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Many-body calculations on the valence photoemission of NiCO and $Ni(CO)_4$

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The valence electron spectra of NiCO and $Ni(CO)_4$ are calculated by the third-order algebraic-diagrammatic-construction Green's-function method. We obtain fairly good agreement with experiment. It is shown that the quasiparticle picture of 1π breaks down due to the one-hole/two-hole–one-particle ($1h/2h1p$) charge-transfer (CT) coupling in the bonded system. The dominant role played by the intraligand relaxation in free CO is replaced by the CT relaxation because of a drastic decrease of the intraligand $1h/2h1p$ coupling strength. The CT relaxation is much stronger because of much smaller $1h/2h1p$ energy separations. When the Ni-CO bond length becomes larger (weak coupling), the intensity increase of the satellite and breakdown of the quasiparticle picture also occur for 4σ ionization. This is not due to the change in the CT $1h/2h1p$ coupling strength but due to the smaller CT $1h/2h1p$ energy separations. The present work emphasizes the importance of $1h1h$ and $1h1p$ interactions in the $2h1p$ states. It is shown that, in the case of 5σ and 4σ levels, the $1h$ state is more stable than the $2h1p$ states. Consequently the main line is interpreted as the $1h$ state, where the screening charge resides on the bonding orbital, which is more polarized toward the ligand than in the ground state. The satellites are dominated by $2h1p$ configurations, where the bonding to antibonding shakeup excitations occur. For 1π ionization the strong mixing of $1h$ and $2h1p$ configurations leads to the breakdown of the quasiparticle picture of the ionization, and thus a distinction between main line and satellite line becomes meaningless. The effects of the relaxation and screening in the $2h1p$ states are also discussed. We show the usefulness of the molecular-orbital Green's-function calculations for understanding ionization in adsorbates.

I. INTRODUCTION

During the past decade there has been a great deal of experimental effort in characterizing the nature of the bonding of CO to a metal surface. Different kinds of surface electron spectroscopic techniques are used to ellucidate the nature of the surface and surface-adsorbate bond by probing the electronic structure of the systems. However, the act of probing the electrons perturbs the ground-state distribution, so that different probes measure different properties. It is fairly important to be able to interrelate the information obtained from the different measurement processes. The adsorption of CO onto a metal surface is one of the systems studied extensively by photoemission and with various different theoretical approaches.[1-31]

The adsorbate core-hole spectra show a multipeak structure.[1-9,22] The multipeak structure is interpreted in terms of the screening of the core hole by the charge-transfer screening (CTS) from the substrate.[1,4-17] Conventional pictures of the CTS are (a) in a simplified band picture, the initially nearly unoccupied (2π) adsorbate (ligand) level is pulled below the Fermi level by the (core) hole and becomes partly filled by the electron transfer from the substrate (metal); (b) while in a molecular-orbital (MO) picture the bonding combinations of the 2π ligand orbital with the metal π orbital, which has dominant metal character in the ground state, becomes more CO-like in the (core) ionized state.[15,16] Besides a more or less semantic question, all major works based on different kinds of theoretical approaches tend to agree to interpret the low-binding-energy (BE) peak as a "well-screened" state. The nature of satellites, however, has been controversially discussed in terms of an unscreened final state as well as a local ligand shakeup transition.[11-17] Recent high-resolution core and valence-electron x-ray photoemission spectroscopy (XPS) spectra of CO on Ni(100) surface show a number of newly resolved structures.[29] These structures are interpreted as the shakeup excitations from the $2\pi^*$ screening orbital to the antibonding orbital or Rydberg-like states in the CTS core-hole state.[29] The broader and asymmetric adsorbate core-level lines in comparison to the free molecule are interpreted either as being due to electron-hole pair shakeup excitations within the $2\pi^*$ resonance[30] or due to vibrational excitations in the final core ionized state, giving broadenings of the order of 2 eV.[31]

In the case of the valence spectrum, the spectrum looks more normal than the core hole spectrum; however, there was an ambiguity concerning the assignments of the 5σ and 1π levels which are reversed compared to the case of free CO. These assignments for CO on Ni are by now well established by angular and photon-energy-dependent ultraviolet photoemission spectroscopy (UPS) studies.[18-24] Recently the valence spectrum of CO on Ni(100) recorded by high-resolution XPS show the satellites which have been observed so far only in the weakly coupled system.[29] The interpretation of the valence spectra of the adsorbates is still qualitative in a sense that many authors interpreted the spectra in the same way as the core-level spectra without performing sophisticated theoretical calculations. Even among different kinds of theoretical calculations performed so far, there is still disagreement on the interpretation of the spectra.[5,13,15,25–27] Recently more experimental effort has been devoted to the understanding of the electronic structure of the valence levels of the adsorbates and bonding structures (see references in Ref. 29). Further theoretical studies on the ionization from the valence levels are thus in need.

The linear molecule NiCO has been used as a model system to study the chemisorption of CO on a nickel surface.[28] A Green's-function calculation of the valence and core spectra of NiCO has been performed within a semiempirical approach, the complete neglect of differential overlap (CNDO/2).[17,27] The Green's-function method itself is called the diagonal two-particle–hole Tamm-Dancoff approximation (*d2ph* TDA) Green's-function method.[32] This simple calculation already shows that the incorporation of many-particle effects is necessary for even a qualitative understanding of the photoelectron spectra of these systems. It is shown that not only the charge transfer (CT) but also other relaxation mechanisms such as local ligand excitations have to be taken into account.[17,27] It is an advantage of the Green's-function method in contrast to the self-consistent-field (SCF) molecular-orbital (MO) approach (SCFMO), such as the ΔSCF method, that one can deal simultaneously with local metal, local ligand, and CT excitations.

The *d2ph* TDA Green's-function calculations of the valence and core-hole spectra of NiCO and $Ni(CO)_4$ by Saddei *et al.* demonstrate the breakdown of the one-electron picture.[17,27] This phenomenon has been found to be a general one in atoms, solids, and molecules (see Refs. 33–38). Saddei *et al.* used the SCF-MO-CNDO method. A general problem with the use of a CNDO basis is the inaccurate description of the $1h/2h\,1p$ (here h denotes a hole and p a particle) coupling strength and energy separations. This leads to an inaccurate description of the spectral features such as energy positions and intensities. A dramatic spectral feature such as the breakdown of the one-electron or even quasiparticle picture of the single or multiple ionizations depends often critically on the coupling strength and energy separations between the initial- and final-hole states.

In the present work we calculate the valence ionization spectra of NiCO and $Ni(CO)_4$ with an *ab initio* method using extended basis sets. The many-electron effects are included via the Green's-function method in the so called ADC(3) (the third-order algebraic diagrammatic construction, equivalent to the extended *2ph* TDA).[38,39] In the case of model systems such as NiCO, we can compare only indirectly the theoretical results with the experimental data from the adsorbates [CO on a Ni(100) surface]. Therefore we also calculate the valence spectrum of $Ni(CO)_4$ and compare the results with experiment to test the accuracy of the present ADC(3) Green's-function calculations.

The present results give an overall good agreement with experiment. Our calculations also show the breakdown of the one-electron picture of ionization in the coordinated systems due to a strong coupling of the single-hole ($1h$) and two-hole–one-particle ($2h\,1p$) CT configurations. The dominant role played by the intraligand excitations in the free CO is replaced in the coordinated system by the metal-ligand CT excitations. We make an analysis of the spectrum in terms of the $1h$ and the $2h\,1p$ CT states instead of the "screened" and "unscreened" states used in an ambiguous way in the literature on the CTS model in the interpretation of ionization spectra of adsorbates, transition-metal compounds, high-temperature superconductors, etc. In general the CTS state ($2h\,1p$ shakedown state) is considered as a screened state and the $1h$ state (Koopmans's state) as an unscreened state. The smaller BE state is a screened state. However, this state is not necessarily the CTS state. We show that in the present case the $1h$ state can be more stable than the $2h\,1p$ CT states and the main (lowest binding energy) line can be the $1h$ state and not the $2h\,1p$ CT state.

To see how the spectral features change with an increase of the Ni—CO bond length, we calculate the spectra of NiCO at different bond lengths. The results show that with an increase of the bond length which leads to a weaker coupling, the satellite intensities increase. We analyze this effect in terms of the energy separations of the $1h$ and $2h\,1p$ configurations and show the importance of the $1h\,1h$ and $1h\,1p$ interactions in the $2h\,1p$ states. We make a comparison of the present results with the CNDO results and discuss the causes of the discrepancies found between these two sets of results. Then we discuss the interpretation of the satellites observed recently by different kinds of spectroscopies. Finally we discuss briefly those additional relaxation, screening, and the substrate broadening effects in the $2h\,1p$ states which are neglected in the present ADC(3) approach and comment on the core-hole spectra. We conclude that many-body calculations such as the ADC(3) approach are quite useful for understanding the hole spectra of adsorbates.

II. THEORY

In this section we present briefly the outline of the theoretical approach. We refer the reader to Refs. 38 and 39 for details of the ADC(3) approach. We use the Green's-function formalism to calculate the IP's (ionization potential) and their spectral intensities directly. Using the spectral representation of the Green's function, the (vertical-electronic) ionization energies are given by the negative-pole positions in the Green's function. The residue provides the pole strength. This is, in the sudden approximation, a measure for the relative intensities of the states which derive their intensity from the same orbital.

The Green's function can be calculated by using a well-established diagrammatic perturbation expansion in terms of the self-energy. The essence of the perturbation expansion lies in the renormalization of the self-energy. In the present work we are concerned with the self-energy which describes the configuration interaction (CI) between the initial $1h$ and final $2h\,1p$ configurations. The second-order self-energy consists of three terms, each describing different many-body effects, namely the non-hole-hopping relaxation, hole-hopping relaxation, and ground-state correlation terms. We start with the renormalization of these three basic 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 the $1h\,1p$ interactions. We approximate the $1p\,1h$ interaction within the framework of the random-phase approximation (RPA). Some of the third-order diagrams are the first in a sequence that constitutes the RPA. Furthermore, using the ladder approximation for the $2h$ interaction, all diagrams appearing in the third order are summed to infinity by the ADC(3) approach. 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 excitations ($3h\,2p$ configurations, etc.) on the ionic states. In the present work we calculate the self-energy by the ADC(3) scheme.

III. NUMERICAL PROCEDURES

The configuration interaction calculations on NiCO have shown that the ground state of NiCO is the $^1\Sigma^+$ state rather than the $^3\Delta$ state. The $3d^{10}4s^0$ Ni configuration gives the dominant contribution to the $^1\Sigma^+$ state of NiCO.[40–44]

The optimized Ni-CO distance obtained for the linear NiCO molecule with the complete active space SCF (CASSCF) wave function is 3.2 bohrs.[44] The experimentally determined Ni(100)/CO distance is 3.5 bohr, with the CO sitting vertically on top of the Ni sites.[45] This distance is close to the Ni-CO distance of a Ni(CO)$_4$ molecular crystal. The C-O distance in our calculation is fixed at that of free CO, as the effect on the electronic structure of NiCO due to a change of the C-O distance from free CO (2.132 bohr) to the Ni(CO)$_4$ C-O distance (2.173 bohr) is quite small.[26] We performed the ADC(3) calculations at $R=3.2$ and 3.5 bohr for the NiCO molecule.

We use basis sets of Cartesian Gaussian functions on the atoms to expand the MO's. The $[14s9p5d]$ basis set of Wachters[46] for Ni is enlarged by two p-type functions with exponential parameter $\alpha_p=0.24,0.08$ to describe the $4p$ orbital of Ni and the diffuse $3d$ functions of Hay ($\alpha_d=0.1316$).[47,48] 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 contractions upon molecular bonding. The final basis set is $[14s11p6d]$ contracted to $(8s6p4d)$ (contraction number of 3 of Wachters). The C and O basis sets are taken from Salez and Veillard, $[11s7p1d]$ contracted to $(5s3p1d)$.[49] The exponential parameters of the d-type functions are $\alpha_d(\mathrm{C})=0.6$, $\alpha_d(\mathrm{O})=0.8$. In a second calculation we added to the Ni basis set a set of three f functions contracted to two f-type functions ($\alpha_f=5.02,1.72,0.4$).[48] The resulting basis sets are somewhat too large for Ni(CO)$_4$ with the given computational resources. For this molecule we thus used on Ni a $[14s11p6d]/(7s5p3d)$ basis and on C and O a $[9s5p1d]/(4s2p1d)$ basis which is taken from the work of Huzinaga.[50]

In the ADC(3) Green's-function calculations for NiCO all orbitals except for the core orbitals and their virtual counterparts were taken into account. This leads to matrices of dimension of around 8000. The eigenvalues and eigenvectors were extracted with a block Davidson method.[51] For σ symmetry about 70 eigenvalues and eigenvectors were calculated. For Ni(CO)$_4$ all occupied valence and the lowest 33 virtual orbitals were taken into account. This leads to matrices of dimension 15 000 which were diagonalized with the block Davidson method to obtain about 100 solutions.

IV. RESULTS AND DISCUSSION

A. Initial-state effect; chemical shift

In Table I we list the orbital energies for free CO and for NiCO at $R=3.2$ and 3.5. We list also the *ab initio* results by Hermann and Bagus[26] and the results of a CNDO calculation.[27] Strictly speaking, the Hartree-Fock (HF) orbital energies (Koopmans's approximation) have no physical relevance because of the neglect of ground-state and final-state correlation and relaxation in the final state. However, the eigenvalue shift due to a change of environment (such as change of bond length or removal of the Ni atom to infinity) should indicate the initial-state effect (neglecting the ground-state correlation energy shift). At $R=3.2$ bohr the ordering of the 5σ and 1π levels (eigenvalues) is reversed compared to that of a free CO molecule. The 5σ orbital in CO which is directed towards the Ni atom is shifted by 1.7 eV to higher BE, whereas the 4σ and 1π orbitals which are predominantly localized on the oxygen are shifted to smaller BE by 1.0 eV. This indicates the presence of a specific initial-state interaction between the CO (adsorbate) 5σ and the Ni

TABLE I. Ionization energies (eV) for CO and NiCO in Koopmans's approximation (eV), R values in bohr.

				NiCO			
		CO		Present work		Ref. 26	CNDO
Level	Present work	Ref. 26	CNDO	$R=3.2$	$R=3.5$	$R=3.5$	$R=3.5$
5σ	15.11	15.15	17.3	16.81	16.49	18.42	19.1
1π	17.49	17.12	21.1	16.41	16.72	18.26	21.4
4σ	21.89	21.80	24.7	21.10	21.42	22.97	25.2
3σ	41.51		45.3	39.84	40.31		45.1

TABLE II. Theoretical and experimental ionization energies of free CO (eV).

Level	ADC(3) IP	*d2ph* TDA CNDO[a] IP	HF-ΔSCF[b] IP	SCF-*X*α-SW[c] IP	Expt.
5σ	13.91(0.89)	16.5(0.97)	13.53	13.9	14.0[d]
		44.0(0.03)			
1π	16.98(0.9)	21.2(0.95)	14.96	17.6	16.9[d]
		40.5(0.05)			~27.0[e]
4σ	20.08(0.79)	23.2(0.82)	19.87	21.0	19.7[d]
	23.00(0.11)	30.2(0.01)			~23[e]
		33.9(0.05)			
		34.5(0.05)			
		44.7(0.07)			
3σ	33.93(0.11)	39.2(0.10)			~31[e]
	38.75(0.17)	40.0(0.03)		34.8	~36[e]
	39.21(0.30)	41.7(0.24)			38.3[e]
	39.55(0.15)	47.2(0.62)			

[a] Reference 27. The intensities are read from the figure.
[b] Reference 26.
[c] Reference 56.
[d] Reference 84.
[e] Reference 69.

atom (substrate). A conventional picture of bonding of NiCO (CO on Ni metal surface) is that the 5σ charge is donated to the metal (substrate) with a simultaneous charge backdonation from the metal valence states into the 2π derived orbital of CO.[52] However, the exact nature of the bonding between CO and metals is still controversial. With an increase of the Ni—CO bond length (at $R = 3.5$), the chemical shifts of the 5σ, 1π, and 4σ levels are 1.4, −0.8, and −0.5 eV, respectively, where negative values are shifts to lower BE. The eigenvalues come closer to those of free CO because of an increase of the bond length. The changes in the chemical shifts from $R = 3.2$ to 3.5 for the 5σ, 1π, and 4σ levels are −0.3, 0.3, and 0.3 eV, respectively. The 5σ orbital thus is less involved in the bonding at the larger distance.

B. The main line IP of NiCO

In Tables II and III we list the ADC(3) results for free CO and NiCO. In the case of free CO the ordering of the IP's is correctly produced by the orbital energies. For 5σ and 1π the main line takes almost all of the strength (with a pole strength of 0.9) and the one-electron picture is valid. For 4σ non-negligible strength (0.21) goes to satellites. For 3σ the intensity is distributed over several lines and the quasiparticle picture breaks down. In the case of NiCO the ordering of the main IP's of the 5σ and 1π levels is reversed compared to that of free CO but is correctly given by Koopmans's approximation at $R = 3.2$. For 5σ and 4σ the main state takes a smaller amount of the original strength and the remaining strength is distributed over small satellites. For the 1π and 3σ ionization the quasiparticle picture breaks down. With an increase of the bond length the quasiparticle picture for 4σ breaks down as well. The outer valence shell levels of free CO become inner valence shell levels in the bonded system due to the presence of high-lying occupied orbitals on the metal atom. The quasiparticle picture for 1π (and 4σ) breaks down due to the metal-ligand CT $1h/2h1p$ coupling which involves the occupied orbitals of the metal atom. Later we shall discuss in detail this aspect of the physics. The *d2ph* TDA CNDO calculation also gives intense satellite lines for 1π ionization but they appear about 8 eV above the main line and the main line contains still about two-thirds of the original strength. The picture which emerges is thus quite different from the ADC(3) calculations.

The present results refer to an isolated NiCO molecule and solid-state effects associated with CO chemisorbed on a Ni metal surface are totally neglected. However, it is interesting to compare the present results with the experimental data from the adsorbate [CO on Ni(100)] to see whether NiCO can be a suitable model for the adsorbate. Here a comparison with the theoretical results for the molecule is made simply by adding the work function which ranges from 5.5 to 6.3 eV (depending on Refs. 6, 18, 20, 21, 24, and 53), to the binding energy of the adsorbed molecule measured relative to the Fermi level of the substrate, to bring them to a common reference level. If we neglect the basis-set truncation error and the incomplete treatment of the many-body effects, whose magnitude can be quite reliably estimated from the results for free CO and from general experience, then the discrepancy between the NiCO molecule IP and adsorbate IP is the part of the adsorbate-free molecule energy shift which cannot be explained by the present linear molecule model. The use of the metal work function is not without problems. Recently Wertheim raised the questions of the usefulness of the bulk metal work function for the adsorbate.[54]

The present ADC(3) results give a far better agreement with experiment than the Hartree-Fock Δ self-consistent-field (HF-ΔSCF) method[5,26,55] and the SCF-$X\alpha$-scattered wave (SW) method.[56] Taking the average value of the experimental data (7.0, 8.0, and 10.9 eV for 1π, 5σ, and 4σ levels, respectively) and 6.3 eV as the estimated work function, the discrepancy between the ADC(3) results and experiment still ranges from 0.3 to 1.4 eV. Of these about 0.1 to 0.4 eV can be estimated from the results for free CO to be due to basis-set errors and errors due to the incomplete treatment of many-body

TABLE III. Theoretical valence IP of NiCO and experimental values for CO on Ni metal surfaces (of eV).

	ADC(3)		*d2ph* TDA CNDO/2[a]	HF-ΔSCF[b]		
Level	$R=3.2$	$R=3.5$	$R=3.5$	$R=3.5$	SCF-$X\alpha$-SW[c]	Expt.
$3d\sigma$	8.63(0.92)	7.75(0.91)	6.2		9.8	7.4[d]
$3d\pi$	9.71(0.91)	9.36(0.92)	6.8		10.6	
$3d\delta$	10.45(0.93)	9.68(0.94)	6.2		10.5	
1π	14.29(0.33)	14.14(0.14)	15.8(0.61)	16.0	16.5	12.3[e]
	14.94(0.14)	14.78(0.20)	24.2(0.04)			13.0[f]
	15.53(0.14)	15.44(0.13)	27.0(0.23)			13.3[g]
	16.06(0.07)	15.79(0.10)	27.2(0.06)			11.8[h]
	18.34(0.06)	17.87(0.05)	40.8(0.03)			13.5[i]
	19.51(0.11)	18.76(0.21)	45.4(0.03)			13.0[j]
						13.3[k]
						13.8[d]
5σ	15.01(0.75)	14.65(0.74)	15.3(0.70)	16.4	16.3	13.6[e]
	17.40(0.08)	17.20(0.07)	23.0(0.13)			13.5[f]
	20.23(0.03)	19.27(0.02)	27.0(0.05)			13.8[g]
						13.6[h]
						14.5[i]
						13.4[j]
						14.5[k]
						13.8[d]
4σ	18.6(0.65)	18.62(0.42)	18.0(0.69)	21.0	21.1	16.6[e]
	21.04(0.06)	19.27(0.11)	20.5(0.03)			16.1[f]
	23.92(0.05)	19.39(0.09)	22.0(0.07)			16.3[g]
		21.01(0.09)	28.6(0.10)			16.6[h]
			33.2(0.03)			17.1[i]
			36.5(0.07)			16.4[j]
						17.5[k]
						17.0[d]
3σ[l]	33.53(0.08)		37.8(0.50)		34.9	35.3[k]
	34.00(0.11)		41.2(0.03)			34.3[d]
	37.27(0.20)		43.5(0.03)			
	37.58(0.09)		49.6(0.18)			
	37.90(0.03)		49.9(0.26)			
	40.06(0.03)					
	44.13(0.04)					
	45.38(0.03)					

[a] Reference 27. The intensities are read from the figure.

[b] Reference 26.

[c] Reference 56.

[d] Reference 29 with the estimated work function of 6.3 eV.

[e] Reference 18.

[f] Reference 21.

[g] Reference 21.

[h] Reference 20.

[i] Reference 53.

[j] Reference 6.

[k] Reference 24.

[l] The ionization energies for 3σ have been calculated by a pole search method (Ref. 86) which employs configuration selection.

effects. The HF-ΔSCF and SCF-$X\alpha$-SW methods give IP's which are ~ 2.0-eV larger than the ADC(3) IP's. As the relative separations of the 5σ and 4σ levels to the lowest 1π level are independent of the work function, we also compare these quantities with experiment. The corresponding theoretical energy separations are 0.7 and 4.3 eV at $R = 3.2$ and 0.5 and 4.5 eV at $R = 3.5$ by the ADC(3) method and 0.4 and 5.0 eV by HFΔSCF method, whereas the averages of the experimental energy separations are 1.0 and 3.9 eV, respectively. The ordering of the valence levels as obtained by the ADC(3) method is in accord with the experimental assignment. The *d2ph* TDA CNDO results are in reasonable agreement with the ADC(3) results; however, the ordering of the 1π and 5σ valence levels is different here. This is also the case for the results by the SCF-$X\alpha$-SW method. Later we shall make a detailed analysis of the causes of the discrepancies between the ADC(3) and *d2ph* TDA CNDO results.

In the case of free CO we list only the theoretical results obtained by the methods used for the calculations on NiCO. The ADC(3), SCF-$X\alpha$-SW, and ΔSCF approaches give a good agreement with experiment except that in the case of the 1π level the ΔSCF method underestimates the IP by as much as 2 eV because of the total neglect of the correlation energy in both ground and ionic state. The *d2ph* TDA CNDO fails badly and overestimates the IP by as much as 4.3 eV. Later we shall make a detailed analysis of the cause of this discrepancy.

The energy shifts (sum of the relaxation and correlation energy shifts) obtained for 1π, 5σ, and 4σ levels of NiCO by the ADC(3) are 2.1, 1.8, and 2.5 eV at $R = 3.2$ and 2.6, 1.8 and 2.8 eV at $R = 3.5$, respectively, whereas the relaxation energy shift obtained at $R = 3.5$ by the ΔSCF method is 2.3, 2.0, and 2.0 eV, respectively. In the case of free CO, the energy shifts for the 1π, 5σ, and 4σ levels calculated by the ADC(3) method are 0.5, 1.2, and 1.8 eV, respectively, whereas the relaxation energy shift obtained by the ΔSCF approach is 2.2, 1.6, and 1.9 eV, respectively. The shift for 1π is considerably too large.

The second-order self-energy diagrams already show that the energy shift beyond the Koopmans's approximation can be divided into three contributions, namely the correlation, non-hole-hopping relaxation, and hole-hopping relaxation energy shifts. In the case of atomic-like localized levels, the deeper the level is the more the non-hole-hopping static relaxation (SR) dominates over the hole-hopping dynamical relaxation (DR). In the former relaxation, the initial hole remains in the same orbital and acts as a classical static charge, inducing the radial distortions of the surrounding electrons, i.e., monopole relaxation. However, in the latter relaxation the hole fluctuates between different orbitals, inducing nonspherical (angular) distortions of the surrounding charge densities.[33-36] The SR in extended systems can be discussed in terms of ΔSCF calculations by breaking the translational symmetry and localizing the hole in an atomic orbital on a particular atom. However, the DR and correlation cannot be discussed in terms of ΔSCF calculations. In the case of CO and NiCO, the occupied orbitals are predominantly localized on either nucleus and all holes are therefore created predominantly on one nucleus or the other. If for CO and NiCO the DR would be negligible, or the DR and correlation energy shifts tend to cancel out, then a ΔSCF scheme will directly give the right ordering of the valence hole levels, leading to binding energies in a reasonable agreement with experiment. This appears at first sight to be the case for the 5σ and 4σ levels of free CO, but for the 1π level the correlation is large and the ΔSCF underestimates the BE by as much as 2.0 eV. The Koopmans's approximation is actually in good agreement with experiment only because of the cancellation of SR and correlation shifts (and negligible DR energy shift because of fewer possibilities of hole hopping). As discussed in detail in the Sec. IV C, the metal-ligand CT relaxation plays in the case of NiCO a significant role, leading even to the breakdown of the quasiparticle picture. In this case the ΔSCF method using the one-electron picture becomes meaningless.

Brundle *et al.* discussed the final-state effects for the valence levels due to a change of environment in terms of the differences in the relaxation shifts obtained by the ΔSCF method.[5] (The relaxation shift defined in the present work should not be confused with the "final-state relaxation shift" defined by Hermann and Bagus[26].) Brundle *et al.* concluded that there is no strong final-state effect because the relative separations of the ΔSCF IP's differ from those of the orbital energies by only 0.3 eV.[5] As the 5σ and 4σ orbitals of CO are localized, these authors argue that there should not be an appreciable change in localization upon ionization. Within the ΔSCF picture the final-state energy shifts between free CO and NiCO are very small (0.1 to 0.5 eV) in spite of a change of environment. However, the ADC(3) results show that the final-state shifts (the differences of the relaxation and correlation energy shifts due to a change of environment) are appreciable. For the 5σ, 1π, and 4σ levels they are 0.6, 1.6, and 0.7 eV at $R = 3.2$ and 0.7, 2.0 and 1.0 eV at $R = 3.5$, respectively. On the whole the final-state effect is very significant in the 1π level. The changes in the final-state shifts with an increase of the bond length are 0.1, 0.4, and 0.3 eV, respectively. These changes in the final-state shifts are small. The large difference between the final-state shifts obtained by the ADC(3) and ΔSCF methods is due to the total neglect of correlation and DR by the latter method. As we shall discuss in detail in Sec. IV C, the character of the dominant relaxation effect changes drastically from free CO to NiCO. In such a case a study of the final-state shifts cannot provide useful information. It is necessary to make a more detailed analysis of the spectrum.

Before we proceed further to an analysis of the spectrum, we would like to comment briefly on the effects of inclusion of f-type wave functions. In Table IV we list the IP calculated at $R = 3.2$ by the present ADC(3) method using the extended basis set of $[14s11p6d3f]/(8s6p4d2f)$. The calculated main-line IP is slightly shifted toward smaller BE by 0.1 to 0.2 eV. However, the satellite positions are hardly shifted at all. The intensities also remain almost unchanged. The effect of the f-type wave functions is thus small.

TABLE IV. Theoretical valence IP of NiCO by an extended basis set with diffuse f wave functions (in units of eV).

Level	ADC(3) $R=3.2$
$3d\sigma$	8.42(0.90)
$3d\pi$	9.84(0.91)
$3d\delta$	10.34(0.93)
1π	14.23(0.37)
	14.91(0.13)
	15.49(0.13)
	19.49(0.07)
5σ	14.80(0.77)
	17.35(0.06)
	20.20(0.03)
4σ	18.43(0.67)
	21.00(0.05)

C. Intensity of the lines and analysis of the configurations

In this section we make an analysis of the spectrum obtained from the ADC(3) calculations of free CO and NiCO. First of all we make an analysis of the valence spectra of free CO and NiCO obtained at $R=3.2$. (If weights are given in the following, they refer to the square of the amplitudes or to their sum.)

1. 5σ level

In free CO, the 5σ spectrum consists of one dominant peak with a pole strength of 0.9. The main line is described by the $5\sigma^{-1}$ single-hole configuration. In NiCO the 5σ main state consists essentially of a single-hole configuration (pole strength 0.75). The rest consists of $5\sigma^{-1}\pi_M^{-1}2\pi$, $5\sigma^{-1}\sigma_M^{-1}n\sigma$, $\sigma_M^{-1}\pi_M^{-1}2\pi$ configurations (here M denotes the metal ion). The satellite in NiCO is dominated (0.9) by the $2h\,1p$ configurations. More than half of the contributions come from $5\sigma^{-1}\pi_M^{-1}2(n)\pi$ and the rest mainly from $4\sigma^{-1}\pi_M^{-1}2(n)\pi$, $\sigma_M^{-1}\pi_M^{-1}2\pi$ configurations. In contrast to free CO where the 5σ level is the outermost one, in NiCO the 5σ level now belongs to the inner valence shell due to the presence of high-lying occupied orbitals derived from the Ni atom. As the present ADC(3) results show, the $5\sigma^{-1}$ configuration interacts strongly with the metal-ligand charge-transfer $2h\,1p$ configurations not only of the non-hole-hopping SR type ($5\sigma^{-1}\leftrightarrow 5\sigma^{-1}\pi_M^{-1}2\pi$) but also of the hole hopping DR type (e.g., $5\sigma^{-1}\leftrightarrow 4\sigma^{-1}\pi_M^{-1}2\pi$, $5\sigma^{-1}\leftrightarrow\sigma_M^{-1}\pi_M^{-1}2\pi$). From this we note that as discussed above the ΔSCF approximation cannot really deal with this level because the DR cannot be treated by the ΔSCF approximation.

We should emphasize the difference between the static charge-transfer relaxation and dynamic charge-transfer relaxation in extended systems. In the former case the hole remains on the same orbital, including a radial distortion of the surrounding electron cloud through the charge transfer from the metal-occupied orbital to the ligand unoccupied orbital. However, in the latter the hole charge oscillates between different orbitals and thus between different spatial regions, leading to varying degrees of localization on either nucleus. When a localized hole charge oscillates between the nuclei together with its equally localized charge-transfer screening charge ($5\sigma^{-1}\leftrightarrow 4\sigma^{-1}\pi_M^{-1}2\pi$), then the localized hole with its π charge-transfer screening cloud which does not reserve the original symmetry of the MO's will propagate as the quasihole: dynamical relaxation. If the hole hopping is very fast and the screening charge cannot follow, then its hole becomes delocalized. In this case the static relaxation will be more efficient (see Ref. 33 for a general discussion in the case of a free molecule).

2. 4σ level

In free CO, the 4σ main peak is described by a $1h$ configuration. The rest of the contribution is from the $5\sigma^{-1}1\pi^{-1}2(n)\pi$ configuration which is coupled with the $4\sigma^{-1}$ configuration by the DR. The satellite is dominated (0.8) by the $5\sigma^{-1}1\pi^{-1}2(n)\pi\ 2h\,1p$ configuration. The $4\sigma^{-1}\leftrightarrow 5\sigma^{-1}1\pi^{-1}2(n)\pi$ DR plays a significant role; a good agreement of the ΔSCF result for the 4σ level with experiment is fortuitous because of a cancellation of correlation and the DR energy shift. In NiCO the main 4σ line consists essentially (pole strength 0.64) of the $1h$ configuration. The remaining dominant contribution is $4\sigma^{-1}\pi_M^{-1}2(n)\pi$. The first satellite (21.04 eV with a pole strength of 0.06) is mainly dominated by the $2h\,1p$ configurations. Not only $4\sigma^{-1}\pi_M^{-1}2(n)\pi$ but also $\sigma_M^{-1}\pi_M^{-1}2(n)\pi$ and $5\sigma^{-1}1\pi^{-1}2\pi$ contribute substantially. The second satellite (23.92 eV with a pole strength of 0.05) consists of several $2h\,1p$ configurations. A substantial contribution (0.3) comes from $M^{-2}\sigma(\pi)$-type configurations (here M denotes π_M or σ_M). For 4σ ionization we thus note a remarkable difference between free CO and NiCO. In NiCO the $4\sigma^{-1}\leftrightarrow 4\sigma^{-1}\pi_M^{-1}2\pi$ SR process (which is a charge-transfer process) dominates rather than the $4\sigma^{-1}\leftrightarrow 5\sigma^{-1}1\pi^{-1}2\pi$ local ligand DR process, whereas in free CO the DR process dominates.

3. 1π level

In free CO the 1π spectrum consists of one prominent peak with a pole strength of 0.9. The dominant configuration is the $1\pi^{-1}$ configuration and the rest is the $1\pi^{-2}2\pi 2h\,1p$ configuration. In contrast to free CO the 1π ionization in the NiCO spectrum shows a dramatic effect; the spectral strength is now distributed over several peaks, the intensities of which are comparable. The lowest line has only one-third of the original strength. In addition to the $1\pi^{-1}$ configuration contribution is from the $1\pi^{-1}\pi_M^{-1}2(n)\pi 2h\,1p$ configuration. The second, third, and fourth peaks (14.94, 15.53, 16.06 eV) consist mainly (0.8–0.9) of $2h\,1p$ configurations, the dominant role is played by the $1\pi^{-1}\pi_M^{-1}2(n)\pi$ configuration. The fifth state (18.34 eV) consists mainly of $\pi_M^{-1}\sigma_M^{-1}n\sigma 2h\,1p$ configurations and the state at 19.51 eV of $1\pi^{-1}\pi_M^{-1}2\pi$ and $1\pi^{-1}\sigma_M^{-1}n\sigma$ configurations. The quasiparticle picture for the 1π level breaks down due to the strong dynamic charge-transfer coupling between the $1\pi^{-1}$ and $1\pi^{-1}\pi_M^{-1}2\pi$ configurations.

4. 3σ level

In both free CO and NiCO, the quasiparticle picture of the 3σ hole breaks down completely due to strong $1h/2h1p$ CI. In the case of free CO in addition to the $3\sigma^{-1}$ configuration, the major contribution to the first peak (33.93 eV) comes from the $4\sigma^{-1}1\pi^{-1}2(n)\pi$ and $5\sigma^{-2}n\sigma$, those to the second, third, and fourth peaks (38.74, 39.21, and 39.55 eV) from the $4\sigma^{-1}5\sigma^{-1}n\sigma$ configuration. These $2h1p$ configurations document a strong hole hopping DR. In the case of NiCO, the quasiparticle picture of 3σ hole breaks down as well and the intensities are distributed over several lines over a wide energy range. There is no particular dominating $2h1p$ configuration. For the 3σ level of CO/Ni(100), one expects a smeared out continuumlike spectrum. To our knowledge, the experimental data available for the 3σ excitations are the measurements by Norton and coworkers[24] and Nilsson and Mårtensson.[29] These groups observed a broad band [10–12 eV FWHM (full width at half maximum)] centered at around 34.3 or 35.3 eV [with respect to the vacuum, shifted by an estimated work function of 6.3 eV (Ref. 53)]. Our theoretical prediction agrees rather well with this experimental observation.

Let us now analyze the valence spectrum of NiCO at $R=3.5$ to study the changes in the spectral features. With an increase of the bond length, the IP of the main line does not change much (0.4, 0.2, and 0.0 eV for 5σ, 1π, and 4σ, respectively). The main-line–satellite-line energy separation also changes very little except for the case of the 4σ level.

(i) 5σ level. With an increase of the bonding distance, the character of the main line hardly changes. The contribution of the $2h1p$ configuration to the satellite increases slightly.

(ii) 4σ level. For the lowest-energy line the contribution of the $1h$ configuration decreases substantially (from a pole strength of 0.64 to 0.42). The dominant contribution comes from several $2h1p$ configurations, e.g., $4\sigma^{-1}\pi_M^{-1}2\pi$, $1\pi^{-1}\pi_M^{-1}n\sigma$, $5\sigma^{-1}M^{-1}n\pi(\sigma)$, $M^{-2}\pi(\sigma)$. The second and third states deriving from 4σ ionization consist dominantly of $2h1p$ configurations like $1\pi^{-1}\pi_M^{-1}n\sigma$ and $5\sigma^{-1}\sigma_M^{-1}n\sigma$. The fourth state also consists of several $2h1p$ configurations like $4\sigma^{-1}\pi_M^{-1}2\pi$, $\sigma_M^{-1}\pi_M^{-1}2\pi$, and $5\sigma^{-1}1\pi^{-1}2\pi$, etc. With an increase of the bond length the quasiparticle picture of 4σ starts to break down. The main reason for this is the increased importance of dynamic charge-transfer relaxation. The detailed explanation will be given later.

(iii) 1π level. As is the case for $R=3.2$, all states are dominated by the $2h1p$ configurations. The quasiparticle picture of 1π ionization breaks down. There are no qualitative differences to the case at $R=3.2$ bohr, but only quantitative ones. The intensity redistribution is somewhat larger at $R=3.5$ bohr than at $R=3.2$ bohr.

The ADC(3) calculation for NiCO shows that at least for 5σ and 4σ, the $1h$ state is more stable than the $2h1p$ state. The lowest-energy states deriving from the 5σ and 4σ ionization consist mainly of the $1h$ configuration where the screening charge resides on the bonding orbital which is more polarized toward the ligand than in the ground state. The satellites are dominated by $2h1p$ configurations where the bonding to antibonding shakeup excitations occur (strong polarization toward CO). We note that in the present work we define the shakeup with respect to the neutral ground-state configuration. The state from where the excitations originate is the neutral ground state (one-step model used by the present approach) not the relaxed hole state (two-step model used by a CI method).

We proceed to a further analysis of main line and satellites. Why is the $1h$ state more stable than the $2h1p$ states in the case of the 5σ and 4σ levels? We make an analysis similar to that by Saddei *et al.*[17] As we shall discuss in detail later, the present results show that the metal-ligand charge-transfer relaxation is more dominant than the intraligand relaxation. We focus on the static and dynamic charge-transfer relaxation. The ADC(3) method sums the bare ladder and bubble $1h1h$ and $1h1p$ Coulomb interactions among the two holes and the excited electron in the intermediate $2h1p$ state of the self-energy to infinite order. For the sake of simplicity we consider these interactions within the framework of the $d2ph$ TDA scheme. The denominator of the self-energy includes the following interaction terms:

$$\varepsilon_v-(\varepsilon_a-\varepsilon_d+V_{vdvd}-V_{vava}-V_{adad}) \, . \tag{1}$$

Here a term V_{vava} describes the bare Coulomb interaction (including the exchange term) between a valence hole (v) and the acceptor (adsorbate) level (a) in the ligand, V_{vdvd} between a valence hole and the donor level in the metal (d), and V_{adad} between the transferred electron (a) with the remaining hole (d). The numerical analysis shows that for all valence levels of interest now, the term inside the parentheses in Eq. (1) (shakeup energy) is still positive. This excludes the possibility of the shakedown state as the lowest ionic state. A stabilization of an unoccupied ligand orbital below the Fermi level due to the presence of a valence hole does not occur within this model. This is in accord with the present ADC(3) results. It should be emphasized that the numerical studies show that all three interactions V_{vdvd}, V_{vava}, and V_{adad} are of the same magnitude and it is incorrect to consider only the V_{vava} term, the valence hole-acceptor interaction. These three interactions will equally govern the changes of the main and satellite lines and their energy separation. A similar physics was also discussed by Domcke *et al.* who studied theoretically the multipeak structure in the nitrogen K-shell spectra of nitroaniline and related highly polar aromatic compounds.[57] They showed that the mechanism leading to the multipeak structure is indeed related to the screening mechanism of the adsorbate spectra proposed by Schönhammer and Gunnarsson.[11] In addition to the Anderson-Newns Hamiltonian of chemisorption,[58] Domcke *et al.*[57] included the terms V_{adad} and V_{vdvd}. Schönhammer and Gunnarsson claimed that these terms can be approximately incorporated into their theory by a renormalization of the original Hamiltonian.[59]

The present ADC(3) results for NiCO show that the dominant relaxation is the charge-transfer relaxation rather than the intraligand relaxation, such as $i^{-1} \leftrightarrow i^{-1} 1\pi^{-1} 2\pi$, which in the case of free CO plays a significant role. Why does the character of the dominant relaxation effects change from free CO to NiCO? The question can be answered by studying the variations in the $1h/2h1p$ coupling strength and energy separations, because these quantities essentially determine the spectral features. From free CO to NiCO, the $1h/2h1p$ energy separations for the intraligand excitations do not increase much (3.7, 3.7, and 1.2 eV for 5σ, 4σ, and 1π levels, respectively). However, the magnitude of the corresponding $1h/2h1p$ coupling matrix element decreases by as much as a factor of 2 to 3. Consequently, the intraligand relaxation plays a minor role. On the other hand, in the case of the valence orbitals of NiCO the $1h/2h1p$ metal-ligand charge-transfer coupling is as strong as the intraligand excitation one. However, the $1h/2h1p$ CT energy separation is much smaller than in the case of intraligand excitation (by as much as ~ 17 eV). Thus in the NiCO one expects that the CT relaxation plays a dominant role. For the 4σ and 1π levels of NiCO, the $1h/2h1p$ CT energy separation is much smaller (by ~ 4 eV) and the magnitude of the metal-ligand CT $1h/2h1p$ coupling matrix element is more than twice larger than what is found for 5σ. This explains why the 4σ and 1π spectra of NiCO show the appearance of strong satellite lines. With an increase of the bond length, the $1h/2h1p$ energy separations for the intraligand excitations do not change at all and the corresponding $1h/2h1p$ coupling matrix element increases by about 20% as the ligand looks more like a free CO molecule. The intraligand relaxation is still small in comparison to the CT relaxation.

With an increase of the bond length, the 4σ main-line intensity decreases very much and the satellite intensity increases. This tendency is in accord with the experimental observation of the strong 4σ satellite in the weak-coupling system CO/Cu, compared to the strong-coupling system CO/Ni.[60] This is conventionally interpreted as due to a smaller degree of CT in the ground state, resulting in a reduced intensity of the main line which is interpreted as the CTS state.[5,16] However, in the present case the main lines of the 5σ and 4σ levels are interpreted as $1h$ state.

How can we then explain the 4σ satellite-intensity increase with an increase of the bond length? We consider the $1h/2h1p$ charge-transfer CI. With an increase of the bond length V_{vdvd} and V_{adad}, which depend on the overlap between the adsorbate and the substrate, decrease. However, V_{vava} increases because the CO ligand becomes similar to free CO. In the case of the 5σ and 4σ levels this results in a much smaller (although still positive) $1h/2h1p$ CT energy separation. In general, with an increase of the bond length, the magnitude of the CT $1h/2h1p$ coupling-matrix element decreases. The smaller the $1h/2h1p$ energy separation becomes, the more effective is the dynamical CT relaxation. This leads to a breakdown of the quasiparticle picture for the 4σ ionization. This explanation is in accord with the well-known rule of thumb for the breakdown of the one-electron picture of single- or multiple-hole excitations in atoms, molecules, and solids which have been tested by a large number of Green's-function calculations of XPS, x-ray emission spectroscopy (XES), and Auger electron spectroscopy (AES) spectra.[33-38,61-63] When the initial- and final-hole states are strongly coupled and/or nearly degenerate, the one-electron picture and/or quasiparticle picture in general breaks down.

In the present case the bond length governs not only the $1h/2h1p$ coupling strength but also energy separations through the changes in the strength of the $1h1h$ and $1h1p$ interactions in the $2h1p$ configuration. In the present case the latter is much more influenced than the former by the bond length and causes the breakdown of the one-electron and/or quasiparticle picture of the hole excitation in NiCO. The present results show that it is not correct to consider only the influence of the coupling strength when we consider the changes in the spectrum. It is important to take into account the $1h1h$ and $1h1p$ interactions in the $2h1p$ states which govern the $1h/2h1p$ energy separations. In the present case the weak-coupling system shows a more dramatic effect than the strong-coupling case. This is analogous to the well-known breakdown of the quasiparticle picture of a $4p$ hole level in the atomic elements from Cd($Z=46$) to Yb($Z=70$). The $4p$ hole spectra of these elements were interpreted in terms of a discrete initial-hole level interacting with a continuum band of finite width. The strength of the coupling, the shape of the band, and the position of the unperturbed discrete levels relative to the band are varied indirectly by the atomic number. The weaker the coupling is (smaller atomic number), the more pronounced is the breakdown of the quasiparticle picture.[33,35,36,62,63]

D. Comparison with the $d2ph$ TDA CNDO/2 results

There are discrepancies between the CNDO and the present results. The diagrams considered by the $d2ph$ TDA scheme are identical to those by the ADC(3) except for neglect of some diagrams in the former method. The ADC(3) method includes more ground-state correlation which leads among others things to an improved treatment of $1h$ states.[38,39] The main differences between the ADC(3) and the $d2ph$ TDA results are, however, expected to arise from the basis sets used.

As pointed out already, the CNDO results obtained for free CO and NiCO show this fact; in comparison to the *ab initio* results, the CNDO eigenvalues are shifted to higher BE by 2 to 4 eV for free CO and 3 to 5 eV for NiCO. For free CO the IP obtained by ($d2ph$ TDA) CNDO deviates by as much as 4.3 eV from experiment and the ADC(3) results. For NiCO, on the other hand, the calculated IP agrees well with the ADC(3) results except for the 1π level. The level ordering is the same as that found in Koopmans's approximation. However, this ordering contradicts the experimental assignment and the calculated relaxation and correlation energy shifts and the main-line–satellite-line energy separations are overestimated very much in comparison to the ADC(3) results.

How does the poor CNDO basis set then influence the spectral features? The main features of the spectrum are determined essentially by the $1h/2h1p$ energy separation and the coupling strength. In the case of free CO the $2h1p$ energy and the coupling strength obtained by the CNDO and the *ab initio* method agree rather well. The energy shift for the main line is also similar. Then the discrepancies between ADC(3) and CNDO are due to the CNDO Koopmans's energy used as the unperturbed energy for the Dyson equation. By using the *ab initio* orbital energies and energy shifts calculated by $d2ph$ TDA CNDO, we obtain 14.3, 17.4, and 20.4 eV for the 5σ, 1π, and 4σ levels which agree well with experiment. The $1h$ state solution can be simply obtained by performing such a shifting because of a smooth behavior of the real part of the self-energy in the energy region of the solution. However, the satellite ($2h1p$ state) cannot be shifted in this way because of a singularity of the real part of the self-energy. Because of the smaller $1h/2h1p$ energy separation in the case of the CNDO calculation compared to the *ab initio* one, the satellite lines appear at higher energies in the former calculation.

In the case of NiCO the metal-ligand CT and intraligand $2h1p$ excitation energies calculated by CNDO agree well with the corresponding *ab initio* results. However, the corresponding $1h/2h1p$ energy separations calculated by CNDO become much smaller because of the much larger Koopmans's energies. The magnitude of $1h/2h1p$ coupling-matrix elements for the intraligand excitations are well approximated by CNDO, whereas for the CT excitations they are overestimated by a factor of about 2 or more. These factors increase the strength of the intraligand and metal-ligand CT relaxation compared to the *ab initio* results. This explains also why the *intraligand* relaxation is more significant in the case of the CNDO results than in the case of the *ab initio* results. The main-line–satellite-line energy separations and the relaxation energy shifts are overestimated because of an overestimated CT coupling strength.

E. Interpretation of the satellites

Satellites in the valence photoemission spectrum of CO on Ni have been observed by several techniques. Recently Nilsson and Mårtensson (NM) observed the satellites at 15 and 22 eV as well as the extended 3σ band in the valence spectrum of CO on a Ni(100) surface by high-resolution XPS.[29] In this paragraph we define the energies with respect to the Fermi level unless otherwise noted. The angle-resolved C 1s and O 1s autoionization spectra of CO/Ni(110) also show the structures at ~13.5, 20, and 23 eV.[64] NM interpreted the 15- and 22-eV satellites to be the same as the 13.5- and 23-eV structures in the autoionization spectrum. Freund and coworkers[64] interpreted the 13.5-eV peak [274.5 eV in kinetic energy (KE); peak 1 in Fig. 21 of Ref. 64] as the autoionization of a 5σ "one-hole shakeup" state (these authors defined the shakeup with respect to the $2h1p$ CTS main-line state) and the 20- and 23-eV (268 and 265 eV KE) peaks as arising from $5\sigma^{-1}1\pi^{-1}2\pi$, $1\pi^{-2}2\pi$, and $4\sigma^{-1}5\sigma^{-1}2\pi$ configurations. However, NM interpreted the 15-eV satellite also as two outer-valence-hole-one excited $2\pi^*$ electron state. The interpretation is based on the assumption that autoionization decay and valence photoemission measure exactly the same final state. However, the question whether this is true in the case of adsorbates has been studied experimentally.[65–67]

Recent experimental studies of the 1s to 2π excitation for strongly coupled adsorbates by resonant photoelectron spectroscopy (RESPES) show that the initial-hole state for both the autoionization and Auger decay process are identical and they are the same as the XPS 1s core-hole state.[65–67] In other words, the 1s to 2π resonantly excited state relaxes to the 1s core-hole state before the Auger decay starts. In contrast to the case of a free molecule, the distinction between Auger and autoionization processes becomes meaningless in the case of strongly coupled adsorbates. NM commented that two RESPES studies of CO adsorbed on Cu(100) by Refs. 65 and 66 show the discrepancy in the energy calibration of the spectra, namely about a 4-eV difference in kinetic-energy scales. However, this energy difference is due to the different reference levels, namely to the Fermi level in Ref. 66 and to the vacuum level in Ref. 65 as stated clearly in the respective articles. Therefore we do not see any inconsistency between these two data. The groups of Refs. 64, 65, and 66 seem to have observed the same structure and Refs. 64 and 66 seem to give a similar interpretation. The authors of Ref. 65 interpreted the Auger back-bonding structure in CO on a Cu(100) surface as the UPS main-line state. Wurth *et al.* concluded that the back-bonding structures observed for CO on Ni(111) at 274.4 eV KE, 519 eV KE [peak 6 in Fig. 4 of Ref. 66(b)], and 515 eV KE [peak 5 in Fig. 3 of Ref. 66(b)] are not UPS main-line states (which are CTS states) but UPS shakeup states. Their interpretation for the lines is as follows: one hole in the 5σ, 1π, and 4σ, respectively, one 2π hole and screening electron at the Fermi level.[66] This state is defined with respect to the $2h1p$ CTS main-line state, but not with respect to the ground state. If we define this state with respect to the ground state, it would be one valence hole, one hole in the metal orbital, and one screening electron. In Ref. 66 the XPS core-hole (CTS) state is considered as the initial-hole state, thus 11.1 eV is obtained as the binding energy. In Ref. 64 the 1s to 2π resonantly excited state is considered as the initial-hole state, and thus 13.5 eV is obtained as the binding energy. We note that the experimental data are measured on different surfaces, namely Ni(110) and Ni(111). The kinetic energies measured may differ because of different binding; CO on Ni(100) is terminally bonded while CO on Ni(111) is predominantly bridge bonded. The 15-eV satellite in the XPS spectrum may correspond to the 13.5-eV peak in the autoionization spectrum if the normal autoionization picture is applicable also for strongly coupled adsorbates. Then the interpretation of the 15-eV satellite will be the 5σ satellite [either a 5σ one-hole shakeup[64] or $5\sigma^{-1}i^{-1}2\pi$ (Ref. 29)]. However, if the resonantly excited state relaxes to the XPS core-hole state before the Auger decay starts, then the 13.5-eV peak has to be interpreted as the 11.1-eV peak and it is improbable that the 15-eV XPS satellite is to be associated with this structure. The interpretation is then probably that the 515-eV Auger peak (16.1 eV ac-

TABLE V. Summary of interpretation of valence ionic states. V is the valence orbital, M is the metal orbital, and S is the screening orbital other than 2π.

Reference No.	1st state	2nd state	3rd state
64 (autoionization)	$V^{-1}M^{-1}2\pi$	V^{-1}	$V^{-1}V'^{-1}2\pi$
29 (XPS)	V^{-1}+screening	not identified	$V^{-1}V'^{-1}2\pi$
66 (Auger)	not observable	$M^{-1}V^{-1}S^{1}$[a]	$M^{-1}V^{-1}V'^{-1}2\pi$
This work[b]	V^{-1}+CTS CI	$V^{-1}M^{-1}2\pi$+CI	strong CI

[a] The configuration $M^{-1}V^{-1}S^{1}$ is taken with respect to the ground state. With respect to the CT state it would be $V^{-1}2\pi^{-1}S^{1}$.

[b] Dominant configurations are given. The other contributions are given as "CI".

cording to the binding-energy scale by the authors of Ref. 66), which was interpreted as the 4σ satellite, may correspond to the 15-eV XPS satellite. The same structure was seen in CO on Cu(110).[65]

The peaks at 20 and 23 eV (peak 2 and 3 in Fig. 21 of Ref. 64) in the autoionization spectrum could be interpreted as the Auger decay from the CTS core-hole state. Umbach[68] studied the K-VV Auger spectra of CO on Ni(100) and interpreted these peaks as the $1\pi^{-2}2\pi$ and $4\sigma^{-1}1\pi^{-1}2\pi$ states. This interpretation is similar to that of the autoionization spectrum by Freund and coworkers[64] except for the different initial-hole states referenced to and the different binding-energy scale. The 22-eV satellite in the XPS spectrum may correspond to the 23-eV (or 21 eV if the reference is chosen as in Ref. 66) structure as NM already suggested.

According to the present ADC(3) calculations, we obtain the satellites at ~11, 16, and 27 to 38 eV for the 5σ, 4σ, and 3σ levels, respectively. The 11-eV satellite could be hidden in the tail of the 15-eV satellite observed in the XPS spectrum. The 16-eV satellite corresponds to the 15-eV XPS satellite. The satellites at 27 to 38 eV correspond qualitatively to the 3σ XPS broad band. The ADC(3) method is expected to be able to describe the lowest one or two satellites reasonably well. The general shape and width of the 3σ spectrum is qualitatively well described by the ADC(3) method. There is a possible explanation for the 22-eV satellite observed in the XPS spectrum if we refer to the spectrum of free CO.[69] At about 25–30-eV binding energy with respect to the vacuum level there are satellites which have been assigned as 1π satellites.[69] The calculations (see also Refs. 70 and 71) give satellites here, obtaining intensity from 1π, 4σ, and 3σ ionization, but their intensities are too small. In NiCO the quasiparticle picture of the 1π ionization breaks down and one cannot expect a one-to-one correspondence between the free CO and NiCO spectra for the assignments of the satellites.

The authors of the aforementioned experimental works[64,66] interpreted the satellite as the shakeup from the bonding orbital to the antibonding orbital in the $2h\,1p$ CTS state; however, the satellites obtained by the ADC(3)

TABLE VI. Theoretical and experimental IP of gas-phase $Ni(CO)_4$ (eV).

Level	KT[a]	ADC(3)	*d2ph* TDA CNDO[b]	HF-ΔSCF[c]	SCF-S[d]	SCF-DV-$X\alpha$[e]	LCGTO-$X\alpha$[f]	Expt.[g]
$9t_2$	10.60	9.15(0.92)	5.1(0.81)	5.1	11.7	9.3	8.86	8.7
$2e$	12.69	11.52(0.92)	7.1(0.8)	5.8	13.0	10.3	10.3	9.7
$8t_2$	17.56	14.61(0.83)	13.5(0.65)		17.0	14.6	13.53	14.7
$1t_1$	17.80	14.95(0.71)	16.5(0.64)	17.3	16.7	14.1		14.0
		21.37(0.07)	17.7(0.1)					
$7t_2$	18.06	15.16(0.68)	16.6(0.5)		17.0	15.0		15.4
		21.29(0.06)	17.9(0.07)					
$1e$	18.16	15.27(0.68)	16.8(0.57)		17.0	15.0		16.1
		22.11(0.02)	18.1(0.05)					
$8a_1$	19.06	15.78(0.72)	15.9(0.59)	18.4	17.6	15.1		16.8
		18.73(0.08)	18.4(0.06)					
$6t_2$	21.88	18.91(0.68)	18.4(0.39)		19.3	16.5		18.3
		19.41(0.05)	20.5(0.15)					
$7a_1$	22.38	18.73(0.15)	23.4(0.1)		20.4	17.2		19.6
		19.35(0.49)	24.3(0.1)					

[a] Koopmans' "theorem," present work.

[b] Reference 27.

[c] Reference 72.

[d] Reference 75.

[e] Reference 73.

[f] Reference 74.

[g] Reference 85.

method are interpreted as the shakeup from the bonding to the antibonding orbital in the $1h$ state. These interpretations, at first glance, appear to be different. However, the difference is a matter of how much the bonding orbital is polarized toward the CO molecule in the presence of a hole. We find this polarization to be small. As a summary we present the different interpretations of the satellite lines in Table V. We have attempted to find a common language and used ground-state orbitals which are appropriate for valence states and satellites.

F. $Ni(CO)_4$

For the ADC(3) calculation on $Ni(CO)_4$ a somewhat smaller basis set was used as mentioned in Sec. III. The ionic states of this molecule have previously been calculated by CI and Green's-function methods by Smith *et al.*[72] But the basis sets did not contain polarization functions on the C and O atoms. This deficiency is amended in the present work. The ADC(3) results are listed together with results by other methods in Table VI. The SCF discrete variational (DV) -$X\alpha$ (Ref. 73) and linear combination of Gaussian-type orbitals (LCGTO) $X\alpha$-ΔSCF results[74] are rather similar. The former method gives good agreement with experiment for the first five levels; however, for the inner-valence-shell orbitals the deviation between theory and experiment increases up to 2.4 eV. On the other hand, the SCF Slater transition-state technique gives better agreement with experiment for the inner-valence-shell but not for the outer-valence-shell orbitals.[75] In comparison with the ADC(3) results, these results deviate from experiment randomly. The ΔSCF results deviate from experiment by as much as 3.3 eV.[72] This shows that the hole-hopping DR and correlation energy shifts are far from negligible. The ΔSCF energy shifts for the $1t_1$ and $8a_1$ levels are very small (0.5 eV). In contrast to the ΔSCF method, the ADC(3) method gives a fairly good agreement with experiment except for the $2e$ levels. The errors in general amount to 0.1 to 1.0 eV except for the $2e$ level (error 1.8 eV). The dominant cause of the errors is expected to be the orbital basis truncation. This was done in $Ni(CO)_4$ but not in NiCO. The errors obtained for $Ni(CO)_4$ are thus expected to be larger than those for NiCO.

The one-electron picture breaks down except for the $9t_2$, $2e$, and $8t_2$ levels. The main line has, in general, order of two-thirds of the strength. Satellites close to the energies of the main lines which have non-negligible intensities are obtained for the $1t_1$, $1e$, $8a_1$, $6t_2$, and $7a_1$ levels. These satellites consist dominantly of $2h\,1p$ configurations which are coupled by the hole-hopping DR, inducing the shakeup excitations from the bonding to the antibonding orbital. We note that a significant contribution comes from $2h\,1p$ configurations where the holes are created in the same orbital (e.g., $9t_2^{-2}3e$ for the $8a_1^{-1}$ satellite). This is analogous to a very strong DR found in the localized atomic levels in solids, e.g., the super-Coster-Kronig transition.[33,36] This explains why the ΔSCF method fails.

The 5σ derived orbitals in $Ni(CO)_4$ are $8t_2$, $8a_1$, the 1π derived orbitals are $1t_1$, $7t_2$, and $1e$, and the 4σ derived orbitals are $6t_2$ and $7a_1$. The relaxation and correlation energy shifts for $Ni(CO)_4$ given by the ADC(3) calculations are 2.9 eV for $8t_2$, $1t_1$, $7t_2$, $1e$, 3.3 eV for $8a_1$, and 3.0 eV for $7a_1$ and $6t_2$. The energy shifts for the 5σ, 1π, and 4σ levels of NiCO obtained at $R=3.5$ by the ADC(3) method are 1.8, 2.6, and 2.8 eV. For the 4σ and 1π levels the energy shifts in $Ni(CO)_4$ are almost the same as those in NiCO; however, for the 5σ level, the shift is about 1.1-eV larger. This shows a difference in the degree of involvement of 5σ derived orbitals in the bonding in $Ni(CO)_4$ and NiCO. As is the case in NiCO at $R=3.5$ the satellite intensity for the 4σ- and 1π-derived levels is not negligible, reflecting the dynamics of the weakly coupled system. The CNDO results also show the same tendency; however, the agreement with experiment is not as good as in the case of NiCO. The valence spectra of the transition-metal carbonyl complexes show prominent satellites which are interpreted as shakeup satellites (here shakeup is defined with respect to the CTS hole state).[3] The present results for $Ni(CO)_4$ show the reliability and accuracy of the present approach.

G. Screening, relaxation, and substrate band broadening effects in the $2h\,1p$ states

So far the present interpretation of the valence-hole spectrum of NiCO is based on the results of the ADC(3) approach. The first effects of relaxation and screening in the ionic excited $2h\,1p$ states, which are totally neglected in the ADC(3) scheme, enter in fourth order. We already emphasized that the features of the spectrum are strongly governed by the $1h/2h\,1p$ energy separations and coupling strengths. The screening effects and relaxation in the $2h\,1p$ ionic state may shift the $2h\,1p$ energy. *Ab initio* extended random-phase-approximation exchange (RPAE) Green's-function calculations of the ionization spectra of atoms and solids as well as ADC(3) calculations of molecular ionization spectra which include such effects show that the energy position of the $1h$ state is less sensitive to the $2h\,1p$ energy but the satellites and the line profiles can be influenced considerably.[33–36,61–63,76] It is necessary to estimate these effects without performing the ADC(4) calculation. It should, however, be noted here that the lowest satellite lines are quite reasonably calculated by the ADC(3) method and the effects mentioned above become important mainly for the higher-energy satellites.

Here we estimate the energy shifts by a simple approximate scheme. Starting with Eq. (1), we calculate the $2h\,1p$ energies by approximating the screening of the $1h\,1h$ and $1h\,1p$ interaction in terms of the $1h\,(1p)$ relaxation shift. We refer to Ref. 77 for a detailed account of this scheme. We note that strictly speaking this scheme is valid only for localized holes. The $2h\,1p$ CT excitation $(i^{-1}\pi_M^{-1}2\pi)$ energies calculated by this scheme are almost the same as the $d2ph$ TDA results.

In order to examine the accuracy of the scheme we consider the case of the final $2h$ energy of the *C-VV* Auger transition from the adsorbate [e.g., CO on Ni(100) surface]. The effective $1h\,1h$ interaction U is almost zero because of the screening of one of the two holes by a 2π CTS electron provided from the substrate when the initial hole is created.[53,56,68,78] Then we should be able to obtain U approximately by calculating the $2h\,1p$ energy where $1p$ is 2π and $2h$ are two valence holes. By estimating the relaxation shift of the 2π level (~ 2 eV), the calculated U ranges from about 2 eV for $5\sigma^{-1}i^{-1}$, 4 eV for $5\sigma^{-2}$ to 8 eV for $4\sigma^{-1}i^{-1}$, the tendency of which coincides with the experimental observation that U is about 4.5 eV for the double 4σ hole and almost zero for the double hole in the 5σ orbital. This tendency is interpreted as due to the delocalization and localization of the double holes.[68] In the present calculation of the Auger final-state energy we neglect the presence of a hole in the substrate which the CTS electron has left. Inclusion of such a hole, namely calculating the $3h\,1p$ energy leads to a very large U. This may arise from the fact that the $1s$ to 2π resonantly excited ($1h\,1p$) state will relax to the $1s$ XPS CTS core-hole ($2h\,1p$) state;[65-67] the hole left in the substrate by the CTS does not play a significant role because the hole will be screened by the metallic screening or will be delocalized.

To conclude, within the present scheme we expect that the $1h/2h\,1p$ energy separations will not be changed much by the relaxation and screening effects. However, we do not know how these effects will modify the $1h/2h\,1p$ coupling. Because of screening the $2h\,1p$ energy becomes nearly equal to a linear sum of single-hole energies. This situation is also found in the $4d^{-2}4f$ configuration of the Ba atom where a $4f$ electron localized in the region of a $4d$ hole acts as the screening electron and screens out one of the $4d$ holes.[63]

It was proposed that the localized valence orbitals of the adsorbate strongly hybridize with the broad substrate band and this leads to resonances.[30] Such adsorbate-derived resonance states lying below the Fermi level are considered to appear above the bottom of the d band[30] in contrast to the MO picture where the bonding orbital is likely to appear below the bottom of the d band.[79] Gumhalter *et al.*[30] argued that the valence UPS spectra of CO on Ni(111) and CO on Ni(100) (Ref. 80) show such a structure. However, there is no indication of $2\pi^*$-derived states at the Fermi level, neither in the recent high-resolution XPS spectrum nor in the angle-resolved photoemission spectra.[29,64,81-83] The latter spectra show the new states originating from two-dimensional CO $2\pi^*$ Ni $3d$ surface bands at energies between 1 and 2.7 eV below the Fermi level.[81-83] These results seem to be incompatible with the model based on the Anderson-Newns Hamiltonian of CO chemisorption.[58] The Blyholder model[52] seems to be able to explain the experimental data without any difficulties.[64,82,83] This implies that the MO approach like the present one could be very useful for understanding the dynamics of the ionization from the adsorbates.

The introduction of the substrate 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 and will not significantly modify the energetics of the hole excitations, the main-line–satellite-line energy separations, the intensities, etc. Therefore, the present MO Green's-function calculations should be able to provide such a basic knowledge of the energetics of the hole excitations in the adsorbates.

V. CORE-HOLE SPECTRUM

About a decade ago the core-hole spectra of the strongly or weakly coupled adsorbates were studied experimentally and theoretically very intensively (see Refs. 4 and 15 for a summary). The ADC(3) method cannot be used to calculate core-hole spectra. However, assuming that the main and/or satellite intensity ratio and energy separation are predominantly determined by the CT excitations, we made a $d2ph$ TDA two-level model calculation of the core-hole spectrum both at $R=3.2$ and 3.5 bohr. The results are listed in Table VII. We should not take these results too literally because of neglect of screening and relaxation of the $2h\,1p$ states, which is expected to be non-negligible in the case of the core-hole ionization. The present interpretation is that as in the case of a valence-hole excitation, the unoccupied orbital is not pulled fully below the Fermi level because of significant $1h\,1h$ and $1h\,1p$ interactions in the $2h\,1p$ CT states. The main line is the $1h$ state where the screening charge resides on the bonding orbital which is more polarized toward the ligand than in the ground state and the satellite is the $2h\,1p$ state where the bonding to antibonding shakeup excitations occur. This interpretation does not contradict the observation of the back-bonding structure in the Auger spectra of the coordinated molecules which is considered as evidence of the 2π CTS of the core-hole main-line state.[53,66-68,76] The Auger transition is dominantly the intra-atomic transition localized at the atomic site. The transition probes the local 2π density charges of the bonding orbital in the main-line state.

Saddei *et al.* performed the $d2ph$ TDA Green's-function calculation of the core-hole spectrum of NiCO ($R=3.5$) using the CNDO/2 approximation.[17] The results show that the lowest IP is the $1h$ state. The main-line–satellite-line energy separation is overestimated very much. The reason is as follows. The energy separations between the CT and intraligand excited $2h\,1p$ configurations calculated by CNDO agree rather well with the *ab initio* results. However, the absolute $2h\,1p$ energies are underestimated as much as 6–8 eV. The magnitude of the $1h/2h\,1p$ CT and local-ligand coupling-matrix element is overestimated very much in the CNDO-based calculation, by a factor of about 4 in comparison to the *ab initio* result.

Bagus and Hermann[12] performed an *ab initio* ΔSCF calculation of NiCO and concluded that the lowest IP peak is the CTS state and the satellite is the shakeup state from the CTS state. However, Saddei *et al.*[17] made an analysis of the results and concluded that the results in Ref. 12 actually show that the lowest IP peak is the $1h$ state and the satellite is the local metal excited state.

The new high-resolution spectrum[29] shows a quite different main-line–satellite-line energy separation and intensity ratio in comparison to previous measurements. Theoretical results available so far agree well with old measurements, but not with the new measurements. Further theoretical studies are thus in need.

TABLE VII. Theoretical main-line–satellite-line energy separations and intensity ratios for C 1*s* and O 1*s* core spectra of NiCO and corresponding experimental data from CO on Ni metal surfaces. Note that the spectra of Ref. 29 show a number of newly resolved structures. The satellite intensity of Ref. 29 is a sum of all satellite intensities. The values of Ref. 12 are at $R \sim 3.5a_0$. In Ref. 17 the intensity ratios are for the first satellite and read from figures.

	Expt.		Theory				
			A simple two-level model Present work				
Level	Ref. 5	Ref. 29	$R=3.2$	$R=3.5$	Ref. 12	Ref. 42	CNDO Ref. 17
			Energy separation (eV)				
C_{1S}	5.2	2.1(5.5)	5.1	3.64	8.6	4.4	9.5
O_{1S}	6.0	5.5	5.75	4.21	7.5	2.9	18.2
			Intensity ratios				
C_{1S}	0.74/0.26	0.29/0.71	0.93/0.07	0.83/0.17	0.8/0.2	0.75/0.25	0.71/0.12
O_{1S}	0.83/0.17	0.36/0.64	0.79/0.21	0.64/0.36	0.88/0.12	0.87/0.13	0.62/0.12

VI. CONCLUSION

In the present work the valence-electron spectra of NiCO and $Ni(CO)_4$ are calculated by the ADC(3) Green's-function method. We obtain fairly good agreement with experiment, suggesting that NiCO can be a good model system for a strongly coupled adsorbate. The outer-valence-shell levels of a free molecule become inner-valence-shell levels in the bonded system due to the presence of high-lying occupied orbitals of the metal atom. This introduces metal-ligand charge-transfer $1h/2h\,1p$ coupling. It is shown that the quasiparticle picture of 1π breaks down due to the $1h/2h\,1p$ CT coupling in the bonded system. The dominant role played by the intraligand relaxation in free CO is replaced by the CT relaxation because of a drastic decrease of the intraligand $1h/2h\,1p$ coupling strength. The CT relaxation is much stronger because the corresponding $1h/2h\,1p$ energy separations are much smaller. When the Ni—CO bond length becomes larger (weaker coupling), the intensity increase of the satellite and breakdown of the quasiparticle picture occurs also for 4σ ionization. This is not due to the change in the CT $1h/2h\,1p$ coupling strength but due to the smaller CT $1h/2h\,1p$ energy separations. The smaller energy separations occurs because of a change of magnitudes of the $1h\,1h$, $1h\,1p$ interactions in the $2h\,1p$ states. The present work emphasizes the importance of $1h\,1h$ and $1h\,1p$ interactions in the $2h\,1p$ states. A similar tendency of the increase in the satellite intensity is also seen in the weakly coupled $Ni(CO)_4$. The observation of the strong 4σ satellite in CO on Cu (weak-coupling system) compared to CO on Ni (strong-coupling system) may be explained by the aforementioned argument rather than the conventional interpretation that the intensity of the main line which is interpreted as the CTS state decreases because of a weaker CT in the ground state. Such an interpretation takes into account only the bonding strength and neglects totally the effects of $1h\,1h$ and $1h\,1p$ interactions.

It is shown that in the case of the 5σ and 4σ levels, the $1h$ state is more stable than the $2h\,1p$ states. Consequently the main line is interpreted as the $1h$ state where the screening charge resides on the bonding orbital which is more polarized toward the ligand than in the ground state. The satellites are dominated by $2h\,1p$ configurations where the bonding to antibonding shakeup excitations occur. For $1h$ ionization the strong mixing of $1h$ and $2h\,1p$ configurations leads to the breakdown of the one-electron picture of ionization and thus a distinction between main line and satellite lines is meaningless.

The ADC(3) approach neglects the relaxation and screening effects in the $2h\,1p$ states. The calculation of these effects by an approximate scheme shows that the energy shifts of the $2h\,1p$ energies are relatively small and are expected not to influence the present results for the lowest satellites appreciably. This is in accord with the general experience that the first few (one or two) satellites can be reasonably calculated by the ADC(3) approach. To conclude, we showed the usefulness of the MO Green's-function calculations for understanding the dynamics of the ionization in adsorbates.

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