy shift for the ligand levels (except $1b_{2u}$) from free C_2H_4 to NiC_2H_4 is about 2 eV which will almost be canceled out by this extra initial-state energy shift. This is expected because the ligand level energies (except for the one which involves in metal-ligand bonding) should not be strongly influenced by the presence of a metal surface. As stated below, the extra polarization of the surrounding metal atoms is expected to be small. The extra final-state energy shift is expected to be small.

Before we discuss the ADC(3) results, we discuss briefly the OVGF data. A comparison with the experimental valence spectrum of the adsorbate is made by adding 8.31 eV to the adsorbate data to align the $1b_{2u}$ peak to the $4a_1$ level. The relevant data are given in Table IV. The final-state energy shifts for the $1b_{2u}$, $1b_{2g}$, $3a_g$, and $1b_{3u}$ levels of NiC_2H_4 are 0.19, 1.16, 1.72, and 1.76 eV, respectively. The changes in the final-state energy shifts are 0.38, 0.47, 0.53, and 0.43 eV, respectively. The increase is fairly independent of the levels. The initial-state energy shifts from the free molecule to NiC_2H_4 for these levels are -3.3, -1.8, -2.15, and -2.12 eV, respectively. The sums of the initial-state energy shifts and the changes in the final-state energy shifts are then -2.92, -1.33, -1.62, and -1.69 eV, respectively. The initial-state energy shifts dominate the C_2H_4 to NiC_2H_4 ionization energy shifts. The experimental $1b_{2u}-1b_{2g}$ ionization energy separation of the adsorbate is 1.2 eV, while the value obtained by the OVGF method is 1.07 eV and by the ADC(3) method 1.04 eV. The OVGF calculation suggests that the separation energy shift of the $1b_{2u}$ level is mainly due to the initial-state energy shift.

The final-state energy shifts obtained for the $4a_1$, $2a_2$, $2a_1$, $1b_2$, and $1b_1$ levels of NiC_2H_4 by the ADC(3) method (see Table V) are 0.57, 1.57, 1.68, 1.67, and 2.59 eV, respectively. The final-state energy shifts for the corresponding levels of the free molecule are -0.26, 0.66, 1.02, 1.31, and 2.17 eV. The changes in the final-state energy shifts from the free molecule to NiC_2H_4 are for the same levels 0.83, 0.91, 0.66, 0.36, and 0.42 eV, respectively. The final-state energy shifts for the ligand ionization levels increase, when the molecule binds to a Ni atom. The increases are due to the availability of the metal-ligand CT screening channels. The initial-state energy shifts from the free molecule to NiC_2H_4 for the $1b_{2u}$, $1b_{2g}$, $3a_g$, $1b_{3u}$, and $2b_{1u}$ levels are -3.3, -1.8, -2.15, -2.12, and -2.17 eV, respectively. The sums of the initial-state energy shifts and the changes in the final-state energy shifts are then -2.47, -0.89, -1.49, -1.76, and -1.75 eV, respectively. The initial-state energy shifts dominate the C_2H_4 to NiC_2H_4 ionization energy shifts. Aligning the experimental ionization energy of the adsorbate and the one of the free C_2H_4 molecule at the $2b_{1u}$ level, the experimental free molecule to adsorbate ionization energy shifts for the first four ligand levels are -1.02, 0.12, 0.13, and 0.14 eV, respectively, while the theoretical predictions (with respect to the experimental ionization energies of free C_2H_4) are -0.62, 0.68, 0.11 and -0.23 eV, respectively. The predictions by the distorted molecule are -0.16, 0.07, 0.28, and -0.7 eV. The experimental $1b_{2u}-1b_{2g}$ ionization energy separation of the adsorbate is 1.2 eV, while the one of NiC_2H_4 is 1.04 eV and the one of the distorted molecule is 2.11 eV. The distorted molecule approximation, in particular, fails to provide a reasonable description of the shift in the ionization energy separation of the $1b_{2u}$ level in going from the free molecule to the adsorbate, in contrast to the present single metal-atom model. The present calculation suggests that the separation energy shift of the $1b_{2u}$ level is mainly due to the initial-state energy shift. It should be noted that it is the free molecule-adsorbate initial-state energy shift and not the free molecule to distorted molecule initial-state energy shift which provides the separation energy shift.

Next we discuss the hole spectral function of NiC_2H_4 where the geometry of C_2H_4 is the same one as of the distorted C_2H_4 discussed above (see Table V). The final-state energy shifts obtained for the $4a_1$, $2a_2$, $2a_1$, $1b_2$, and $1b_1$ levels of NiC_2H_4 (with distortion of the adsorbate) by the ADC(3) method are 0.79, 1.63, 2.86, 1.99, and 2.57 eV, respectively. The final-state energy shifts of the corresponding levels of the distorted molecule are -0.26, 0.88, 0.7, 1.63, and 2.46 eV, respectively. The changes in the final-state energy shifts by bonding to a Ni metal atom for the same levels are 1.05, 0.75, 2.16, 0.36, and 0.11 eV, respectively. The corresponding changes for the free molecule are 0.83, 0.91, 0.66, 0.36, and 0.42 eV. The substantial differences in the changes for the $3a_g$ and $2b_{1u}$ levels are due to the ambiguity of the final-state energy shifts, because the one-electron picture for these two levels breaks down more severely in the present case than in the case with the undistorted C_2H_4. The relevance of this fact has been discussed above. This comparison indicates that the final-state energy shifts are rather independent of the distortion of the molecule. The initial-state energy shifts from the distorted molecule to NiC_2H_4 (with distortion of the adsorbate) for the first five ligand levels are -2.88, -1.81, -3.31, -1.29, and -2.10 eV, respectively, while the corresponding shifts for the free molecule [free molecule to NiC_2H_4 (without ‘‘distortion’’)] are -3.3, -1.8, -2.15, -2.12, and -2.17 eV, respectively. There are large changes for the $3a_g$ and $1b_{3u}$ levels. If we consider the initial-state energy shifts from the free molecule to NiC_2H_4 (with distortion) the corresponding shifts are -2.54, -1.18, -1.96, -1.49, and -1.79 eV, respectively. The changes in the initial-state energy shifts with respect to the nondistorted free molecule from NiC_2H_4 (without ‘‘distortion’’) to NiC_2H_4 (with distortion) for the same levels are 0.76, 0.62, 0.19, 0.63, and 0.38 eV, respectively. The changes are rather uniform except for the $3a_g$ and $2b_{1u}$ levels. Thus the relative level positions in the ground state do not change significantly. The changes in the final-state energy shifts (with respect to the undistorted free molecule) from NiC_2H_4 (without distortion) to NiC_2H_4 (with distortion) for the same levels are 0.22, 0.06, 1.18, 0.32, and -0.02 eV, respectively. The changes are small except for the $3a_g$ level. The value for the $3a_g$ level is ambiguous because of the severe breakdown of the one-electron picture for this level of NiC_2H_4 (with distortion) (the main line spectral intensity is 0.29) in comparison to the one of NiC_2H_4 (without distortion) (here the main line spectral intensity is 0.69). Thus this shows also that the final-state energy shifts of NiC_2H_4 are rather independent of the distortion of the adsorbed molecule. One concludes that both the initial- and the final-state energy shifts are rather independent of the distortion of the adsorbate. Aligning the theoretical ionization energies of NiC_2H_4 (with distortion) to the experimental one of the free C_2H_4 molecule at the $2b_{1u}$ level, the theoretical values of the ionization energy shifts for the first four ligand levels are 0.0, 1.0, 1.12, and 0.36 eV, respectively, while the experimental

TABLE V. Calculated ionization energies and pole strengths (⩾0.02) of NiC_2H_4 with the distorted C_2H_4 and the experimentally observed ionization energies of C_2H_4 adsorbed on a Ni(110) surface (all energies are in eV). 6.95 eV is added to the experimental ionization energies listed in Refs. 18, 19 (see text).

Level	KT	IP	I	Exp.
$5a_1$	5.00	5.21	0.86	
		10.97	0.02	
$4a_1$ $(1b_{2u})$	12.74	10.97	0.07	
		11.95	0.76	11.95
$2a_2$ $(1b_{2g})$	14.92	12.56	0.19	
		13.29	0.48	13.15
		13.51	0.20	
$3a_1$	16.59	13.86	0.58	
		14.98	0.09	
		15.82	0.02	
		15.87	0.05	
		16.03	0.02	
		16.13	0.05	
$2b_1$	17.72	13.55	0.02	
		14.16	0.69	
		14.30	0.03	
		15.36	0.02	
		17.83	0.02	
		18.61	0.04	
$2a_1$ $(3a_g)$	17.84	13.86	0.20	
		14.85	0.02	
		14.98	0.29	14.95
		15.25	0.02	
		15.40	0.02	
		16.03	0.07	
		16.13	0.20	
$1a_2$	18.21	14.21	0.10	
		14.44	0.56	
		16.42	0.13	
		18.73	0.04	
$1b_2$ $(1b_{3u})$	18.94	16.24	0.30	
		16.95	0.37	16.15
		17.03	0.08	
		17.48	0.03	
		19.48	0.02	
$1a_1$	21.10	14.98	0.05	
		15.25	0.05	
		16.13	0.02	
		17.21	0.04	
		17.96	0.03	
		18.12	0.12	
		18.24	0.09	
		18.47	0.34	
		18.69	0.03	
		19.40	0.02	
$1b_1$ $(2b_{1u})$	23.24	19.44	0.05	
		19.74	0.02	
		20.07	0.10	
		20.20	0.04	
		20.35	0.03	
		20.50	0.07	
		20.67	0.33	19.65
		22.04	0.02	
		22.17	0.03	
		22.38	0.02	

ones are −1.02, 0.12, 0.13, and 0.14 eV. NiC_2H_4 (without distortion) provides −0.62, 0.68, 0.11, and −0.23 eV, respectively. At a first glance the agreement seems to be very poor for NiC_2H_4 (with distortion). However, when we align the ionization energies at the $3a_g$ level, the theoretical ionization energy shifts for the first four ligand levels (except the $3a_g$ level) are −1.12, −0.12, −0.76, and −1.12 eV, respectively, while the experimental ones are −1.15, −0.01, 0.01, and −0.13 eV. For NiC_2H_4 (without distortion) they are −0.73, 0.57, −0.34, and −0.11 eV, respectively. The former aligning provides worse agreement for NiC_2H_4 (with distortion) because of the much more severe breakdown of the one-electron picture of ionization for the $1b_{3u}$ and $2b_{1u}$ levels, in comparison to NiC_2H_4 (without distortion). Except for the first two ligand ionization energy levels, the breakdown of the one-electron picture of ionization is very severe. Thus the NiC_2H_4 model with the distortion may not be an as suitable model as NiC_2H_4 without the distortion, except for the first two ligand levels. The $1b_{2u}-1b_{2g}$ ionization energy separation for NiC_2H_4 (with distortion) is 1.34 eV, while the experimental one is 1.2 eV and the one of NiC_2H_4 (without distortion) is 1.04 eV. The effect of the geometrical distortion of the molecule on the ionization energy separation shift of the $1b_{2u}$ level is small. Thus the shift of the $1b_{2u}$ level is due mainly to the metal-ligand bonding and not to the distortion of the molecule.

In order to study the valence-level photoemission spectrum of C_6H_6 on a Ni metal surface, we performed the same type of calculation for NiC_6H_6 as done here.[57] It is found that the tilting of the C-H bonds out of the molecular plane and away from the metal has only a small influence on the spectrum (maximally a difference of 0.2 eV is calculated). Thus it is expected that the molecular distortion upon chemisorption does not influence the spectrum in a significant way. Both initial- and final-state energy shifts are hardly influenced by the distortion of the molecule.

Recently, Weinelt *et al.*[18,19] studied experimentally and theoretically the ground-state electronic structure of ethylene on a Ni(110) surface. They calculated the electronic structure, by performing LCGTO-LDF model cluster calculations for $Ni_{24}(C_2H_4)_2$ and $Ni_{25}(C_2H_4)_2$ for the di-σ and the π geometry, respectively. Similar electronic level structures were found for both chemisorption geometries. In an approximation (by which it is possible to save the computational effort of the SCF calculation for each ionic state) they compared the ground-state level energies for both geometries to their ARUPS data. This procedure is only applicable if the relaxation of the levels is rather uniform. They claimed that this requirement is fulfilled satisfactorily if the spatial characteristics of the orbitals in question are sufficiently similar. However, the characteristics of the bonding orbitals (which are going to be involved in the metal-ligand bonding) may differ significantly from other ligand levels. As a result the degree of the metal-ligand charge-transfer screening may differ. The present study shows that this is the case. Weinelt *et al.* aligned the ground-state energy levels of the free molecule and the large π-type (di-σ-type) cluster model at the $1b_{3u}$ level. They found that the π orbital $(1b_{2u})$ derived levels are shifted on the average by 1.7 eV for both geometries. The remaining ligand levels are shifted by less than 0.2 eV for the π model and between −0.3 and 0.2 eV for the di-σ

model. If we make the same alignment procedure for the present single-metal-atom model without distortion of the molecule then the $1b_{2u}$ is shifted by 1.2 eV and the remaining ligand levels are hardly shifted. Then the relative shift of the $1b_{2u}$ level is 1.2 eV, while the $Ni_{25}(C_2H_4)_2$ model provides 1.5 eV (1.7 eV−0.2 eV=1.5 eV). Although the latter shift includes the combined effect of the distortion of the molecule and the mixing with the substrate orbitals, the agreement is good. For NiC_2H_4 with distortion of the molecule, the $1b_{2u}$ level is shifted by 1.1 eV, while the remaining ligand levels are shifted by amounts of between −0.5 and 0.3 eV. The magnitude of the relative level shift agrees well with that of the larger cluster models.

As stated in the beginning of this section, an extra initial-state energy shift of the ligand levels, which is about 2 eV (in the absence of distortion), is required to align the experimental data of the adsorbate in addition to the work function. This 2-eV shift which moves all the ligand levels equally is somehow an artificial shift caused by a single metal atom. Except for this extra shift, the present single metal-atom model seems to be able to describe the ground-state levels rather well. The study by Weinelt *et al.* shows that the initial-state shift is rather independent of geometrical changes in the adsorption site. In previous work on CO adsorption on a Pd (Pt) metal surface,[20] we have shown that the final-state energy shift is fairly independent of the number of metal atoms to which the molecule binds. The final-state energy shift is also fairly independent of geometrical changes of the adsorption site. Thus we expect that the final-state energy shift will not change significantly with an increase in the number of metal atoms. In spite of the much more complicated adsorption geometries of hydrocarbon molecules (such as C_2H_2, C_2H_4, and C_2H_6) on a Ni metal surface, the success of the single metal-atom cluster models for the ionized hydrocarbon adsorbates probably arises from the localized polarization of the metal surface in response to the ionized adsorbate.

It is not the geometrical distortion of the molecule but mainly the metal-molecule bonding which provides the changes in the ionization energy separations from the free molecule to the adsorbate. From the present investigation it also emerges that Demuth's approach fails because of the neglect of the metal-ligand CT screening. As it is the metal-ligand bonding and not the distortion of the molecule which mainly provides the changes in the separations of the ionization energies 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 necessary for this purpose.

It is informative to make a comparison between the free molecule spectrum and the NiC_2H_4 spectra both obtained by the ADC(3) method. First let us consider the case of NiC_2H_4 without distortion of the adsorbed molecule. In contrast to the case of the free molecule, where the one-particle picture of the ionization is valid for the first five ionization levels, for the ligand ionization levels of NiC_2H_4 ($4a_1$, $2a_2$, $2a_1$, $1b_2$, and $1b_1$ levels) the initial single hole configuration interacts strongly with the $2h1p$ configurations so that a substantial part of the original strength goes to satellite lines and the one-electron picture of ionization begins to break down for the $1b_2(1b_{3u})$ and $1b_1(2b_{1u})$ levels. The $2h1p$ configurations involve not only the intraligand excitations but also the metal-ligand CT and the intrametal excitations. The latter are found to play a dominant role for the reduction of the original spectral unit strength. One obtains 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. In the present model (in the ground state), the $3a_1$, $2b_1$, $1a_2$, and $1a_1$ metal levels are shifted below the $2a_2$ level. This is unphysical, the presence of these levels below the ligand levels introduces a somewhat artificial splitting of the ligand level main line spectral intensity into several closely spaced lines. For the metal levels (with a small admixture of ligand character) the one-electron picture breaks down except for the $5a_1$ and $3a_1$ levels. When the C_2H_4 molecule is distorted in NiC_2H_4 the breakdown of the one-electron picture becomes much more severe. It begins to break down already for the $1a_2(1b_{2g})$ level. Thus the final-state energy shifts discussed in the previous paragraph become ambiguous for NiC_2H_4 with the distorted adsorbate. However, one should still be able to use the energy separation between the $4a_1(1b_{2u})$ and $1a_2(1b_{2g})$ levels for a comparison.

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. As has been discussed in detail for the case of CO on a Ni metal surface,[20] 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, in general, constant and 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 region.

For the CO adsorption systems and related ones, recent 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.[20,24–29,34–39] In the NiC_2H_4 (undistorted adsorbate) spectrum the main line spectral intensities of the valence levels of the free molecule tend to split by the metal-ligand charge-transfer excitations into a few relatively closely spaced levels. The sum rule holds approximately also in the present case. In our model the metal levels are treated as discrete levels and the band effect such as the broadening of the spectrum is neglected. The introduction of the adsorbate band broadening may influence significantly 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 major features of the energetics of the hole excitations (in the case the poles of the self-energy are well separated). However, when the split levels are located close together, they may converge to a single peak with the spectral intensity equal to the sum of the spectral intensities of the closely 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, the main line intensities are distributed over a few closely spaced line (for the $2a_1$, $1b_2$, and $1b_1$ levels) in the case of NiC_2H_4 without adsorbate distortion. However, when we take into account the band broadening effect, we expect broad peaks of larger spectral intensities for these levels, as in fact observed experimentally. Moreover, 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 [which is neglected in the ADC(3) scheme] may shift the $2h1p$ energy. As a result the satellite line positions are expected to move closer to the main line positions.[20] As a result it is likely that a single prominent peak will be observed.

In order to simulate the band effect, we take into account only the closely spaced satellite lines around the main line and calculate the center of gravity. In the case of NiC_2H_4 (with no distortion of the molecule) we obtain for the $1b_{2u}$, $1b_{2g}$, $3a_g$, $1b_{3u}$, and $2b_{1u}$ levels 12.93 (0.79), 14.16 (0.86), 16.28 (0.81), 17.79 (0.79), and 20.96 (0.69) eV for the main line positions (the values inside the brackets are the spectral intensities). The discrepancies between theory and experiment are (when the $1b_{2u}$ level is aligned) 0.03, 0.35, 0.66, and 0.33 eV, respectively. The agreement is improved in this way. The calculated $1b_{2u}-1b_{2g}$ energy difference is 1.23 eV, while the experimental one is 1.20 eV, the agreement is also improved. Note that the calculated IP and pole strengths are similar to those obtained by the OVGF method.

In the case of NiC_2H_4 (with distortion) for the first five ligand ionization levels we obtain 11.95 (0.76), 13.18 (0.87), 15.01 (0.35), 16.71 (0.78), and 20.47 (0.59) eV, respectively. The discrepancies between theory and experiment are (when the $1b_{2u}$ level is aligned) 0.03, 0.06, 0.56, and 0.82 eV, respectively. The agreement is improved as is the $1b_{2u}-1b_{2g}$ energy difference which is calculated to be 1.23 eV compared to the experimental value of 1.20 eV. However, the effect of the distortion is very small, particularly on the $1b_{2u}-1b_{2g}$ energy difference.

IV. CONCLUSION

In the present work we studied the valence photoemission spectrum of C_2H_4 adsorbed on a Ni metal surface by performing *ab initio* MO many-body calculations of the valence-hole spectral functions of NiC_2H_4. We draw the following conclusions from our calculations.

(i) We obtained an overall good description of the spectrum. The present single metal-atom model represents the π-bonding complex, although the adsorption geometry of C_2H_4 on the Ni(110) surface seems to be more complicated.[18,19] In spite of the simplicity of the present model, it gives a reasonably good description of the ionization of the ligand levels.

(ii) The intraligand relaxation (plus correlation) shifts are rather independent of the distortion of molecular geometry. Thus the assumption on which Demuth's approach is based, namely, that the final-state energy shifts due to the intraligand relaxation are independent of the distortion of the molecule, is true in the present case. However, the KT energy shifts from C_2H_4 to the distorted C_2H_4 which are not negligible do not explain the adsorbate-free molecule ionization energy separation shifts. There are changes in both initial- and final-state energy shifts due to the metal-ligand bonding. The shift of the $1b_{2u}$ level relative to the rest of the ligand levels from the free molecule to the adsorbates is shown to be mainly due to the chemical shift and caused by the metal-ligand bonding, not by the geometrical distortion of the molecule upon chemisorption, which emerges as a secondary effect.

The use of a single metal-atom model already provides a reasonable description of the observed spectral features. In order to provide a proper description of the adsorbate spectrum, it is necessary to take into account the metal-ligand bonding. Not only the intraligand excitations but also the metal-ligand CT excitations and the intrametal excitations are important for the screening processes. One cannot describe the spectral feature changes such as the ionization energy separation changes simply by separating the metal surface from the molecule and trying to simulate the electronic structure of the adsorbate only by distorting the free molecule (rehybridizing orbitals) together with the use of a free molecule approximation. One cannot utilize the photoemission spectrum for the determination of the geometry of the chemisorbed molecule, simply by using a free molecule approximation.

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[1] G. C. Bond, in *Advances in Catalysis* (Academic, New York, 1964), Vol. 15, p. 91.

[2] M. J. S. Dewar, Bull. Soc. Chim. Fr. **18**, C79 (1951); J. Chatt and L. A. Duncanson, J. Chem. Soc. London **1953**, 2939 (1953).

[3] J. E. Demuth, IBM J. Res. Dev. **22**, 265 (1978).

[4] J. E. Demuth, Surf. Sci. **79**, L603 (1978).

[5] J. E. Demuth, Surf. Sci. **84**, 315 (1979).

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

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

[8] N. Rösch and T. N. Rhodin, Phys. Rev. Lett. **32**, 1189 (1974).

[9] T. E. Felter and W. H. Weinberg, Surf. Sci. **103**, 265 (1981).

[10] R. J. Koestner, J. C. Frost, P. C. Stair, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **116**, 85 (1982).

[11] H. Ibach, H. Hopster, and B. Sexton, Appl. Surf. Sci. **1**, 1 (1977).

[12] H. Steiniger, H. Ibach, and S. Lehwald, Surf. Sci. **117**, 685 (1982).

[13] J. A. Horsley, J. Stöhr, and R. J. Koestner, J. Chem. Phys. **83**, 3146 (1985).

[14] R. G. Carr, T. K. Sham, and W. E. Eberhardt, Chem. Phys. Lett. **113**, 63 (1985).

[15] T. K. Sham and R. G. Carr, J. Chem. Phys. **84**, 4091 (1986).

[16] C. E. Anson, B. J. Bandy, M. A. Chesters, B. Keiller, I. A. Oxton, and N. Sheppard, J. Electron Spectrosc. Relat. Phenom. **29**, 315 (1983).

[17] J. A. Stroscio, S. R. Bare, and W. Ho, Surf. Sci. **148**, 499 (1984).

[18] M. Weinelt, W. Huber, P. Zebisch, H.-P. Steinrück, B. Reichert, U. Birkenheuer, and N. Rösch, Phys. Rev. B **46**, 1675 (1992).

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

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

[21] M. Blomberg, U. Brandemark, J. Johansson, P. Siegbahn, and J. Wennerberg, J. Chem. Phys. **88**, 4324 (1988), and references therein.

[22] C. W. Bauschlicher Jr., J. Chem. Phys. **84**, 260 (1986), and references therein.

[23] M. R. Blomberg, U. B. Brandemark, P. E. M. Siegbahn, K. B. Mathiesen, and G. Karlström, J. Phys. Chem. **89**, 2171 (1985).

[24] M. Ohno and P. Decleva, Surf. Sci. **258**, 91 (1991); **269/270**, 264 (1992); Chem. Phys. **156**, 309 (1991).

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

[26] P. Decleva and M. Ohno, J. Chem. Phys. **96**, 8120 (1992).

[27] M. Ohno and P. Decleva, Chem. Phys. **169**, 173 (1993).

[28] M. Ohno and P. Decleva, J. Chem. Phys. **98**, 8070 (1993); Surf. Sci. **284**, 372 (1993); **296**, 87 (1993); Chem. Phys. **171**, 9 (1993).

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

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

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

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

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

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

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

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

[37] 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).

[38] M. Ohno and W. von Niessen, Phys. Rev. A **51**, 1052 (1995).

[39] M. Ohno and W. von Niessen, Surf. Sci. **366**, 209 (1996).

[40] S. Bao, P. Hofmann, K.-M. Schindler, V. Fritzsche, A. M. Bradshaw, D. P. Woodruff, C. Casado, and M. C. Asensio, Surf. Sci. **307–309**, 722 (1994).

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

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

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

[44] C. Salez and A. Veillard, Theor. Chim. Acta **11**, 441 (1968).

[45] 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.

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

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

[48] N. Rösch, W. G. Klemperer, and K. H. Johnson, Chem. Phys. Lett. **23**, 1498 (1973).

[49] The ethylene was distorted. The C-C bond was lengthened to 2.78 a.u., as determined by EELS (Ref. 50). The H atoms were raised above the C-C axis so that the CCH angle is 107° (by EELS data Refs. 51–54). The HCH angle was also fixed at 107° (by EELS data Refs. 51–54).

[50] H. Ibach and S. Lehwald, J. Vac. Sci. Technol. **18**, 625 (1981).

[51] J. E. Demuth, H. Ibach, and S. Lehwald, Phys. Rev. Lett. **40**, 1044 (1978).

[52] J. E. Demuth and H. Ibach, Surf. Sci. **85**, 365 (1979).

[53] J. C. Bertolini and J. Rousseau, Surf. Sci. **83**, 531 (1979).

[54] S. Lehwald and H. Ibach, Surf. Sci. **89**, 425 (1979).

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

[56] M. S. Banna and D. A. Shirley, J. Electron Spectrosc. Relat. Phenom. **8**, 255 (1976).

[57] M. Ohno and W. von Niessen, Phys. Rev. B (to be published).