# A COMPARISON OF SURFACE ELECTRON SPECTROSCOPIES

## E.W. PLUMMER, C.T. CHEN and W.K. FORD

Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-3859, USA

#### W. EBERHARDT

Exxon Research and Development Laboratory, RT22E, Annandale, New York 08801, USA

### **R.P. MESSMER**

General Electric Co., Corporate Research and Development, Schenectady, New York 12301, USA

and

#### H.-J. FREUND

Institut fur Physikalische and Theoretische Chemie, Universitat Erlangen-Nurnberg, Egerlandstrasse 3, D-8520 Erlangen, Fed. Rep. of Germany

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The objective of all surface electron spectroscopic techniques is to illucidate the nature of the surface and surface-adsorbate bond by probing the electronic states of the systems. All spectroscopies sample the system by measuring the response to an incident probe, yet the desired information is usually the ground state of the system. This paper will discuss and compare several types of spectroscopies: photoemission, photoadsorption or electron loss, Auger spectroscopy and inverse photoemission. The adsorption of CO will be used as the model system because much data exists for gas-phase CO, carbonyls and adsorbed CO.

# 1. Introduction

The interaction of electrons with other electrons and with the nuclei determines almost all of the physical and chemical properties of any piece of matter. The structure of a surface is dictated by the electron–electron and electron–ion interactions and not the other way around. Likewise the reactivity of a surface depends upon both the static and dynamic charge distributions at the surface. Clearly it is the objective of all surface electron spectroscopists to illucidate the characteristics of electrons at or near the surface. The problem is that the act of probing the electrons perturbs the ground-state distribution, so





Fig. 1. Schematic illustration of four electronic processes; ionization, inverse photoemission, optical excitation and Auger decay.

that different probes measure different properties. The objective of this paper is to interrelate the information obtained from the different measurement processes.

Fig. 1 is a schematic illustration of four electron spectroscopies commonly used to study surfaces: photoemission, inverse photoemission, photoabsorption or electron energy loss and Auger decay. The photoemission process [1,2] is the absorption of a photon which causes the emission of an electron thereby leaving the system positively charged. In contrast, inverse photoemission is the process where an electron is captured emitting a photon and thereby leaving the system negatively charged [3,4]. The well known optical excitation shown in fig. 1c leaves the system in a neutral but excited state [5,6]. Auger decay is commonly used to measure the surface concentration of impurities but recently both experimentalists and theorists have begun to interpret the energy positions [7,8] and symmetries [9] of the Auger peaks in an attempt to understand the bonding of an atom or molecule to the surface. The Auger process in an atom or molecule leaves the system with a +2 charge. These four processes have quite different final states, a positive ion for photoemission, a negative ion for inverse photoemission, a neutral for optical excitations and a double ionic state for the Auger decay. Therefore it is obvious that the energies measured in each experiment will be unique to the specific process. We hope to show in this paper that there is a commonality among the measurement processes by using the CO molecule adsorbed onto a metal surface as a prototype system.

It is very tempting to look at the complex processes shown in fig. 1 and immediately conclude that a single-particle picture will surely fail. Obviously no one would believe that a ground-state calculation for the molecular orbital energies would suffice for any of the processes shown, but an appropriate calculation for the ground and excited state of the system being studied has consistently produced reasonable agreement with experiment. In the preceding paper Avouris and Demuth have illustrated the use of Hartree–Fock calculations for explaining excitation spectra [10] and Messmer [11] has reviewed the use of various theoretical approaches to calculate the electronic structure [11].

Photoemission, especially angle-resolved photoemission utilizing synchrotron radiation as a light source has become the work horse of electron spectroscopy [1,2]. Due to the large effort in this area in the last 10 years a relatively clear understanding of the photoionization process has developed. We will attempt to use the concepts generated in this field to explain excitation processes in the other three spectroscopies shown in fig. 1. Inverse photoemission has been an active research area in surface science for a much shorter time than photoemission, but there is no doubt that it will soon be developed to the same level of sophistication. Excitation spectroscopy as well as Auger spectroscopy have been used as tools to study solids for many more years than either photoemission or inverse photoemission, but the interpretation of the data is much more difficult, because the measurement process does not define the parameters of the initial and final states as closely as either angle-resolved photoemission or inverse photoemission. There seems to be an unspoken uncertainty principle in surface science: The product of the difficulty of the experiment times the difficulty of the theoretical interpretation is a constant. A very nice confirmation of this uncertainty principle appeared in the literature this year [9]. The collection of Auger spectra from surface adsorbates is a simple straightforward if tedious experiment, but the theoretical interpretation has been very complicated [7,8]. Umbach and Hussain have measured the angular dependence of the Auger spectra using light from an undulator at the Stanford Synchrotron Radiation Laboratory [9]. The experiment is difficult but the assignment of the peaks in the Auger spectra only requires multiplication of spherical harmonics.

In section 2 the photoemission process will be discussed, concentrating on the process involved in photoionization from adsorbed CO. Section 3 will discuss excitation spectra, concentrating on the core to bound excitations that are now being observed with the new generation synchrotron light sources [12–14]. Section 4 will discuss Auger spectra and Section 5 will compare inverse photoemission and core to bound excitations as probes of the unoccupied states.

# 2. Photoemission

Angle-resolved photoemission has become to electronic structure what X-ray scattering is to crystallography and neutron scattering is to phonon structure. It is not too much of an exaggeration to claim that the three-dimensional bulk and two-dimensional surface band structure can be measured for any crystal that can be cleaned and does not charge when exposed to the incident light. In almost all cases that have been studied a single-particle calculational scheme gives good first-order agreement with experiment [1,15]. Even in the cases where the single-particle picture has deficiencies they are usually small (but important) effects [15] and in many situations can be corrected by the use of many-body corrections [15,16].

The adsorption of CO onto a metal surface is one of the most studied systems with photoemission and with various theoretical techniques. The photoemission observations for strongly chemisorbed CO are fairly universal and summarized in fig. 2 and table 1 for CO bound to Co atoms [17,18]. The molecular orbitals for free CO are shown in fig. 3. There are four general observations from fig. 2 and table 1.

(1) The CO core levels shift to lower binding energy by 4-5 eV on interaction with the metal.

(2) New intense satellite lines appear on the core level spectra when CO is coordinated to a transition metal.

(3) The CO 5 $\sigma$  and 1 $\pi$  peaks invert their ordering on the surface compared to the gas phase.

(4) The reduction in binding energy (ignoring the  $5\sigma$  level) caused by adsorption is larger for the core levels than for the valence levels. The O<sub>1s</sub> level in chemisorbed CO shifts upwards by 4–5 eV compared to gas-phase CO while the equivalent shift in the  $4\sigma$  level is only 3.3 eV.

The shift of the core levels to lower binding energy could be a result of either charge transfer due to bonding or to screening effects in the final state [19–25]. Calculations and measurements that will be described subsequently indicate that there is very little initial-state shift in the carbon or oxygen core levels when CO is bound to a transition metal or in a carbonyl complex [26,27]. Therefore the  $\sim 5$  eV shift is due to screening. This screening of the photoin-duced hole can be from two sources, (a) image potential screening of the lowest unoccupied orbital of the molecule. Image screening gives  $\sim 0.7$  eV of shift as seen for physisorbed CO on Ag [28] while charge transfer can produce 4 to 5 eV shift in CO [19–25]. In CO the lowest unoccupied orbital is the  $2\pi$  shown



Fig. 2. Valence and core photoionization spectra of free CO,  $Co_4(CO)_{12}$  and  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  CO on Co(0001) [17]. The horizontal scale is the binding energy referenced to the vacuum level.

in fig. 3, so screening is accomplished by transferring charge from the valence band of the metal to the  $2\pi$  orbital. This screening mechanism was referred to as the "excited atom" model by Lang and Williams [19] and has been confirmed by numerous theoretical calculations [20–24].

Fig. 4 shows a charge density difference plot for  $Cr(CO)_6$  by Baerends [29]. The plot is the difference between a self-consistent calcuation for  $Cr(CO)_6^+$  with a localized  $C_{1s}$  hole in one CO (shown by arrow) and a self-consistent calculation for a neutral  $Cr(CO)_6$  with the one CO where the hole is replaced by a relaxed  $CO^+$  molecule with a hole in the  $C_{1s}$ . This figure clearly shows that the extramolecular screening is caused by a  $\pi$ -like orbital. If we take the "excited atom" model literally and extend it to molecules, we conclude that we should be comparing the binding energies measured for adsorbed CO with the gas-phase excitation energies, not with the ionization potentials. This will be the subject of the next section.

Table 1

Energy levels of	free CO and CO	bound to a metal	; $\Delta E$ is differend	e between free	and coordinated
CO					

Energy level	I Free CO	II CO <sub>4</sub> (CO) <sub>12</sub>	a)	III CO on Co(0	)01) <sup>b.c)</sup>	
	Binding energy	Binding energy (eV)	$\Delta E$ (eV)	Binding energy (eV)	$\frac{\Delta E}{(\text{eV})}$	
5σ	14.0	13.5	0.5	13.6	0.4	
1π	16.9			13.4	3.5	
4σ	19.7	16.8	3.0	16.4	3.3	
3σ	38.9	34.7	4.2	34.9	4.0	
$2\sigma(C_{1s})$	296.1	292.2	3.9	291.6	4.5	
$1\sigma(O_{1s})$	542.4	538.3	4.1	537.9	4.5	

<sup>a)</sup> See ref. [18].

<sup>b)</sup> See ref. [17b].

<sup>c)</sup> 5.7 eV work function for  $(\sqrt{3} \times \sqrt{3})$  R30° overlayer.

The large and new satellite lines seen in the core level spectra of coordinated CO are intimately related to the charge-transfer process. It is generally agreed theoretically [22-25] that the lowest binding energy core level peak is the screened core while the satellite line is the unscreened excited state. In more weakly bound adsorption systems the unscreened peak can become the most intense peak in the spectrum [28,30,31] because the coupling to the substrate is so small that charge cannot be efficiently transferred. As in most spectroscopies there are sum rules governing the intensity and energy position of the peaks in the spectra. Manne and Åberg [32] proved within the context of Hartree–Fock theory that there are two appropriate sum rules. The first sum rule says that the sum of all of the intensities of the core level lines must be a constant. If  $I_i$  indicates the intensity of a given peak then

$$\sum_{j} I_{j} = \text{const.} \tag{1}$$

This implies that intensity must be borrowed from the "main line" to produce new satellite lines when CO binds to a transitin metal. The second sum rule concerns the first moment of the spectrum:

$$\epsilon_{\rm HF}(i) = \sum_{\substack{j \ \text{bound}}} I_j E_j + \int_{\rm cont.} I_j(E) \ E \ dE.$$
<sup>(2)</sup>

 $\epsilon_{\rm HF}(i)$  is the initial-state binding energy of the *i*th hole in the Hartree–Fock (HF) approximation. The right-hand side of eq. (2) is a sum over all discrete excitations plus an integral over the continuum or shake-off states. It is this integral over the continuum that makes utilization of the second sum rule so



Fig. 3. Wavefunctions for the free CO molecule. The binding energies are given in parentheses. The carbon end of the molecule is on the left.

difficult. In spite of this complication Freund et al. [26] have shown that the sum rules work for small molecules and carbonyls. We have no reason to believe that they do not work for CO adsorbed on the surface.

Fig. 5 shows the  $O_{1s}$  core level spectrum for gas-phase CO and Fe(CO)<sub>5</sub> taken at the same pressure in the gas cell. An analysis of the main line intensity shows that there is a 28% loss in intensity per CO molecule in the Fe(CO)<sub>5</sub> spectrum compared to the free CO spectrum. All of this lost intensity is in the new satellite lines since a sum like eq. (1) over the bound-state excitations for the  $O_{1s}$  spectra of Fe(CO)<sub>5</sub> compared to CO shows that the Fe(CO)<sub>5</sub> spectrum has 0.93 of the integrated intensity of the CO spectrum. Eq. (2) for the sum rule on the first moment cannot be accurately tested because the continuum is



Fig. 4. Electron density difference plots from Baerends for  $Cr(CO)_6$  [29]. The core electrons are not included. The plot is the difference in the total charge density of the  $Cr(CO)_6$  molecule with a  $C_{1s}$  hole in the carbon atom marked by the arrow minus the charge density of a neutral Cr, five neutral CO molecules and one CO ion with a  $C_{1s}$  hole.

too difficult to measure. Freund et al. [26] assumed that the intensity in the continuum was the same for CO and  $Fe(CO)_5$  and summed eq. (2) over the bound states. The first moment was 546.6 eV for CO and 546.1 eV for Fe(CO)<sub>5</sub>. The first moments are shown in fig. 5. These numbers are in embarrasingly good agreement with calculated initial-state shifts.

The message from this discussion of core level intensities is: The experimentalist should always look at the first moment of any complicated spectra.

The shift of the  $5\sigma$  ion state energy relative to the  $1\pi$  ion state energy or the  $5\sigma$  shift with respect to the energy of any of the other molecular orbitals of CO seen in fig. 2 and table 1 is a consequence of the bonding. In the Blyholder model for CO adsorption there is  $\sigma$  donation from the  $5\sigma$  of CO to the metal and back donation from the metal d electrons into the empty  $2\pi$  CO level [33]. All experimental data and theoretical calculations [34–39] for chemisorbed CO or for transition-metal carbonyls show a drop in the  $5\sigma$  level with respect to the other CO energy levels due to the bonding. It should be pointed out, as noted by many others, that for CO adsorption the magnitude of the drop in the CO  $5\sigma$  level is not directly related to the bond strength [40].

The final item listed as a general property of adsorbed CO was the



Fig. 5.  $O_{1s}$  core hole spectra of gaseous Fe(CO)<sub>5</sub> and CO taken at the same pressure [26]. The excitation energy was 1254 eV. The vertical arrows indicate the first moment of each spectrum, 546.4 eV, for CO and 546.1 eV for Fe(CO)<sub>5</sub>.

nonuniform shift in the energy levels of CO not involved in the bond to the metal. It is apparent that this nonuniform shift is a consequence of an orbital-dependent screening, which in principle can be calculated by any scheme which properly treats the final ionic state of the system. The next section will demonstrate that you do not need to calculate anything to understand this phenomena. Instead all that is required is a table of the excitation energies in gas-phase CO.

#### 3. Electronic excitations

In the last section the claim was made that the ionization potentials of CO adsorbed onto the surface are related to the excitation energy of the specific

CO molecu	le		N <sub>2</sub> molec	ule	
Initial energy level	Ionization (eV)	Excitation to $2\pi^{\text{b}}$ (eV)	Initial energy level	Ionization (eV)	Excitation to $2\pi^{c}$ (eV)
5σ	14.0	8.07 <sup>1</sup> П 6.04 <sup>3</sup> П	5σ	15.5	$9.2 {}^{1}\Pi_{g}$ 7.9 ${}^{3}\Pi_{g}$
$1\pi$	16.9	$13.7 \ {}^{1}\Sigma^{+}$ $8.3 \ {}^{3}\Sigma^{+}$	$1\pi$	16.8	$\frac{14.2  {}^{1}\Sigma_{u}^{+}}{7.6  {}^{3}\Sigma_{u}^{+}}$
4σ	19.7	13.12 П 11.79 <sup>3</sup> П	4σ	18.6	$12.8 {}^{1}\Pi_{u}$ $11.0 {}^{3}\Pi_{u}$
3σ	38.9		3σ		
$2\sigma(C_{1s})$	296.1	287.3 <sup>1</sup> П 285.9 <sup>3</sup> П	N <sub>1s</sub>	409.9	400.96 <sup>1</sup> П 400.16 <sup>3</sup> П
$1\sigma(O_{1s})$	542.4	534.1 <sup>1</sup> 11 533.6 <sup>3</sup> 11			

Table 2 Excitation and ionization energies in CO and  $N_2^{(a)}$ 

<sup>a)</sup> Ref. [45] discusses the assignments used in this table.

<sup>b)</sup> See ref. [41] for valence excitations and refs. [42,43] for core excitations.

<sup>c)</sup> See ref. [41] for valence excitations and refs. [42,44] for core excitations.

level of interest to the empty  $2\pi$ . This hypothesis was based on the theoretical observation and prediction that a hole on the CO is screened by filling the first unoccupied energy level of CO (the  $2\pi$ ). Let us try to make this hypothesis more quantitative so that it can be tested. In table 2 we have compiled the observed excitation energies of gas-phase CO and N<sub>2</sub> [41-45]. The first problem encountered is the multiplet structure due to spin coupling. There are singlet and triplet excited states arising from excitations of each  $\sigma$ -symmetry orbital in the ground state and a manifold of six states for excitation in table 2. For the  $\sigma$  initial states the singlet excitation is optically allowed so the triplet energy must be obtained from non-dipole scattering experiments. If we assume that the spin splitting observed in the gas phase is unaffected when CO is adsorbed and that the hole screening will occur by filling the lowest-energy state, we can use table 2 to predict orbital binding energies of adsorbed molecules.

First let us address the issue of nonuniform shifts which was postponed until the excitation energies shown in table 2 were presented. Look at the differences between the triplet excitation energies and the ionization potentials for CO. The differences are 8.8, 10.2, 7.9 and 7.9 eV for the O<sub>1</sub>, C<sub>1s</sub>,  $4\sigma$  and  $5\sigma$ levels respectively. Likewise for N<sub>2</sub> the differences are 9.7, 7.6 and 7.6 eV for



Fig. 6. Total charge density difference plots for excitation to the  $2\pi$  state of CO. (a)  $O_{1s} \rightarrow 2\pi$ , (b)  $C_{1s} \rightarrow 2\pi$ , (c)  $4\sigma \rightarrow 2\pi$ , (d)  $5\sigma \rightarrow 2\pi$ .

the N<sub>1s</sub>,  $4\sigma$  and  $5\sigma$  levels respectively. There is another way of demonstrating the state dependence of the response of the CO molecule to excitations into the  $2\pi$ . That is, the numbers listed above are the energies required to remove the  $2\pi$  electron from the CO molecule containing a hole in the various specified orbitals.

Fig. 6 shows the total charge density difference plots for excitation from  $O_{1s}$ ,  $C_{1s}$ ,  $4\sigma$  and  $5\sigma$  orbitals to the  $2\pi$  orbital, respectively [45]. These plots are the excited-state charge density minus the ground-state charge density using a generalized valence bond (GVB) theoretical scheme. Each figure shows that the redistribution of charge upon excitation is very dependent upon the orbital from which the excitation takes place. For example in fig. 6a for an  $O_{1s} \rightarrow 2\pi$  excitation the excess charge induced by the rearrangement is on the oygen end of the molecule, while a  $C_{1s} \rightarrow 2\pi$  excitation shown in fig. 6b produces an excess charge on the carbon end. In figs. 6c and 6d the charge density plots for excitation. In detail the  $\sigma$  hole delocalizes so that the electron-hole interaction energy is less than for the case of the core hole excitation shown in figs. 6a and 6b. This is the reason that the  $2\pi$  excited electron is bound more tightly to the molecule with a core hole compared to a valence hole.

Let us now turn to comparing actual orbital binding energies of adsorbed

molecules to the excitation energies shown in table 2. The philosophy (once more) is that the screening is accomplished by filling the lowest-energy  $2\pi$ orbital and the readjustment of the other valence orbitals for a given hole. The  $2\pi$  level is pinned at the Fermi energy so the excitation energy is equal to the binding energy if there is no perturbation of the CO molecular states by the substrate, i.e. no bonding. If we wish to minimize the perturbation of the substrate, then physisorbed molecules would be an obvious starting point. These systems can be difficult to analyze because the weak coupling does not allow charge transfer to occur. It is safer to start with weakly chemisorbed systems and then return to physisorption and strong chemisorption. In table 3 the electron binding energies for a variety of adsorbed CO and N<sub>2</sub> systems has been compiled. The heat of adsorption  $H_a$  is in the 0.5 eV range for weak chemisorption, the three weak chemisorption systems in this table are CO on Cu(001) (column I), N<sub>2</sub> on Ni(110) (column V) and CO on NiAl (column IV). The CO adsorbed on Ag(110) is an example of physisorption (column II) and CO on Ni(100) (column III) is an example of strong chemisorption.

First examine the CO on Cu system. The binding energies and the differences between the binding energies and excitation energies are given. In all cases the lowest-energy excitation is used. The agreement is very good except for the  $5\sigma$  level where there is a 2.4 eV discrepancy between CO and adsorbed CO. We already indicated that this is the level of CO that is shifted because of the bonding. The small shift in C<sub>1s</sub> level of 0.7 eV can be a result of the interaction of the CO with the surface either through the backbonding into the  $2\pi$  or polarization of the molecule by the surface. The N<sub>2</sub> adsorbed on Ni(110) even shows better agreement than for CO on Cu. Column V shows that the difference between the binding energy on the surface and the excitation energy is only a few tenths of a volt for the valence levels. The two core levels are generally thought to be a consequence of the two inequivalent N<sub>1s</sub> core levels when N<sub>2</sub> is adsorbed on the surface [52]. Umbach [31] has a different interpretation, but for the purposes of this paper we will treat these two peaks as different  $N_{1s}$  levels. Therefore the average discrepancy is -0.3 eV. This  $N_2$ adsorption system offers qualitative support to "excited atom" type models of screening and it also indicates that the large shift in the CO  $5\sigma$  is not directly related to the bond energy because of the large shift in the CO on Cu system.

If this model works for weak chemisorption it should work even better for physisorption. Column II lists the data for CO adsorbed on Ag(110) [29]. The core levels look very good but the valence levels are off by  $\sim 3$  eV. There is a trival explanation for this apparent discrepancy. The charge-transfer process is not very efficient in these weakly coupled systems so the peaks for the screened state are much less intense than the unscreened satellite lines. For example the lowest binding energy peak in the C<sub>1s</sub> spectrum has a binding energy of 286.4 eV but only 20% of the intensity of the unscreened peak at 290.6 eV. It is very hard to see these weak peaks in the valence band spectra because of their

CO on Cu <sup>a</sup> )         CO on Ag(110) <sup>b</sup> )         CO on Ni(100) <sup>c)</sup> CO on Ni(100) <sup>c)</sup> $H_a = 0.6 \text{ eV}$ $H_a = 0.15 \text{ eV}$ $H_a = 0.15 \text{ eV}$ $H_a = 0.13 \text{ eV}$ $H_a = 0.04 \text{ eV}$ Energy         BE $\Delta E$ Energy         BE $\Delta E$ Energy         BE $\Delta I$ Energy         BE $\Delta E$ Energy         BE $\Delta E$ Energy         BE $\Delta I$ $5\sigma$ $8.4$ $0.1$ $1\pi$ $11.9$ $3.5$ $1\pi$ $7.5$ $-0.9$ $1\pi$ $8.4$ $0.1$ $1\pi$ $8.4$ $11.8$ $-0.01$ $4\sigma$ $10.6$ $-1.2$ $4\sigma$ $11.6$ $-1.2$ $4\sigma$ $11.6$ $-1.2$ $4\sigma$ $11.6$ $-0.9$ $6^{-1}$				Π			III			IV			>		
Energy         BE $\Delta E$ Energy         BE $\Delta I$ 5 $\sigma$ 8.4         0.1         1 $\pi$ 11.9         3.5         1 $\pi$ 7.5         -0.9         1 $\pi$ 8.4         -         -         8.4         -<	_ CO on Cu <i>II</i> <sub>a</sub> ~ 0.6 e	(e <b>V</b>		CO on Ag $H_{\rm a} = 0.15$	g(110) <sup>b)</sup> i eV		CO  on  Ni $H_a \sim 1.3 \text{ e}$	(100) <sup>e)</sup> V		CO  on  N $H_a \sim 0.9 \text{ or }$	iAl(110) ' eV	(1	$N_2 \text{ on } N$ $H_a \sim 0.4$	i(110) <sup>e)</sup> . eV	
$5\sigma$ $8.4$ $2.36$ $5\sigma$ $9.1$ $3.01$ $5\sigma$ $8.0$ $+1.96$ $5\sigma$ $8.7$ $+1.66$ $-1.2$ $4\sigma$ $11.66$ $-1.2$ $4\sigma$ $11.6$ $-1.2$ $4\sigma$ $11.6$ $-1.2$ $4\sigma$ $11.6$ $-1.2$ $3\sigma$ $3\sigma$ $3\sigma$ $3\sigma$ $2\sigma(C_{1s})$ $286.6$ $0.7$ $2\sigma(C_{1s})$ $286.6$ $-0.3$ $2\sigma(C_{1s})$ $285.6$ $-0.3$ $2\sigma(C_{1s})$ $285.8$ $-1$ $1\sigma(O_{1s})$ $533.7$ $+0.1$ $1\sigma(O_{1s})$ $531.5$ $-2.1$ $1\sigma(O_{1s})$ $531.7$ $-2$ $\sigma(O_{1s})$ $533.7$ $+0.1$ $1\sigma(O_{1s})$ $531.5$ $-2.1$ $1\sigma(O_{1s})$ $531.7$ $-2$ $\sigma(O_{1s})$ $533.7$ $+0.1$ $1\sigma(O_{1s})$ $531.5$ $-2.1$ $1\sigma(O$	Energy level	BE (eV)	AE (eV)	Energy level	BE (eV)	Δ <i>E</i> (eV)	Energy level	BE (cV)	Δ <i>E</i> (eV)	Energy level	BE (eV)	Δ <i>E</i> (eV)	Energy level	BE (cV)	$\Delta E$ (cV)
$ \begin{bmatrix} 1\pi & 8.4 & 0.1 & 1\pi & 11.9 & 3.5 & 1\pi & 7.5 & -0.9 & 1\pi & 8.4 \\ 4\sigma & 11.8 & -0.01 & 4\sigma & 14.8 & 3.01 & 4\sigma & 10.6 & -1.2 & 4\sigma & 11.6 & -1 \\ 3\sigma & 3\sigma & 3\sigma & 3\sigma & 3\sigma & 3\sigma & 3\sigma \\ 2\sigma(C_{1_s}) & 2.86.6 & 0.7 & 2\sigma(C_{1_s}) & 286.4 & 0.5 & 2\sigma(C_{1_s}) & 285.6 & -0.3 & 2\sigma(C_{1_s}) & 285.8 & -1 \\ 1\sigma(O_{1_s}) & 533.7 & +0.1 & 1\sigma(O_{1_s}) & 533.9 & +0.3 & 1\sigma(O_{1_s}) & 531.5 & -2.1 & 1\sigma(O_{1_s}) & 531.7 & -1 \\ \hline {}^{0} & Core level data from ref. [30] and valence from ref. [46]. \\ \overset{(1)}{}^{0} Ref. [28]. \\ \overset{(2)}{}^{0} Valence levels from ref. [30], core levels from ref. [48]. \\ \hline {}^{0} Ref. [49]. \\ \overset{(2)}{}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [30] and valence from ref. [30] hor Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence data from ref. [30] hor Valence data from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence avecter data from ref. [30] hor Valence avecter data from ref. [31] for Ni(100) [51]. \\ \hline {}^{0} Valence avecter data from ref. [30] hor Valence avecter data from ref. [30] hor Valence avecter data from r$	50	8.4	2.36	50	9.1	3.01	5σ	8.0	+1.96	5σ	8.7	+ 2.66	50	8.0	0.1
$4\sigma$ 11.8 $-0.01$ $4\sigma$ 14.8       3.01 $4\sigma$ 10.6 $-1.2$ $4\sigma$ 11.6 $-1.2$ $3\sigma$ <td>17</td> <td>8.4</td> <td>0.1</td> <td>1 1</td> <td>11.9</td> <td>3.5</td> <td>1#</td> <td>7.5</td> <td>-0.9</td> <td>11</td> <td>8.4</td> <td>0.0</td> <td><math>1\pi</math></td> <td>- 7.7</td> <td>0.1</td>	17	8.4	0.1	1 1	11.9	3.5	1#	7.5	-0.9	11	8.4	0.0	$1\pi$	- 7.7	0.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4σ	11.8	-0.01	4σ	14.8	3.01	40	10.6	- 1.2	$4\sigma$	11.6	-0.2	4σ	10.8	- 0.2
$\frac{2\sigma(C_{1_s})}{1\sigma(O_{1_s})} = \frac{2.86.6}{5.38.6} = \frac{0.7}{0.7} = \frac{2\sigma(C_{1_s})}{2\sigma(C_{1_s})} = \frac{286.4}{5.33.9} = \frac{0.5}{10\sigma(O_{1_s})} = \frac{2\sigma(C_{1_s})}{531.5} = \frac{285.6}{-2.1} = \frac{0.3}{10\sigma(O_{1_s})} = \frac{231.7}{531.7} = \frac{1}{0} = \frac{1}{000} = \frac{1}{000} = \frac{1}{000} = \frac{1}{0000} = \frac{1}{00000} = \frac{1}{00000000000000000000000000000000000$	30			3 о			30			3σ			3σ		
$1\sigma(O_{1_{5}})  533.7  + 0.1  1\sigma(O_{1_{5}})  533.9  + 0.3  1\sigma(O_{1_{5}})  531.5  -2.1  1\sigma(O_{1_{5}})  531.7  -$ <sup>a)</sup> Core level data from ref. [30] and valence from ref. [46]. <sup>b)</sup> Ref. [28]. <sup>c)</sup> Valence levels from ref. [47] and core data from ref. [48]. <sup>d)</sup> Ref. [49]. <sup>e)</sup> Valence data from ref. [50]. core levels from ref. [31] for Ni(100) [51].	2σ(C <sub>1s</sub> )	2.86.6	0.7	$2\sigma(C_{1,s})$	286.4	0.5	$2\sigma(C_{1_S})$	285.6	-0.3	$2\sigma(C_{\rm hs})$	285.8	- 0.1	z	399.3	-0.9
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$														400.5	+ 0.3
<ul> <li><sup>30</sup> Core level data from ref. [30] and valence from ref. [46].</li> <li><sup>b)</sup> Ref. [28].</li> <li><sup>c)</sup> Valence levels from ref. [47] and core data from ref. [48].</li> <li><sup>d)</sup> Ref. [49].</li> <li><sup>c)</sup> Valence data from ref. [50]. core levels from ref. [31] for Ni(100) [51].</li> </ul>	$l \sigma(O_{1s})$	533.7	+ 0.1	$l\sigma(O_{1_{s}})$	533.9	+0.3	$1\sigma(O_{1_{5}})$	531.5	- 2.1	$1\sigma(O_{1_{s}})$	531.7	-1.9			
<sup>b)</sup> Ref. [28]. <sup>c)</sup> Valence levels from ref. [47] and core data from ref. [48]. <sup>d)</sup> Ref. [49]. <sup>c)</sup> Valence data from ref. [50]. core levels from ref. [31] for Ni(100) [51].	a) Core le	vel data frc	m ref. [30	] and valen	ice from 1	ref. [46].		-							
<sup>c)</sup> Valence levels from ref. [47] and core data from ref. [48]. <sup>d)</sup> Ref. [49]. <sup>e)</sup> Valence data from ref. [50], core levels from ref. [31] for Ni(100) [51].	<sup>h)</sup> Ref. [2)	<u>3</u> ].													
e) Valence data from ref. [30]. core levels from ref. [31] for Ni(100) [51].	<sup>d)</sup> Ref. 149	c levels fror N.	n ref. [47]	and core d	ata from	ref. [48].									
	c) Valence	; data from	ref. [50].	core levels	from ref.	[31] for N	li(100) [51].								

Table 3

System	$C_{1s} \rightarrow 2\pi$		$O_{1s} \rightarrow 2\pi$		Oxygen-
	Singlet energy (eV)	$\Delta E$ (eV)	Singlet energy (eV)	$\Delta E$ (eV)	(eV)
CO <sup>a)</sup>	287.3	0	534.1	0	246.8
Fe(CO) <sub>5</sub> <sup>b)</sup>	287.7	0.38	533.4	-0.7	245.7
$Fe_2(CO)_9^{b}$	287.9	0.58	533.1	-1.0	245.2
Cr(CO) <sub>6</sub> <sup>b)</sup>			532.2	-1.9	
CO on Ni(111) <sup>c)</sup>	287.5	0.2	533.1	-1.0	245.6

Table 4 Core-to-bound excitation energies ( $\Delta E$  = coordinated CO – free CO)

a) Ref. [42].

<sup>b)</sup> Ref. [53].

<sup>c)</sup> Ref. [13].

overlap with other peaks. The "excited atom" model would predict a screened  $4\sigma$  level at 11.8 eV, the screened  $1\pi$  at 8.4 eV and the equivalent  $5\sigma$  level at 6.1 eV. These are very difficult to see because the screened  $4\sigma(1\pi)$  level is nearly degenerate with the unscreened  $1\pi(5\sigma)$  and the screened  $5\sigma$  overlaps the d-bands of Ag. Before we discuss the NiAl data it will be beneficial to present the strong chemisorption case, CO on Ni.

Column III shows that there are much larger changes in the CO binding energies compared to the gas-phase excitation energies for this strongly chemisorbed system than appear for weak chemisorption or physisorption. The C<sub>1s</sub> and O<sub>1s</sub> binding energies move towards each other by 1.8 eV and the  $4\sigma$  and  $1\pi$  levels of the chemisorbed system are approximately 1 eV less in energy than the excitation energy. It is our contention that all of the information about bonding to the transition metal that can be extracted from photoemission binding energies is contained in the differences shown in table 3. The most obvious next question is "Do the excitation energies observed for coordinated CO shift in the same way as the binding energies?"

The electron energy loses in the valence region of the loss spectra are complicated and the assignment is still being discussed. Avouris and Demuth have discussed the state of these measurements [10]. Let us concentrate in this paper on the core to bound excitations. In table 4 we have listed data for core to bound excitations in gas-phase CO, carbonyls [53] and CO adsorbed on Ni(111) [13]. In general the  $C_{1s} \rightarrow 2\pi$  excitation energy moves up in energy and the  $O_{1s} \rightarrow 2\pi$  energy moves down. Fig. 7 shows the data for condensed CO and CO chemisorbed on Ni(111) by Jugnet et al. [13]. The lineshape is asymmetric most likely due to hybridization of the  $2\pi$  of chemisorbed CO with the unoccupied energy states of Ni. What is listed in table 4 and shown by the arrows in fig. 7 is the first moment of the spectrum.



Fig. 7. Core level excitation spectra for solid Co and chemisorbed CO on Ni(111) [13]. The vertical arrows indicate the position of the first moment of the spectra.

Jugnet et al. [13] have offered an explanation of the shifts in the core to bound energies based upon the spatial character of the  $2\pi$  orbital in the C<sub>1s</sub> hole and O<sub>1s</sub> hole situations. Their argument is based on the observation that the  $2\pi$  is more on the carbon side with an oxygen hole than it is with a carbon hole so the excited molecule interacts via the  $2\pi$  with the substrate more readily with an oxygen hole than it does with a carbon hole. The explanation of the shift in the core to bound excitation energies derived from our GVB calculations shown in fig. 6 is apparently different than that of Jugnet et al. [13]. Again referring to figs. 6a and 6b, we see that in fig. 6a (the  $O_{1s} \rightarrow 2\pi$  excitation) that the redistribution of charge leaves the  $\pi$ -space on the C-end of the molecule open, thus making it a potential  $\pi$ -acceptor from interaction with a metal  $\pi$ -donor. On the contrary, fig. 6b shows (the  $C_{1s} \rightarrow 2\pi$  excitation) that the charge distribution leaves excess charge in the  $\pi$ -space of the C atom thus diminishing its potential  $\pi$ -acceptor capability if adjacent to a metal  $\pi$ -donor. We believe that it is impossible to understand this phenomena by concentrating solely on the  $2\pi$  orbital, but it is premature to conclude that there is a substantial difference in the two calculations discussed above. The apparent discrepancy may be a consequence of the language used to describe the computational results.

In general the observation of table 4 is that the excitation energies change in the same way as the binding energies. For example the  $(O_{1s} \rightarrow 2\pi)$  minus  $(C_{1s} \rightarrow 2\pi)$  energy goes from 246.8 eV for gas-phase CO to 245.6 eV for CO on Ni(111), a shift of -1.2 eV. The equivalent shift in the surface binding energies with respect to the gas-phase excitation energies is -1.8 eV. Now let us return to the surface of the alloy NiAl [49]. The experiments indicate that CO only binds to the Ni atoms in the (110) surface but with a bond energy considerably reduced compared to CO on Ni. In NiAl the Ni d bands are nearly full making this material look like Cu except the d bands are close to the Fermi energy. Column IV of table 3 shows that the valence band energies are close to those seen on Cu, but the core levels are still shifted by 1.8 eV towards each other. We speculate from these data that CO on NiAl is significantly bonded through the  $d-2\pi$  interaction, and it is this interaction that causes the shift in the core to bound excitation energies and the binding energies on the surface.

Let us summarize what has been proposed in this section.

(1) The electron binding energy of each orbital of a molecule adsorbed on a surface is directly related to the energies in the excitation spectra.

(2) The differences between the gas-phase excitation energies (lowest spin state) and surface binding energies reflects the perturbation of the molecule by the surface.

(3) A corrolorary to (2) is that all of the interesting surface modification of the CO is contained in the energy difference between surface binding energy and gas-phase excitation energy.

With this model we can make a few predictions which can easily be checked. Before we stick our collective necks out notice that the agreement between the gas-phase excitation energies and adsorbate binding energies was especially good for those weakly chemisorbed systems where there is believed to be little  $2\pi$  backbonding in the ground state, i.e. CO on Cu and N<sub>2</sub> on Ni. These are the systems where there are large satellite lines observed in the photoemission spectra and the coverage dependence of the energy of the molecular stretch goes the wrong direction. This implies that whenever there is relatively strong  $2\pi$  bonding the core to bound excitation energies will shift and the strong satellite lines will disappear. With this argument in hand we can make a few safe predictions.

(1) When the core to bound transition energies are measured for CO on Cu it will be observed that they are much closer to the gas-phase values than what was seen in fig. 7 for CO on Ni [13].

(2) The co-adsorption of K and CO to a Cu surface causes the strong satellite lines to go away [54]. The core to bound excitation energies for CO + K will look much more like CO on Ni than CO on Cu.

(3) When the core to bound excitation energies for CO on Ni(100) are re-measured with a much better calibration of the monochromator it will be found that the energy difference between the  $O_{1s} \rightarrow 2\pi$  and  $C_{1s} \rightarrow 2\pi$  is ~ 245.5 eV instead of the value quoted by Stohr and Jaeger [12] of 246.5 eV.

There are surely unresolved problems left over. For example, Avouris et al. [5] have argued from their data that the 6 eV loss seen in inelastic electron scattering from CO adsorbed on many substrates is the  $5\sigma \rightarrow 2\pi$  triplet state. This is just impossible in our model. You cannot have an excitation energy less than the binding energy. If the interpretation of the excitation spectra is correct then there must be another  $5\sigma$ -derived level  $\sim 3$  eV above what everyone identifies as the  $5\sigma$  level of adsorbed CO. A second severe problem arises because of the expected two-peak core level spectrum from the singlet-triplet spin couplings [43]. The spin splitting on the O<sub>1s</sub> core is small enough that one could claim that no one would observe such a satellite line but the 1.45 eV splitting expected for the C<sub>1s</sub>  $\rightarrow 2\pi^{-1}\Pi$  to  $^{3}\Pi$  states should have been observed, especially in the carbonyls.

### 4. Auger spectroscopy

There has been an increased interest in the last few years in the possibility of using Auger spectroscopy as a tool to determine the energy levels and bonding configuration of chemisorbed molecules [8,9,55,56]. For example, Jennison et al. [8] claim that the  $2\pi$  backbonding for coordinated CO is directly responsible for a high kinetic energy peak in the Auger spectrum from carbonyls. Everyone is compiling tables of the changes in the hole-hole interaction energy U as a function of the hole configuration in the CO molecule as it bonds to the surface. We will show in this section that once you understand the hole screening mechanism in an adsorbed molecule like CO, predicting the energies seen in the Auger spectra is straigtforward. Understanding the intensities is much more difficult.

The standard procedure for analyzing an Auger spectrum from a gas-phase molecule is to break the process up into two independent ionization processes



Fig. 8. Schematic diagram of the energy level schemes in the initial and final states of an Auger decay. The left shows gas-phase CO going from a  $C_{1s}$  hole configuration to a double-hole  $(1\pi, 5\sigma)$  final configuration.

plus a hole-hole interaction term, which also contains spin-coupling corrections:

$$E_{\rm K}, (i, j, k; {}^{\rm s}{\rm X}) = E_{\rm B}(i) - E_{\rm B}(j) - E_{\rm B}(k) - U(i, j, k; {}^{\rm s}{\rm X}).$$
(3)

Here  $E_{\rm K}$  is the kinetic energy of a peak in the Auger spectrum.  $E_{\rm B}(i)$  is the binding energy of the initial hole while  $E_{\rm B}(j)$  and  $E_{\rm B}(k)$  are the binding energies of the *j* and *k* valence levels involved in the Auger decay. Obviously the energies of the various Auger states will depend up the particular state <sup>s</sup>X the energy of which depends on the spin couplings. Eq. (3) is often rearranged to give the two-hole binding energy  $E_{\rm B}(j, k)$ :

$$E_{\rm B}^{i}(j, k; {}^{\rm s}{\rm X}) = E_{\rm B}(i) - E_{\rm K}(i, j, k; {}^{\rm s}{\rm X}) = E_{\rm B}(j) + E_{\rm B}(k) + U(j, k; {}^{\rm s}{\rm X}).(4)$$

Let us use the configuration shown on the left of fig. 8 to illustrate the use of these equations. The initial state after ionization is a CO molecule with a  $C_{1s}$ 

hole. It costs 296.1 eV in energy to ionize the CO. If it decays leaving  $1\pi$  and  $5\sigma$  holes then from table 1 we know that  $E_B(5\sigma) = 14.0$  eV and  $E_B(1\pi) = 16.9$  eV. Kelber et al. [8] have identified the peak in the C<sub>1s</sub> Auger spectrum (curve a of fig. 9) at a kinetic energy of 253.9 eV as this  $5\sigma$ ,  $1\pi$  hole state. Applying eq. (3) we find that

 $U(5\sigma, 1\pi) = 11.3 \text{ eV},$ 

The common practice in the literature [8,9,55] is to use eq. (3) or (4) to analyze the Auger data from CO adsorbed on the surface or bound in a transition-metal complex. The conclusion always is that the hole-hole interaction energy becomes very small when CO is bound to a metal atom or atoms. In general it is misleading to use eq. (3) or (4) for adsorbed CO because it is not really a hole-hole interaction on the surface, instead it is a electron-hole, electron-hole interaction.

The features in Auger spectra from an adsorbed molecule are (intimately) related to the excitation spectra of the chemisorbed molecule, except now we have two holes. Fig. 8 illustrates on the right a typical Auger decay for CO adsorbed on the surface. The initial state after ionization of a C<sub>1s</sub> electron is the " $2\pi$  screened" molecule, i.e. the molecule is in an excited neutral state with the metal furnishing one electron. After the Auger decay there are holes in the  $1\pi$  and  $5\sigma$  levels of CO but again the molecule is completely screneed by charge transfer from the metal into the  $2\pi$ . The final state of the Auger process has holes in the  $5\sigma$  and  $1\pi$  levels and two new electrons in the  $2\pi$ . With this understanding of the surface Auger process we can write down a new form for eq. (3):

$$E_{K}^{*}(i, j, k; {}^{s}X) = E_{B}^{*}(i) - \Delta E(j, l) - \Delta E(k, l) - U_{l}^{0}(i, j, k; {}^{s}X),$$
(5)

where  $\Delta E(j, l)$  is the excitation energy of state j to the first unoccupied state and  $U^0$  is the e-h, e-h interaction [59]. The asterisks mean that we have measured energies with respect to the Fermi energy. Eq. (5) is in fact the same equation used by Umbach and Hussain [9] to analyze their CO on Ni(100) Auger spectrum. We have already pointed out in the last section that the  $\Delta E$ in eq. (5) are the binding energies of the CO levels with respect to the Fermi energy. If you apply eq. (3) with all of the energies referenced to the Fermi energy the only difference will be in the language, i.e. talking about a hole-hole interaction that goes to zero or in our language an electron-hole. electron-hole interaction that is small.

Fig. 9 shows a series of  $C_{1s}$  Auger spectra starting with gas-phase CO on the bottom and ending up with CO adsorbed on Ni(100) at the top [9]. The kinetic energy is measured with respect to the vacuum level. Curve a is the  $C_{1s}$  Auger spectrum for gas-phase CO. The first two major peaks have been assigned by Ågren and Siegbahn [57] as resulting from a  $5\sigma^{-1}1\pi^{-1}$  and  $4\sigma^{-1}5\sigma^{-1}$  hole configurations. The broad peak at ~ 230 eV kinetic energy is a  $3\sigma^{-1}5\sigma^{-1}$ 

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Fig. 9. A series of  $C_{1s}$  Auger spectra, starting with the gas-phase CO spectrum at the bottom and ending with the spectrum of CO on Ni(100) on the top [9]. All of the Auger spectra are referenced to the vacuum level as the zero of kinetic energy. The CO and carbonyl data are from Chen et al. [53].

configuration while the lowest peak is assigned to a  $3\sigma^{-1}1\pi^{-1}$  or  $3\sigma^{-1}4\sigma^{-1}$  configuration. The first set of data in table 5 shows the energy levels as assigned by Ågren and Siegbahn [57] for gas-phase CO. The column  $\Sigma E_{\rm B}$  is the sum of the single-particle binding energies and the last column is the hole-hole interaction calculated using eq. (4). Notice that the U's range from ~ 11 eV to 19 eV if the level assignments are correct.

A slightly simpler experiment is shown in fig. 9b where the photon energy is tuned to the  $C_{1s} \rightarrow 2\pi$  excitation ( $\hbar \omega = 287.3$  eV) [54]. The initial state is an excited neutral and the final state is a single ion. The appropriate equation is then

$$E_{\mathbf{K}}(i, j, k, l; {}^{s}\mathbf{X}) = \Delta E(i, l) - E_{\mathbf{B}}(j) - \Delta E(k, l) - U'_{\mathbf{i}}(j, k, l; {}^{s}\mathbf{X}), \qquad (6)$$

where  $\Delta E$  is the excitation energy in the neutral molecule and now U' is the hole, electron-hole interaction energy. In the experiment shown in curve b of fig. 9 the excited state in eq. (6) is the CO  $2\pi$ , where we are always exciting to the singlet state. There is a special decay mode where the  $2\pi$  electron produced by the initial core to bound excitation is involved in the Auger process leaving only a single hole state. The shaded peaks in fig. 8b are these decay channels. Spin coupling really complicates the analysis of these spectra since in general we will have a two-hole, one-electron configuration, but we can put as stated above all of this spin coupling into U'. The second set of data in table 5 is for the core to bound case with the configuration for the peaks assigned by Ågren and Siegbahn [58] for ionization of CO. When we calculate the energies of the excited state with the  $2\pi$  orbital occupied  $E_{\rm B} + \Delta E$  shown in column IV, the lowest spin energy state given in table 2 was used. As expected the U' which is the hole, electron-hole interaction is considerably smaller than the hole-hole interaction shownin part A of table 5. U' varies from 0 to ~ 3 eV.

The Auger spectrum shown in curve d of fig. 9 is a superb test of the ideas presented in this paper. It is an "Auger" decay after  $C_{1s} \rightarrow 2\pi$  excitation in  $Cr(CO)_6$ . The initial state after excitation is like the one shown on the top right of fig. 8 except the metal is neutral. The simplest Auger process involves the  $2\pi$ electron to produce single hole states like those seen in the  $C_{4s} \rightarrow 2\pi$  Auger spectrum of CO in curve b. There is a difference in the carbonyl case because the metal can screen the Auger created valence hole. So we invision a process going from  $Cr^{neutral}(CO)^{excited}$  with a  $C_{1s}$  hole and an extra electron in the  $2\pi$ level to a final configuration of Cr<sup>+</sup>(CO)<sup>excited</sup> where now the CO excited molecule has a valence hole and an extra  $2\pi$  electron. You could view this as the crossed Auger process where a CO valence level falls into the C<sub>1s</sub> hole and the Cr 3d electron is emitted. Either way that you look at this process the single-hole peaks in the Auger spectrum should be "screened" peaks of photoemission. If the metal does not respond to screen the CO by transferring charge into the  $2\pi$  level then the single-hole peaks in the Auger should be the unscreened peaks. Curve c is a direct photoemission spectra from Cr(CO)<sub>6</sub>

## Table 5 Auger spectra

# (A) Gas-phase CO (ionized $E_B = 296.1 \text{ eV}$ )

Configuration [8]	Kinetic energy experiment (eV)	Two-hole binding energy (eV)	$\sum E_{\rm B}$ (eV)	U (eV)
$1\pi^{-1}5\sigma^{-1}$	253.9	42.2	30.9	11.3
$4\sigma^{-1}5\sigma^{-1}$	250.3	45.8	33.7	12.1
$4\sigma^{-1}1\pi^{-1}$	.245	51.1	36.6	14.5
$3\sigma^{-1}5\sigma^{-1}$	230	65.9	52.9	13
$3\sigma^{-1}4\sigma^{-1}$	221	75	58.6	16
$3\sigma^{-1}1\pi^{-1}$	221	75	55.8	19
$1\pi^{-1}1\pi^{-1}$		55.8	33.8	

(B) Gas-phase CO ( $C_{1s} \rightarrow 2\pi$  excitation at 287.3 eV)

Peak No.	Configuration [8]	Kinetic energy (eV)	Binding energy (eV)	$E_{\rm B} + \Delta E$ eq. (6) (eV)	U <sup>1</sup> (eV)
	$5\sigma^{-1}$	273.3	14	14	
	$1\pi^{-1}$	270.5	16.8	16.9	
	$4\sigma^{-1}$	267.5	19.8	19.7	
6	$1\pi^{-1}5\sigma^{-1}2\pi$	264.3	23.0	22.9	0.1
5		262.5	24.8		
4	$4\sigma^{-1}5\sigma^{-1}2\pi$	259.9	27.4	25.7	1.7
3	$4\sigma^{-1}1\pi^{-1}2\pi$	255	31.7	28.7	+3.0
	$3\sigma^{-1}$	248.6	38.7	38.9	
2	$3\sigma^{-1}5\sigma^{-1}2\pi$	242.5	44.8	44.9	0
1	$3\sigma^{-1}4\sigma^{-1}2\pi$	234.5	52.8	50.7	+2.0
	$3\sigma^{-1}1\pi^{-1}2\pi$			25.2	

(C) Cr(CO)<sub>6</sub> (C<sub>1s</sub>  $\rightarrow 2\pi$  excitation at 287.7 eV)

Peak no.	Configuration	Kinetic energy (eV)	Binding energy <sup>a)</sup> (eV)	$\frac{E_{\rm B} + \Delta E}{(\rm eV)}$ (eV)	$U^1$
9	$\operatorname{Cr} 3d^{-1}$	279.0	8.7	8.5	
8	$1\pi^{-1}2\pi$ or $5\sigma^{-1}2\pi$	273.7	14.0	13.9	
7	$4\sigma^{-1}2\pi$	269.9	17.8	17.8	
6	$1\pi^{-1}1\pi^{-1}2\pi$ or $5\sigma^{-2}2\pi$	263.2	24.5	22.3	2.2
5	$4\sigma^{-1}1\pi^{-1}2\pi$	260.7	27.0	25.8	1.2
4	$4\sigma^{-1}4\sigma^{-1}2\pi$	258.2	29.5	29.6	-0.1
3	$3\sigma^{-1}2\pi$	252.0	35.7	35.8	
2	$3\sigma^{-1}1\pi^{-1}2\pi$	244.2	43.5	44.1	0.6
1	Cr 3p	237.2	50.5		

<sup>a)</sup> Cr(CO)<sub>6</sub> binding energies taken from ref. [18].

taken at a photon energy 10 eV lower than the  $C_{1s} \rightarrow 2\pi$  Auger spectrum. The kinetic energy of this spectrum is 10 eV less than shown on fig. 9. The Cr 3d peak lines up with the highest kinetic energy peak in the Auger spectrum and the  $4\sigma$  and  $1\pi + 5\sigma$  peaks also line up. The intensity in the Cr 3d peak in the Auger spectrum is due almost entirely to direct photoemission while the  $4\sigma$  and  $(5\sigma + 1\pi)$  peaks increase their intensity by a factor of  $\sim 3$ . The intensity of these screened single-hole states surely indicates that there is Cr 3d-CO  $2\pi$  coupling.

Part C of table 5 shows a comparison of the peaks in the Auger spectrum for the  $C_{1s} \rightarrow 2\pi$  excitation in  $Cr(CO)_6$  and the prediction from the single-particle picture using eq. (6). Given that we do not know how to properly account for the spin coupling the agreement between the experimental binding energies and the values predicted from eq. (6) using measured binding energies [19] and the excitation energies of table 2 is very good. The hole, electron-hole interaction is ~ 2 eV for all of the two-hole states. In making the assignments in table 5 for  $Cr(CO)_6$  we have been guided solely by making U' uniform, but the assignment we reach is exactly what Umbach and Hussain [9] obtained from the angular dependence of the  $O_{1s}$  Auger spectra for CO adsorbed on Ni(100). Their  $C_{1s}$  Auger spectra for two collection angles are shown in curve f of fig. 9.

Once we have understood the details of the  $C_{1s} \rightarrow 2\pi$  excited  $Cr(CO)_6$ Auger spectrum, the other curves shown in fig. 9 are easy to understand. Curve e is the gas phase  $Cr(CO)_6$  Auger spectrum taken with X-ray excitation [18]. If we remove the direct photoemission contribution from curve d and shift it by 3.7 eV in kinetic energy it lines up with  $Cr(CO)_6$  Auger spectrum, feature for feature. The 3.7 eV shift in kinetic energy corresponds to a 9 eV shift in binding energy. This number should be the energy required to remove a Cr 3d electron after the CO molecule has been excited from  $C_{1s} \rightarrow 2\pi$ . Curve f is the  $C_{1s}$  Auger spectra for CO adsorbed on Ni(100) [9]. They have the same features as the carbonyl spectra and our assignment for the two-hole state is exactly what Umbach and Hussain [9] measured from the angular dependence. They pointed out that the highest kinetic energy peak was due to a single-hole state on the CO screened by a  $2\pi$  electron. We can identify the main peak as a  $4\sigma^{-1}2\pi$  configuration while the high kinetic energy shoulder is the  $1\pi^{-1}2\pi$ configuration.  $U^0$  for the  $C_{1s}$  surface spectrum is zero [9].

The extension of the "excited atom" model for screening in molecules works as well to determine energies of Auger peaks as it did for determining binding energies. But we are left with several outstanding problems:

(1) The change in intensity of certain Auger peaks between gas-phase CO and coordinated CO is unexplainable at present. For example, curve b of fig. 9 shows the intensity of the  $4\sigma$  hole state is small, as expected from fig. 3 where you can see that the  $4\sigma$  is a lone pair on the oxygen end of the molecule. Curve d for the core to bound Auger spectrum of Cr(CO)<sub>6</sub> shows that the  $4\sigma$  hole

intensity is much bigger than the  $1\pi$  single-hole state intensity. This seems to be the case on the surface also. The  $4\sigma$  is not involved in the bonding so its wavefunction character should not change when CO binds to a metal. This implies that all of the change in intensity is due to perturbation of the  $2\pi$ electron by the metal.

(2) We have assumed in all of this discussion that any hole is screened before an Auger decay occurs and that the dominant final state in the Auger decay is the screened hole state. As the interaction with the substrate decreases these assumptions will begin to fail. Very recent measurements of the  $C_{1s}$  Auger spectra of CO on Cu(110) show clearly that for a weakly chemisorbed system the core hole is completely screened before the Auger decay occurs [60].

#### 5. Inverse photoemission

Very little needs to be said about inverse photoemission, except every concept learned for photoemission will be relearned for inverse photoemission. Relaxation, charge transfer, shake-up, etc., will all become words in the inverse photoemission literature. For the specific case of CO adsorption that we have been discussing there is one conceptual difference. For photoemission it is easy to transfer charge from the metal into the empty  $2\pi$  level to screen the photoinduced hole. This is possible because the first unoccupied state of CO is not to far above the Fermi energy. In contrast it will not be possible to raise the first occupied state ( $5\sigma$ ) high enough by adding one electron to have charge transfer from the CO to the metal. In general the screening of the hole and the additional electron in any atom or molecule will be different. If charge transfer occurs in the photoemission then it will not be the dominant mechanism in inverse photoemission.

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