

## Deexcitation Electron Spectroscopy: A Probe for the Localisation of Valence Wavefunctions in Free and Adsorbed Molecules\*

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### Abstract

Deexcitation electron spectroscopy (DES) is the measurement of the kinetic energy distribution of electrons emitted in the decay of highly excited states of molecules formed by core to bound resonant photon absorption. This spectroscopy has the potential of becoming a new probe of the localised properties of the valence electronic states in molecules as well as furnishing new insights into the dynamics of the electronic decay and screening processes. This paper describes the basic principles of DES by following the evolution of the DES spectra in CO, from the isolated CO molecule in the gas phase, through the transition metal carbonyls, to CO adsorbed on a surface. In all three cases the energetics, intensities and dynamics of DES will be compared with photoelectron spectroscopy (PES) and Auger electron spectroscopy (AES).

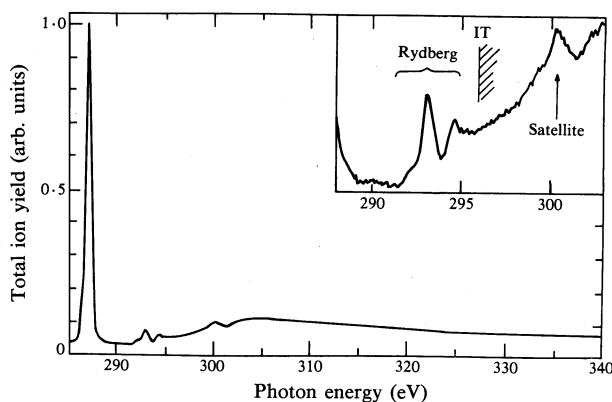
### 1. Introduction

The availability of tunable soft X-ray synchrotron sources has made it possible to easily measure the resonant absorption energies of free and coordinated molecules (Stöhr and Jaeger 1982). An important extension of this capability is to monitor the electronic deexcitation of a molecule that has been excited by a core to bound transition. The electronic decay of a highly excited neutral molecule produces in general a singly charged positive ion, so that the possible final states are the same as in a direct valence photoemission spectrum, but the intensities of the lines are determined by the localised nature of the initial state core hole, similar to Auger electron spectroscopy (AES). Therefore deexcitation electron spectroscopy (DES) is complementary to both photoelectron spectroscopy (PES) and AES, aiding in the peak assignment in both of these spectroscopies. The DES also yields quite new information about the dynamics of the excitation and decay process as well as the charge transfer and screening process for coordinated molecules. By DES one can study the time evolution of a core hole excited state on a timescale given by the natural lifetime of the core hole. These types of measurements have been reported for atoms (Eberhardt *et al.* 1978), simple gas phase molecules using synchrotron radiation for the excitation (Eberhardt *et al.* 1983, 1985*a*) or by electron-electron

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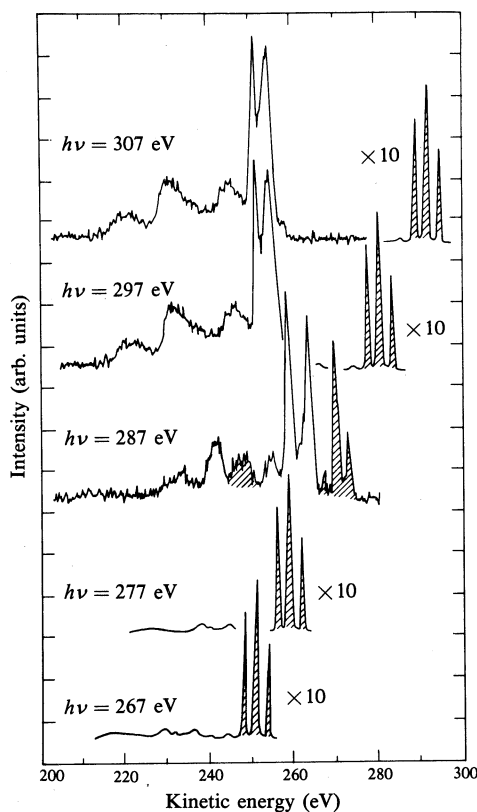
coincidence measurements (Haak *et al.* 1984; Ungier and Thomas 1983), but Loubriel *et al.* (1981) were the first to appreciate the potential of DES for the investigation of an adsorbate system, namely CO on Pt(111) (see also Johnson *et al.* 1983).

There has been an increasing interest in AES as a tool for probing the local bonding configurations of chemisorbed molecules because of the site specific nature of the core hole decay process (Baker *et al.* 1981; Jennison *et al.* 1981; Kelber *et al.* 1981; Jennison 1982; Koel *et al.* 1982; Fuggle *et al.* 1982; Umbach and Hussain 1984; Laramore 1985). The complexity of the Auger process has detracted from the usefulness of AES except as a finger-print of a given bonding scheme. We will show by using DES that the Auger spectra of molecules adsorbed on a metal surface are much easier to interpret than anticipated (Chen *et al.* 1985) and that DES from an adsorbed molecule contains very valuable information about the interaction of the molecule with the surface. To illustrate both the deexcitation process itself and the potential application to chemisorption problems we have investigated the deexcitation of the  $C_{1s} \rightarrow 2\pi$  excited CO molecule starting with gas phase CO, progressing to single metal carbonyl complexes and then to CO adsorbed on a metal surface. In all of these cases the DES will be compared with PES and AES.



**Fig. 1.** Total ion yield of CO as a function of photon energy near the threshold energy for ionisation of the  $C_{1s}$  electron. The total ion yield closely resembles the absorption spectrum. The strongest feature is the  $C_{1s} \rightarrow 2\pi$  transition. The weaker features shown in the insert correspond to transitions into Rydberg states or multi-electron excitations (Ungier and Thomas 1984). The ionisation threshold (IT) is also indicated.

The total ion yield spectrum for gas phase CO in the  $C_{1s}$  core ionisation threshold region is shown in Fig. 1. The total ion yield closely resembles the absorption. The spectrum is dominated by the core  $\rightarrow 2\pi$  bound state excitation at 287.3 eV (Hitchcock and Brion 1980) with less intense Rydberg and shake-up states at higher photon energies (Ungier and Thomas 1984). The  $C_{1s}$  ionisation threshold is at 296.1 eV. The absorption of such a high energy photon causes emission of one or more electrons either via a direct photoemission process or through a subsequent electronic decay of the excited molecule. It is the kinetic energy distribution of these electrons that is of interest to most electron spectroscopists.



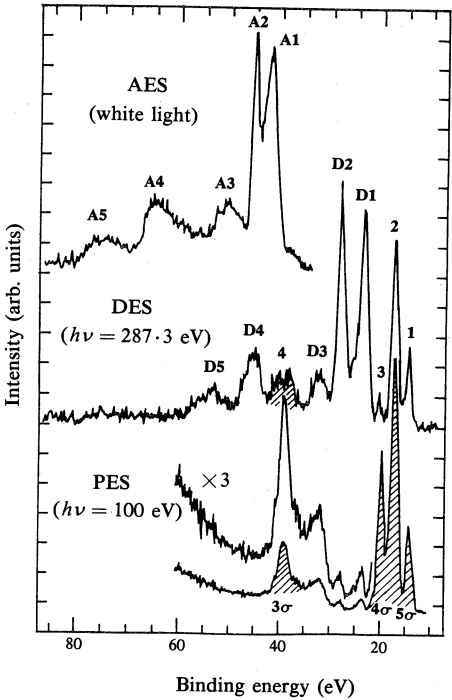
**Fig. 2.** Kinetic energy distribution curves of gas phase CO at various photon energies near the  $C_{1s}$  ionisation threshold. This is intended to be an illustrative figure and should not be used for any quantitative evaluation.

Fig. 2 illustrates the photon energy dependence of the electron emission spectra from gas phase CO. For photon energies below the  $C_{1s} \rightarrow 2\pi$  excitation energy the only channel open is the direct photoexcitation of the valence states of CO. The spectrum labelled  $h\nu = 267$  eV shows the dominant single hole states plus a series of weak two hole-single particle states (shake-up states) characteristic of the ultra-violet or soft X-ray photoemission spectrum of CO (Krummacher *et al.* 1983; Schirmer and Walter 1983; Eberhardt and Freund 1983). An increase in the photon energy from 267 to 277 eV only shifts the spectrum up by 10 eV kinetic energy because no new channels have opened up, but at 287.3 eV photon energy the photon absorption cross section increases dramatically because of the  $C_{1s} \rightarrow 2\pi$  channel (see Fig. 1). This photoabsorption process creates a highly excited neutral molecule without the emission of an electron. The excited molecule will decay either by fluorescence or preferentially by a radiationless transition emitting an electron; this process is DES. The measured energy distribution for this decay process is shown in the spectrum labelled  $h\nu = 287$  eV in Fig. 2. Since the absorption cross section has increased so dramatically at this photon energy, the intensity of the emitted electrons is much larger than that observed at slightly higher or lower photon energies. If the photon energy is increased from 287 to 297 eV, the CO molecule can be ionised by removing a  $C_{1s}$  electron. This core hole decays via an Auger decay process resulting in the ejection of a second electron. The intense peaks in the  $h\nu = 297$  eV spectrum of Fig. 2 result from this Auger decay. As the photon energy is again increased from

**Table 1.** Energy  $E_0$  added to the molecule by the probe for various processes

Process	$E_0$
PES	Photon energy
AES	Core ionisation energy
DES	Core to bound excitation energy

**Fig. 3.** Comparison of the DES, AES and PES spectra of gas phase CO. Peaks 1–4 are single hole states. The D1–D5 peaks are two hole–one electron final states and A1–A5 are Auger two hole final states.



**Table 2.** Binding energies and dominant single particle configurations for the peaks in the DES and AES spectra of Fig. 3

These assignments are given in the single particle notation, even though substantial configuration mixing might occur (Correia *et al.* 1985). Here  $\Delta E$  is the energy difference between the two hole final state and the equivalent two hole–one electron final state

DES spectra			AES spectra			$\Delta E$ (eV)
Label	$E_B$ (eV)	Config.	Label	$E_B$ (eV)	Config.	
1	14	$5\sigma^{-1}$				
2	16.8	$1\pi^{-1}$				
3	19.8	$4\sigma^{-1}$				
D1	23	$5\sigma^{-2}2\pi$	A1	42	$5\sigma^{-2}$	20
	23	$5\sigma^{-1}1\pi^{-1}2\pi$		43	$5\sigma^{-1}1\pi^{-1}$	20
D2	27.8	$4\sigma^{-1}5\sigma^{-1}2\pi$	A2	45.6	$4\sigma^{-1}5\sigma^{-1}$	18
		or $5\sigma^{-1}1\pi^{-1}2\pi$				
D3	31.8	$4\sigma^{-1}1\pi^{-1}2\pi$	A3	51	$4\sigma^{-1}1\pi^{-1}$	19
4	39	$3\sigma^{-1}$				
D4	45	$3\sigma^{-1}5\sigma^{-1}2\pi$	A4	66	$3\sigma^{-1}5\sigma^{-1}$	21
D5	53	$3\sigma^{-1}1\pi^{-1}2\pi$	A5	75	$3\sigma^{-1}1\pi^{-1}$	22
		$3\sigma^{-1}4\sigma^{-1}2\pi$			$3\sigma^{-1}4\sigma$	

297 to 307 eV, the weak direct photoemission peaks from the outer valence states of CO continue to increase in kinetic energy while the Auger electron spectrum remains constant in kinetic energy. It is the comparison of the energies and intensities of the peaks in the PES, DES and AES that is the subject of the present paper.

There are three general types of peak displayed in Fig. 2. The first set of peaks moves linearly with changing photon energy and is associated with PES. The second set of peaks is fixed in kinetic energy, independent of photon energy above a given threshold energy, and is associated with AES. The final set of peaks occurs for only discrete photon energies where a resonant core to bound excitation occurs, and in our language is associated with DES. The same physical process has been previously referred to as autoionisation, resonant photoemission or resonant Auger spectroscopy. Many of the previous studies of this deexcitation process have dealt with the phenomenon in terms of interference effects giving rise to Fano profiles in the absorption cross section (Guillot *et al.* 1977; Schmidt *et al.* 1983), which are more pronounced for lower energy excitations where the valence cross section is still appreciable compared with the core to bound absorption cross section. The experiments described in the present paper utilise the 1s core level where, in general, the photon energy required for a core to bound excitation is sufficiently large that the direct valence photoemission is very weak and interference effects are minimal. Moreover, here the emphasis is on the energies and intensities of the peaks in the electron emission spectrum and consequently we believe that a more descriptive acronym (DES) is justified.

Electron emission spectra of the type shown in Fig. 2 are normally not displayed on a kinetic energy scale. Instead they are plotted as a function of binding energy. Binding energy has a simple physical meaning and is independent of the exciting photon energy. The binding energy  $E_B(i)$  for a given peak (i) in the spectra is defined by

$$E_B(i) = E_0 - E_K(i), \quad (1)$$

where  $E_0$  is the energy added to the system by the exciting probe and  $E_K(i)$  is the measured kinetic energy of the peak (i). The energy added to the system depends upon the process or the type of spectroscopy and is listed in Table 1. For gas phase CO the energy added in PES is the photon energy  $h\nu$ , while it is the ionisation potential of the  $C_{1s}$  (296.1 eV) or  $O_{1s}$  (542.4 eV) level for AES and the  $C_{1s} \rightarrow 2\pi$  (287.3 eV) or  $O_{1s} \rightarrow 2\pi$  (534.1 eV) excitation energy for DES. Fig. 3 shows plots of the PES, AES and DES spectra on a binding energy scale. The peaks in the PES and DES spectra in general correspond with various states of  $CO^+$  with the intensity dictated by the specific process, while the peaks in the AES spectrum correspond to the energy states of  $CO^{2+}$ . The assignments of the peaks in Fig. 3 are given in Table 2.

## 2. DES of CO

The PES and AES have been discussed many times in the literature so the discussion here will centre on DES and its relationship to these better known spectroscopies. Fig. 4 shows schematically the possible decay channels for a CO molecule initially excited by a photon of energy 287.3 eV into the one hole-one electron state (1h-1e) characterised by a  $C_{1s}$  hole and an electron in the previously unoccupied  $2\pi$  level.

The centre panel shows the single particle representation of the excited CO molecule, which is in a  $^1\Pi$  state. The  $^3\Pi$  state is 1.46 eV lower in energy than the singlet state (Ungier and Thomas 1983; Shaw *et al.* 1984) but it cannot be excited by absorption of a photon and there is no mechanism to flip the spin of the  $2\pi$  electron before the decay of the core hole. The  $^1\Pi$  state of CO ( $C_{1s} \rightarrow 2\pi$ ) can decay either through fluorescence or preferentially via a radiationless transition. One class of radiationless decay events, shown on the left-hand side of Fig. 4 involves the  $2\pi$  electron so that the final state is a single valence hole configuration identical to the dominant states in PES. The peaks labelled 1–4 in Fig. 3 are these single hole states. The second class of events in the decay of the core excitation in DES is shown on the right of Fig. 4 where the  $2\pi$  electron is only a spectator. Compared with the molecular ground state, this configuration is in general described by two holes in the valence orbitals and an additional  $2\pi$  electron. The states are also observed in a PES spectrum and are referred to as shake-up states. In a PES spectrum like the one shown in Fig. 3, the intensity of the shake-up states is usually much weaker than the single hole states. The 2h–1e states in the DES spectrum all have an electron in the  $2\pi$  orbital, while in principle the shake-up states in the PES spectrum could have the extra electron in any of the unoccupied orbitals. For CO the configurations where the extra electron was promoted into the  $2\pi$  orbital dominate the shake-up portion of the PES spectrum (Eberhardt and Freund 1983), so there should be a very close correspondence between the binding energies observed in the PES and DES spectra. Fig. 3 shows clearly that this expectation is fulfilled.

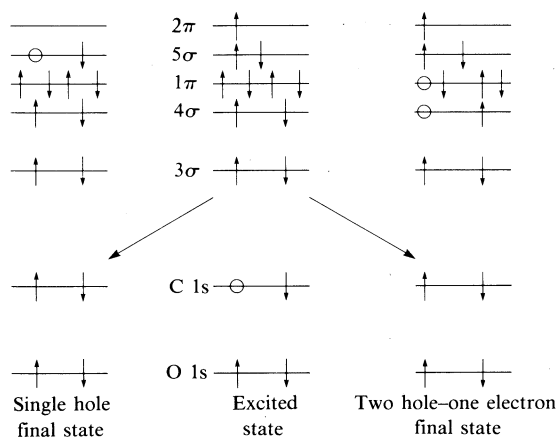


Fig. 4. Schematic illustration of the decay channels for the  $C_{1s} \rightarrow 2\pi$  excited state of CO.

Despite the expected coincidence in energy, the peak intensities in PES and DES are quite different. The intensity differences are easily explained by the different matrix elements governing the two processes. The DES matrix element is a Coulomb matrix element between the core hole excited state as the initial state and the valence hole plus ejected electron or the two hole–one electron plus free electron as the final state. Because of the strong localisation of the core hole in the initial state, the matrix element is dominated by the overlap between this localised core hole wavefunction and the final state valence hole wavefunction. Only valence hole states having an

amplitude at the site of the core hole will have a non-vanishing matrix element. Qualitatively the intensity of the DES single valence hole final state configurations reflects the projection of the respective valence hole wavefunction onto the location of the core hole created in the initial photoabsorption event. There is one preliminary calculation of the intensities of single hole states in the DES spectrum of CO excited  $C_{1s} \rightarrow 2\pi$ . Freund and Liegener (1986), using the procedure developed by Liegener (1983, 1984) for calculating Auger spectra, produced relative intensities of 1 ( $5\sigma$ ), 1.9 ( $1\pi$ ) and 0.1 ( $4\sigma$ ), which should be compared with the experimental values of 1, 2.2 and 0.3 respectively.

The relationship between DES and both PES and AES will now be elaborated. The energies of the peaks plotted on a binding energy scale are identical to those seen in PES but the intensities of the peaks are given by a Coulomb matrix element and therefore should be very similar to the intensities seen in the Auger spectrum. It is not the objective of the present paper to address the assignment of the peaks in the AES or PES spectra, instead we list in Table 2 the measured binding energies for these spectra. The assignment of the single hole states in the DES spectrum can be derived in a straightforward way. The situation is different for the two hole-one electron final states. For example, the peak in the PES spectrum at the same binding energy as peak D2 (Fig. 3) is commonly assigned to  $5\sigma^{-1}1\pi^{-1}2\pi$  (Eberhardt and Freund 1983). However, in analogy to the Auger spectrum we are tempted to assign this peak as  $4\sigma^{-1}5\sigma^{-1}2\pi$ , the implication being that it is the same state as A2 but with a  $2\pi$  electron present as a spectator. A calculation of the DES intensities will clearly help to resolve this ambiguity. The main points in comparing PES, AES and DES are: (i) there is a one-to-one correspondence between the energies in the DES and PES spectra for all peaks observed in both spectra; (ii) there is a qualitative similarity in the intensities seen in the 2h-1e portion of the DES and AES spectra, with nearly a rigid shift of  $\sim 19$  eV in binding energy ( $\sim 10$  eV in kinetic energy). This means that it takes  $\sim 19$  eV to remove the  $2\pi$  electron from the 2h-1e states formed in the deexcitation of the  $C_{1s} \rightarrow 2\pi$  state, almost independent of the two hole configuration.

### 3. Carbonyls

When CO is coordinated to a metal atom either in a carbonyl complex or adsorbed on a metal surface there are quite dramatic changes in both the PES and AES spectra, caused by changes in both the initial state (bonding) and the final state (screening). Therefore the DES spectrum of a carbonyl should be quite different from the equivalent spectrum for gas phase CO. On the other hand, the absorption spectrum in the energy range of the  $C_{1s}$  threshold of a carbonyl is very similar to gas phase CO. The absorption spectrum of  $Fe(CO)_5$  is compared with that of free CO in Fig. 5. There is an increase of approximately 0.4 eV in the  $C_{1s} \rightarrow 2\pi$  resonant absorption energy, compared with the 3.2 eV reduction in the  $C_{1s}$  binding energy for  $Fe(CO)_5$  with respect to CO (Plummer *et al.* 1978). The large reduction in the  $C_{1s}$  binding energy is almost solely a result of the ability of the metal atom to transfer charge to screen the hole on the CO molecule (Freund *et al.* 1981), while the small shift in the core to bound state energy may reflect the perturbation of the CO molecule caused by bonding to a metal atom (Jugnet *et al.* 1984; Plummer *et al.* 1985; Bagus *et al.* 1985).

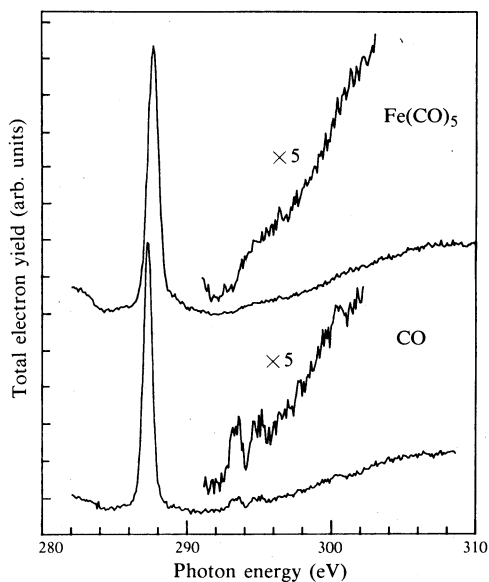
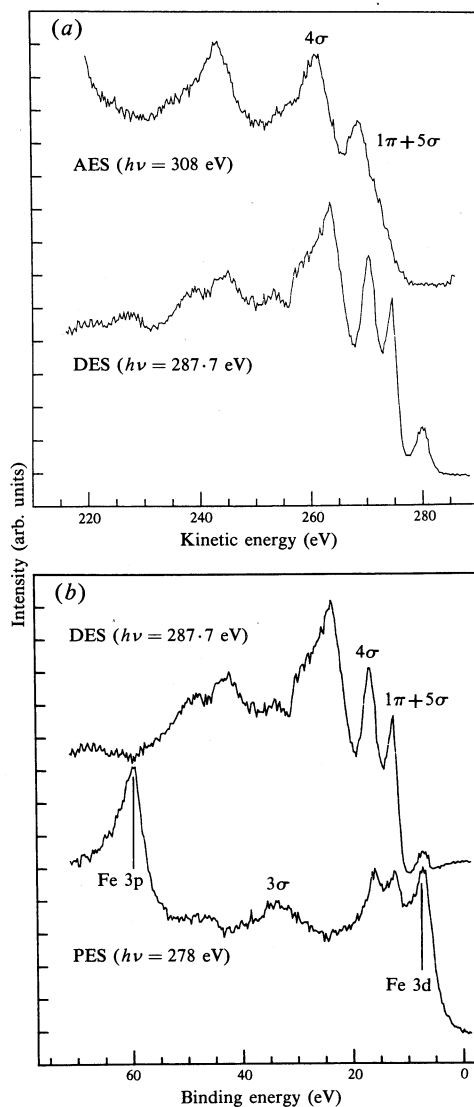


Fig. 5. Comparison of the absorption spectra of gas phase CO and  $\text{Fe}(\text{CO})_5$  taken near the  $\text{C}_{1s}$  threshold.

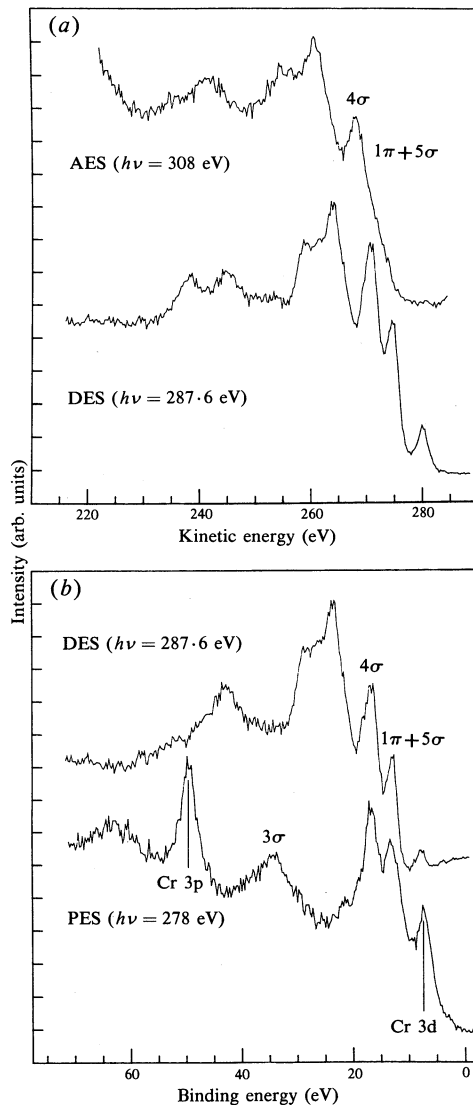
Figs 6 and 7 compare the DES, AES and PES spectra from a thin film of carbonyl [ $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  respectively] condensed onto a cold substrate. In Figs 6*b* and 7*b* the PES spectra were recorded for a photon energy just 10 eV below the core to bound absorption energy and show the metal 3d and 3p levels as well as the three CO induced valence states,  $3\sigma$ ,  $4\sigma$  and  $1\pi+5\sigma$ . Within the uncertainty introduced by the calibration of the monochromator and analyser and the statistical noise, the binding energies measured in the PES and DES spectra for the single hole states are identical ( $\sim 0.3$  eV difference). Upon coordination of CO to a transition metal, such as in  $\text{Fe}(\text{CO})_5$  or  $\text{Cr}(\text{CO})_6$ , we notice two major changes in the DES spectra. The  $5\sigma$  and  $1\pi$  orbitals become energetically almost degenerate and the  $4\sigma$  intensity in DES increases by about one order of magnitude (cf. Fig. 3). The shift of the  $5\sigma$  orbital relative to the other valence orbitals is generally observed when CO is bound to a metal atom or a surface (Bagus 1986). More interesting, however, is the huge increase in the intensity of the  $4\sigma$  single hole state in DES in the carbonyls compared with isolated CO. The ratio of the intensity of the  $4\sigma$  orbital to the sum of the  $1\pi+5\sigma$  orbitals in gas phase CO is 0.1 and increases by about one order of magnitude in  $\text{Cr}(\text{CO})_6$  or  $\text{Fe}(\text{CO})_5$ . It is difficult to give an exact value because of the uncertainties in the background subtraction in the experimental curves. Our interpretation for this dramatic effect is that the  $5\sigma$  interaction with the metal atom allows the  $4\sigma$  orbital to screen the  $\text{C}_{1s}$  core hole. Because of the  $5\sigma$  hybridisation with the transition metal states, the  $\sigma$  space around the C atom is expanded and can be partially occupied by the  $4\sigma$  orbital upon creation of the core hole excited state. In the isolated CO molecule, in contrast, there is no  $\sigma$  space around the C atom available for this to happen.

This interpretation is corroborated by calculations of the  $\text{C}_{1s}$  core hole screening in  $\text{Cu}_5\text{CO}$  (Messmer *et al.* 1980) and  $\text{NiCO}$  (Chen 1985) clusters. The  $4\sigma$  charge transfer in a  $\text{Cu}_5\text{CO}$  cluster is larger than that in isolated CO by a factor of 5. So





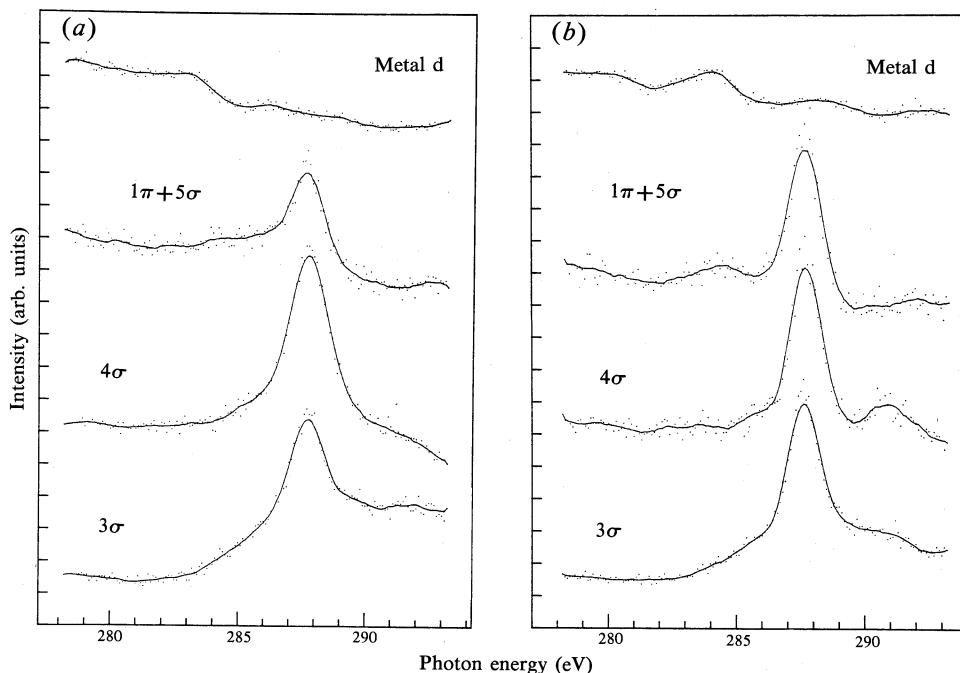
**Fig. 6.** Comparison of DES, AES and PES spectra of  $\text{Fe}(\text{CO})_5$ . The single hole states in the spectra are labelled.



**Fig. 7.** Comparison of DES, AES and PES spectra of  $\text{Cr}(\text{CO})_6$ . The single hole states in the spectra are labelled.

far we do not have a direct theoretical comparison for the single hole state intensities available, but Laramore (1984, 1985) has calculated the Auger intensities for isolated CO and CO adsorbed onto Ni(100) and found an increase by about a factor of 25 for the intensity ratio of the  $4\sigma^{-2}$  to  $5\sigma^{-2}$  final state configurations when CO is adsorbed onto a metal surface. In the coordinated NiCO, Laramore (1985) has also calculated the single hole state intensities and found an intensity ratio of 0.4 : 1 for the intensity of the  $4\sigma$  single hole state relative to the combined  $5\sigma$  and  $1\pi$  single hole states. This is theoretical confirmation of the trends we observed in our spectra, being fully aware that NiCO is not the same as  $\text{Fe}(\text{CO})_5$  or  $\text{Cr}(\text{CO})_6$ , and also taking into

account the uncertainties in the experimental determination of the peak intensities. It is also obvious from these results that the DES spectra are extremely sensitive to changes in the chemical environment. Finally we point out that again the intensities are quite different in the PES and DES spectra of the carbonyls, as they were for gas phase CO.



**Fig. 8.** Constant initial state (CIS) spectra for (a)  $\text{Fe}(\text{CO})_5$  and (b)  $\text{Cr}(\text{CO})_6$  at a photon energy near the  $\text{C}_{1s}$  threshold energy for several different initial state energies.

The increased signal resulting from using a condensed film instead of a gas beam opens up the possibility of doing more sophisticated absorption type measurements. The absorption spectrum shown in Fig. 5 was obtained by measuring with very poor energy resolution all of the electrons emitted from the film with the general energy of the  $\text{C}_{1s}$  Auger peaks, i.e.  $\sim 250$  eV, as the photon energy was scanned. It is more informative to run a photon scan keeping the binding energy fixed. Such a scan, usually called a constant initial state (CIS) spectrum, is shown in Fig. 8 for  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$ . The top curve in each figure has set the difference between the photon energy and the measured kinetic energy equal to the binding energy of the metal d levels. There is no resonance in the cross section when the  $\text{C}_{1s} \rightarrow 2\pi$  transition is reached, which means that the signal from the metal d levels in the DES spectra of the carbonyls is due to direct photoemission. The other three curves all show a resonance at the same photon energy even though the binding energies are different. This means that all of the CO valence states resonate at the core to bound energy. The important observations are:

- (i) The binding energies in the DES and PES spectra of the carbonyls are the same within experimental error.

- (ii) The relative intensities of the outer valence states in the DES spectra of the carbonyls are dramatically different from those observed for CO.

Before leaving the carbonyls it is important to examine the relationship between the AES and DES spectra. These two spectra are plotted in Figs 6a and 7a for  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$ . In both cases the curves are reproduced on a kinetic energy scale (with respect to the vacuum level), instead of a binding energy scale as was done for gas phase CO in Fig. 3. Qualitatively the DES and AES spectra are similar in shape, especially after removing from the DES spectra the features that are a result of direct photoemission. The AES spectra are nearly rigidly shifted downwards in kinetic energy by  $\sim 3$  eV for both carbonyls. This should be compared with the 10 eV shift in the gas phase CO spectra. If the binding energy of the  $\text{C}_{1s}$  level in the condensed film is used in conjunction with the core to bound excitation energy to calculate the binding energies in the two spectra, it is found that there is an approximate shift of 9 eV between the two spectra. The equivalent shift in gas phase CO was 20 eV. Obviously the reduction in the difference between the DES and AES spectra in the carbonyls compared with CO is due to the ability of the molecule to screen the holes produced on a given CO ligand.

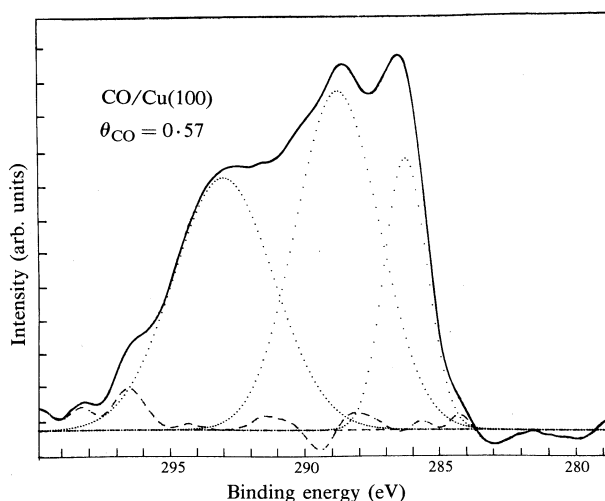


Fig. 9. The  $\text{C}_{1s}$  core level photoemission spectra of CO adsorbed on Cu(100). [From Heskett and Plummer (1986).]

#### 4. Adsorbed CO

We have investigated the properties of the DES spectra for several CO adsorption systems, but CO adsorbed onto a Cu surface is surely the most interesting because this single system illustrates many of the potential capabilities of DES (Chen *et al.* 1985). The CO forms a weak chemisorption bond with Cu, where the heat of adsorption is  $\sim 0.6$  eV and the C–O force constant is  $17.6 \text{ mdyne } \text{\AA}^{-1}$  ( $1 \text{ dyne} = 10^{-5} \text{ N}$ ). This can be compared with the metal–CO bond energy in  $\text{Cr}(\text{CO})_6$  of  $\sim 1.3$  eV and a force constant of  $17.2 \text{ mdyne } \text{\AA}^{-1}$  which is very similar to the bond formed on transition metal surfaces. The weak CO–metal coupling for CO on Cu produces

anomalous photoemission spectra. Norton *et al.* (1978) showed that the X-ray excited  $C_{1s}$  and  $O_{1s}$  core level photoelectron spectra exhibited very intense satellite lines. Subsequently, there have been spectra published for Cu(100) (Eberhardt *et al.* 1985*b*; Heskett and Plummer 1986), and Cu(111) (Baker *et al.* 1981). All these spectra show qualitatively the same features displayed in Fig. 9. The lowest binding energy peak is at  $286.5 \pm 0.1$  eV with two strong satellite peaks at  $2.7 \pm 0.3$  and  $7.2 \pm 0.5$  eV higher binding energy. It is generally agreed now that the lowest binding energy peak is the fully screened core hole state. The  $C_{1s}$  hole produced by photoionisation is screened by charge transfer from the metal into the first unoccupied molecular orbital of the neutral CO molecule, i.e. the  $2\pi$  orbital. The  $2\pi$  level is pulled down below the Fermi energy by the attractive core hole (Lang and Williams 1977). The assignment of the other two peaks in the  $C_{1s}$  core level photoelectron spectra shown in Fig. 9 varies from one paper to another depending upon the theoretical approach utilised. Nevertheless, one or more of these satellite peaks can be associated with a basically unscreened state of  $CO^+$ . The multiple peak spectrum is a consequence of the weak coupling of the CO to the Cu substrate, making it difficult to transfer charge efficiently to screen the core hole.

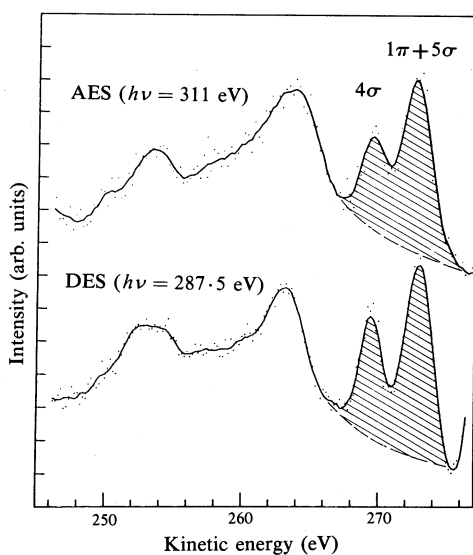


Fig. 10. Comparison of DES and AES spectra on a kinetic energy scale for CO adsorbed on Cu(110) (Chen 1985). The  $C_{1s} \rightarrow 2\pi$  transition occurs at a photon energy of 287.5 eV. The shaded peaks are the 'single hole states'.

By tuning the photon energy to the  $C_{1s} \rightarrow 2\pi$  transition for CO adsorbed on Cu, we can create what is believed to be the fully screened state of adsorbed CO. The subsequent decay of this excited neutral molecule produces a deexcitation spectrum which could be quite different from the Auger spectrum resulting from the ionisation process characterised by the core level spectrum shown in Fig. 9. This depends on whether all three of the states of CO with a  $C_{1s}$  core hole formed by the photoionisation process decay via an Auger process. Then the resulting spectrum

will be very complex. Alternatively the excited core hole configurations (satellite lines) could decay into the fully screened core hole configuration before the core hole decays. This question is answered by comparing the DES and AES spectra from CO adsorbed on Cu. These two spectra are shown in Fig. 10, plotted on a kinetic energy scale. The bottom curve is taken with a photon energy of 287.5 eV which is the measured core to bound excitation energy (Chen *et al.* 1985), and the top curve is for a photon energy of 311 eV, above the ionisation threshold. The two curves are nearly identical. We also examined the core hole decay spectra in the photon energy range 287–318 eV and found no substantial change in shape. Baker *et al.* (1981) have published the same shape Auger spectrum using >2 keV electrons.

Our first observation is that all of the excited  $C_{1s}$  hole configurations produced by photoionisation of the  $C_{1s}$  level decay into the fully screened state before the  $C_{1s}$  hole decays. This also explains why the width of the satellite lines is much larger than the width of the fully screened peak (see Fig. 9 and Eberhardt *et al.* 1985*b*). This is in contrast to the case of isolated CO where the core electron shake-up lines have about the same width as the main line, because there is no decay possibility for the shake-up states into the core hole ground state.

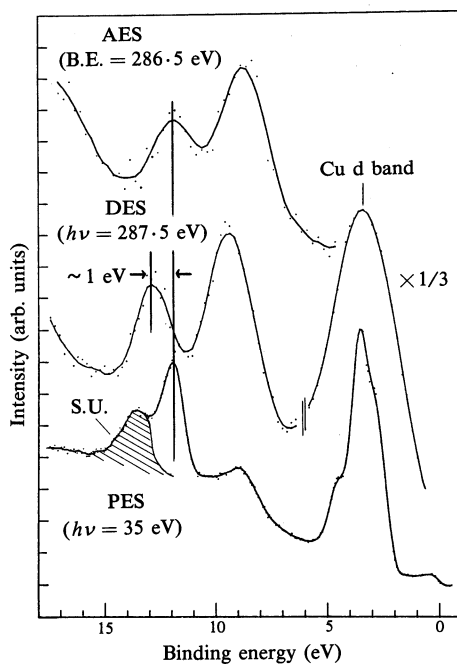


Fig. 11. Detailed comparison of the single hole portions of the DES, AES and PES spectra of CO adsorbed on Cu(110) (Chen 1985).

The second important observation is made by comparing the PES for CO on Cu(110) with the DES spectrum as shown in Fig. 11. The photoemission exhibits rather strong satellite lines (labelled S.U.) just as in the core level photoemission. The origin is actually much the same. The DES and the AES spectra, however, do not show any evidence of these shake-up states. Hence, the DES or AES process itself

occurs on a timescale much slower than the photoemission process. The DES and AES seem to be essentially adiabatic processes, whereas photoemission takes place in the 'sudden' regime, where shake-up processes are observed.

The third and final important observation is made by comparing all three spectra, PES, AES and DES, on a common binding energy scale as shown in Fig. 11. Before we discuss the results of this comparison, we present in detail the steps involved in transforming the kinetic energy scale shown in Fig. 10 into a binding energy scale. The first step is to reference the analyser kinetic energy scale to a fixed zero, which we take to be the Fermi energy. This can be accomplished by using the Fermi edge in the PES spectrum as a reference point. The second step is to subtract the kinetic energy from the initial energy  $E_0$  described in equation (1) (Section 1). For the AES spectrum the energy stored in the system is the binding energy of the  $C_{1s}$  hole, i.e. 286.5 eV. The  $E_0$  for the DES spectrum is 287.5 eV. It is easy to see that we already have two problems. First our assumption, that the core to bound excitation formed the fully screened state of CO on the surface, implicitly assumed that the core to bound excitation energy on the surface would be the same as the binding energy of the fully screened state. However, there is 1 eV difference between these two energies. The second problem is related to the first. Since the AES and DES spectra line up on a kinetic energy scale (see Fig. 10) they cannot line up on a binding energy scale because the energy added in each case is different. This is one of the most important conclusions of this work, so we will describe the calibration procedure step-by-step.

Let us begin by converting the Auger spectrum from kinetic energy to binding energy. The scale shown in Fig. 10 is the kinetic energy with respect to the vacuum level of the analyser which does not give us a good reference point. The kinetic energy scale can be calibrated by measuring the Fermi edge or peak in the Cu d bands for a given photon energy. This procedure assumes that the monochromator is calibrated. Our procedure was to set the zero of the monochromator at zero order and then measure the PES spectrum at a variety of photon energies to assure that the change in photon energy corresponded with the same change in kinetic energy. Probably the best calibration is the core to bound energy in CO since it does not shift appreciably from free CO to adsorbed CO (Jugnet *et al.* 1984; Plummer *et al.* 1985). Using this calibration procedure, the Auger spectrum can be plotted as a function of binding energy with respect to the Fermi energy. The first two peaks (shaded in Fig. 10) occur at the same binding energy as we recorded for the valence  $4\sigma$  (11.8 eV) and  $1\pi+5\sigma$  (8.4 eV) orbitals in the low photon energy PES spectrum. This fact has been pointed out for the Auger spectrum of CO on Cu(111) by Baker (1981). Since the binding energies for these single hole valence states in the Auger spectrum agree with the photoemission binding energies, the configuration of the final states in the AES and PES spectra must be the same (for these states), i.e. fully screened valence hole states. The single hole portion of the AES spectrum is plotted in Fig. 11 and compared with the DES and PES spectra. The main peaks in the PES and AES spectra line up, but the DES spectrum does not.

The calibration of the DES spectrum is easier than the AES spectrum. A photoabsorption curve is run to identify the resonant  $C_{1s} \rightarrow 2\pi$  excitation energy for CO adsorbed on Cu(110). With our monochromator calibration we measured this energy to be 287.5 eV. The monochromator is set at this photon energy and a spectrum is accumulated as a function of kinetic energy. Since the d bands of Cu do not resonate with the core to bound excitation of CO, they are always present in

the spectra excited by the direct photoemission process. Therefore the d band of Cu can be used as a reference for the binding energy scale. When the DES spectrum is calibrated in this fashion the two single hole states in the spectrum are  $\sim 1$  eV higher in binding energy than the equivalent peaks in either the PES or AES spectra.

The obvious explanation of the shift in the DES spectrum compared with either the PES or AES spectra is that the state of CO formed by the  $C_{1s} \rightarrow 2\pi$  excitation is in fact an excited state of the fully screened core hole state responsible for the AES spectrum. This excited state decays into the fully screened core hole state before the deexcitation process with the excess energy of  $\sim 1$  eV given up to the substrate. If this is the real situation then the energy stored in the molecule before the core hole decays is 286.5 eV in both AES and DES, and there is no problem with binding energies. The question arises as to the form of the excited and fully screened states of CO with a hole in the  $C_{1s}$  level and an extra electron in the  $2\pi$  level. We know from gas phase measurements that the optically excited  $C_{1s} \rightarrow 2\pi^1\Pi$  state of CO is not the lowest energy state with this electronic configuration (Ungier and Thomas 1983; Shaw *et al.* 1984); instead the  $^3\Pi$  state is 1.46 eV lower in energy. In gas phase CO or in carbonyls it is very unlikely or impossible to flip the spin in the  $^1\Pi$  state before the core hole decays, but on a surface the electron in the  $2\pi$  level can interact with the continuum of states in the solid. The initially excited  $^1\Pi$  state decays into the  $^3\Pi$  state by exchange of electrons with the metal.

The ratio of intensities of the two valence peaks in the DES spectrum is 0.6, increased with respect to the value of 0.1 for gas phase CO but appreciably less than the value for  $Cr(CO)_6$ . Possibly this correlates with the fact that the CO on Cu bond is weaker than the carbonyl bond.

Finally it is important to point out that an incorrect calibration could not solve the results displayed in Figs 10 and 11. Let us assume for the sake of argument that we made a mistake in our calibration of the core to bound excitation energy and it is the same as the binding energy of the  $C_{1s}$  electron. Then the energy added in both DES and AES is the same and the binding energy of the single hole states of CO are the same in DES, AES and PES. The problem will be that the d bands of Cu appearing in the DES spectra due to a direct photoexcitation process will have a binding energy too small by 1 eV. Every other measurement of the core to bound energies in adsorbed CO shows that this energy is larger than the measured core hole binding energy (Stöhr and Jaeger 1982; Jugnet *et al.* 1984; Chen 1985; Plummer *et al.* 1985).

## 5. Summary

We have shown that the electron spectrum generated in the decay of a core to bound state excitation has common features with both photoemission and Auger spectra of the same molecule. The final states observed are largely identical to the final states observed in photoemission, whereas the intensities are determined by a Coulomb-type matrix element as for the Auger decay. We feel that this type of electron spectroscopy, has potential to become a spectroscopy of its own standing. The DES can be applied to isolated molecules as well as to chemisorption systems and supplies information about the local charge density of the valence electron wavefunctions around the nuclear centre where the core hole was created in the core to bound state transition. Thus we are able to gain new insight into static and dynamic charge transfer and

screening processes in these systems. Additionally DES also offers the possibility to study the time evolution of a core hole excited state on a timescale that is given by the natural lifetime of the core hole. In order to gain a better understanding of some of the details in the spectra we urgently need calculations of DES intensities. The DES calculations are the ideal testground for any Auger calculation, because the peak assignment is not obscured by the hole-hole interaction as in Auger spectroscopy.

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