TILDEN LECTURE*

New Perspectives in Surface Chemistry and Catalysis

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1 Introduction

Surface Chemistry is an area where information at the molecular level has been difficult to obtain and, in the main, we have had to resort to studying the gas phase and then extrapolating the information to develop models of the molecular events occurring at the solid surface. The problems facing the surface chemist have therefore largely revolved around the difficulty of finding experimental methods which can (i) monitor directly the outermost atoms at a solid surface as distinct from sub-surface atoms, (ii) then be able to distinguish one kind from another, and (iii) then monitor the different chemical environment of a given surface atom. These are three distinct milestones on the road to the complete understanding of molecular events at surfaces. Let us see how far along that road we can go.

Fifteen years ago our knowledge of chemisorption on metals was confined largely to information relating to the patterns of reactivity, nitrogen exemplifying obviously rather stringent requirements for chemisorption, being only adsorbed by a few metals at room temperature, whereas oxygen is the most ubiquitous. Such an approach tells us nothing about the molecular nature of the surface species although other techniques such as flash-desorption developed in the late fifties and early sixties would suggest that nitrogen is dissociatively chemisorbed whereas carbon monoxide epitomizes molecular adsorption. We will return to this particular point later. What is missing is surface definition at the molecular level, both chemical and structural, and also information on the adsorbate; for example, what is the nature of interadatom bonding in a diatomic molecule or adatom—substrate bonding?

I would like to consider how one particular experimental development, electron spectroscopy, has, over the past five years, enabled a more detailed picture of chemisorption to be developed. I shall confine myself in the main to just core-level and valence-level spectroscopies (Figure 1). The two relaxation processes, the Auger effect and *X*-ray fluorescence, which may accompany photoemission are not considered. Although Auger Electron Spectroscopy was developed in the early sixties as a surface sensitive technique its inherent complexity (it is a three-electron process) and the possible damaging influence of the

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electron beam has limited its application compared with *X*-ray and u.v. photoelectron spectroscopy (XPS or ESCA and UPS).

In photoelectron spectroscopy the kinetic energy E_K of the electron emitted by a photon of energy $h\nu$ is measured and using the relation

$$E_K = h\nu - (E_{\text{initial}} - E_{\text{final}}) = h\nu - E_B$$

the binding energy E_B can be calculated. If we invoke Koopmans' Theorem then the eigenvalue of a given orbital is equal to its binding energy, *i.e.* it is the energy needed to extract the orbital electron to infinity as long as there is no readjustment of the other electrons in the atom or molecule (the frozen orbital approximation). The concept of single electron orbitals with specific binding energies is of course an ideality, but to consider a molecule as being built up of energy levels corresponding to the binding energy of its molecular orbitals is a highly productive one even though it contains some half-truths.

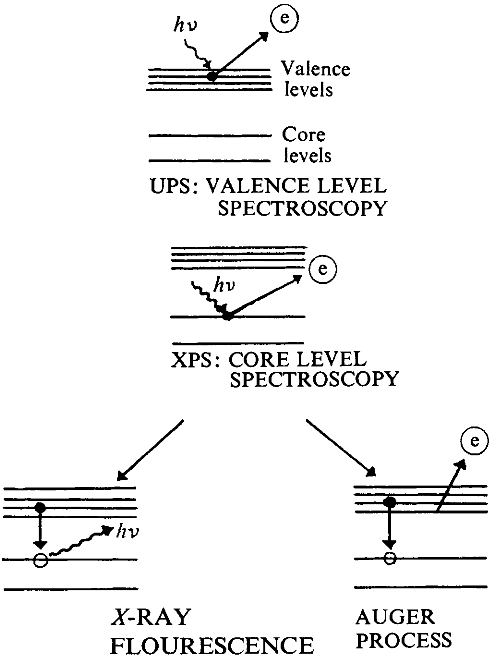

Figure 1 *Photoelectron spectroscopy*

My interest in photoelectron spectroscopy stems from a study with C. M. Quinn of the energy distribution of photoelectrons from nickel[1] using photons of energy 6.2 eV. This work illustrated that photoelectrons were emitted from a region very close to the surface (< 20 Å) and that, after oxygen interaction, their energies

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[1] C. M. Quinn and M. W. Roberts, *Trans. Faraday Soc.*, 1965, **61**, 1775.

were different from those from the clean metal. Clearly with such low-energy photons it was only possible to explore the band structure close to the Fermi level. But the enormous interest in the sixties in the *X*-ray and u.v. photoelectron spectroscopy of gases, largely through the elegant work of Siegbahn, Turner, and Price led us to consider the possibility of investigating the molecular nature of adsorbed species on well defined atomically clean surfaces. We were encouraged by two quite different types of experiment carried out by Siegbahn and his colleagues. First they had shown that, for example, the C(1*s*) binding energies for a series of halogenated hydrocarbons (*e.g.* CBr_4, $CHBr_3$, CH_2Br_2, $CHBr_3$, or CH_4) increased by roughly equal increments as each hydrogen was replaced by a bromine atom. In the case of fluorinated hydrocarbons the C(1*s*) shift can be as much as 8 eV. We have therefore a relationship between chemical shift and the electron density on the carbon atoms. Secondly, some experiments on iodostearic acid had shown[2] clearly the possibility that *X*-ray photoelectrons could be sensitive at the monolayer level since a substantial $I3d_{5/2}$ signal was observed for ostensibly a monolayer. It should, however, be recalled that iodostearic acid is a comparatively large molecule (*ca.* 50 Å) whereas we would require sufficient sensitivity to study, at the sub-monolayer level, the adsorption of relatively small molecules such as nitrogen, carbon monoxide, and simple hydrocarbons. Two questions therefore needed to be resolved, first, whether the escape depth of photoelectrons was sufficiently small (a few ångströms) to give a sensitivity at the sub-monolayer level. In this respect our work with nickel[1] and the results of Bordass and Linnett[3] who reported in 1969 a u.v. photoelectron spectrum for methanol adsorbed on tungsten were encouraging. Secondly there were the experimental difficulties associated with coupling the photoelectron technique with the stringent requirements for preparing well defined metal surfaces.

A u.h.v.-compatible photoelectron spectrometer was constructed[4] in conjunction with Vacuum Generators; the instrument was of a dual-chamber design with multiphoton (He and *X*-ray) sources. It allowed the *in situ* generation of atomically clean metal surfaces and the study of adsorption at these surfaces using both valence-level (He-I and He-II radiation) and core-level (Al-Kα radiation) spectroscopies, and was coupled to a Digico computer for storage and analysis of the experimental data. We therefore had facilities which enabled us, *at least in principle*, to investigate electron binding energies of both the valence and core levels, to distinguish between different chemical environments of a given atom by increasing chemical shifts, and lastly to have analytical information on the atomic composition of the surface. Whether each of these were to be realized in practice remained to be seen.

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[2] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U.Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, 'ESCA Applied to Free Molecules' North-Holland, Amsterdam, 1969.

[3] W. T. Bordass and J. W. Linnett, *Nature*, 1969, **222**, 660.

[4] C. R. Brundle, M. W. Roberts, D. Latham, and K. Yates, *J. Electron Spectroscopy*, 1974, **3**, 241.

By first studying the physical adsorption[5] of such molecules as CO_2, H_2O, and Hg on atomically clean gold surfaces the viability of the experimental approach was established. We then turned our attention to chemisorption.

2 Adsorption of Carbon Monoxide on Metals

Carbon monoxide adsorption on molybdenum films was a particularly attractive system to start with because it illustrated some of the central features which needed to be resolved in order to establish the potential of photoelectron spectroscopy for investigating systems of interest to those of us concerned with chemisorption and catalysis. It was known that CO adsorption on such transition metals as molybdenum and tungsten[6,7] at 295 K occurs with a high heat of adsorption (*ca.* 300 kJ mol^{-1}); on cooling to 80 K further adsorption of carbon monoxide occurs[6] with a comparatively low heat of adsorption (*ca.* 60 kJ mol^{-1}). The room-temperature adsorption is usually referred to as the β-state and the adsorption at 80 K we designate as the γ-state. Figure 2 shows the O(1*s*) spectrum of CO in the β-state and that its binding energy is 530 eV; the γ-state has associated with it an O(1*s*) spectrum with a range of binding energies up to a maximum of about 536 eV. When the valence levels are explored using He (I and II) radiation the β-state exhibits a single peak at about 5.6 eV below the Fermi level (E_F) whereas the γ-state is characterized by two peaks at about 7 eV and 11 eV below E_F. The 5.6 eV peak can be assigned to the O(2*p*) level while the 7 eV and 11 eV peaks have counterparts in the spectrum of CO(g). If the adlayer (the Virgin state) is formed at low temperature (80 K) and then warmed to 395 K, the initial O(1*s*) binding energy which is at about 531 eV decreases to 530 eV at 295 K and the two peaks at 7 eV and 11 eV in the He spectrum disappear, being replaced by a broad hump at about 5.5 eV below E_F. We make the following observations:

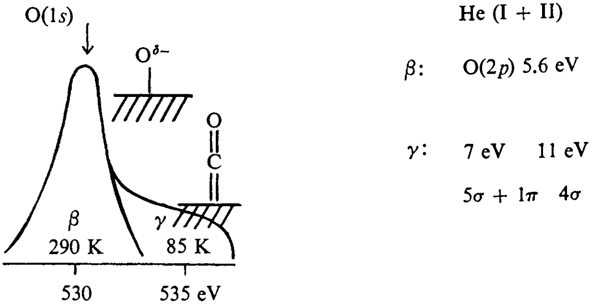

Figure 2 *Core-level* O(1*s*) *spectra together with data from valence-level studies using* He *radiation for* CO *adsorption on* Mo *at* 290 K *and* 85 K

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[5] C. R. Brundle and M. W. Roberts, *Proc. Roy. Soc.*, 1972, A331, 383.

[6] (*a*) R. R. Ford, *Adv. Catalysis*, 1970, **21**, 51; (*b*) D. O. Hayward, in 'Chemisorption and Reactions on Metallic Films', ed. J. R. Anderson, Academic Press, London, New York, 1971.

[7] J. G. Little, C. M. Quinn, and M. W. Roberts, *J. Catalysis*, 1964, **3**, 57.

(i) CO adsorbed with different heats of adsorption is distinguished by different O(1*s*) binding energies.

(ii) Strongly chemisorbed CO is characterized by substantially lower O(1*s*) binding energy than that which is weakly adsorbed. Furthermore the O(1*s*) value of 530 eV (β-state) is the same as for chemisorbed oxygen on molybdenum.

(iii) The β-state does not exhibit orbital structure in the He spectra which can be assigned easily to molecular carbon monoxide. The peak at 5.5 eV is attributed to the O(2*p*) level.

(iv) The γ-state exhibits peaks at 7 eV and 11 eV which can be assigned to the (5σ and 1π) and 4σ orbitals in CO(g). The assignment of these peaks gave rise to considerable debate and speculation[8a,9,10] but is now well established experimentally as a result of the synchroton radiation studies of Gustafsson *et al.*[8b] The outer 5σ orbital is primarily centred on the C atom and looks like a lone pair in that it extends out well beyond the C atoms. The 1π level, which accommodates four electrons, is centred on the oxygen in that the charge distribution is about 3:1 around the oxygen compared with the carbon. Lastly the 4σ is like an oxygen lone pair and extends beyond the O atom.

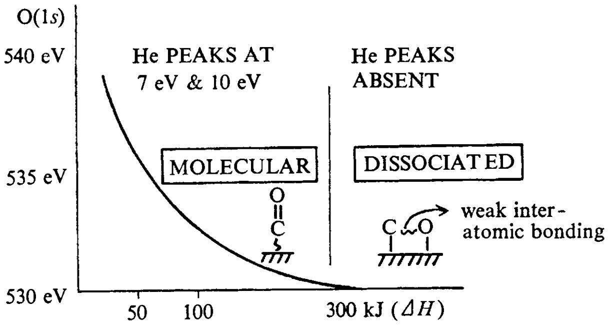

Figure 3 *Correlation between* O(1*s*) *binding energy for adsorbed* CO *on different metals, its heat of adsorption* (ΔH)*, and the presence/absence of peaks in the* He *spectra characteristic of molecular* CO

There is therefore a *prima facie* case for considering carbon monoxide to be dissociated, or at least that the C—O bond is very weak, in the β-state. The relationship between heat of adsorption and the O(1*s*) binding energy noted above led us to explore whether there was a more general correlation.

[8] (*a*) D. R. Lloyd, *Faraday Disc. Chem. Soc.*, 1974, No. 58, p. 136; (*b*) T. Gustafsson, E. W. Plummer, D. E. Eastman, and J. L. Freeouf, *Solid State Comm.*, 1975, **17**, 391.

[9] D E. Eastman and J. K. Cashion, *Phys. Rev. Letters*, 1971, **27**, 1520.

[10] T. A. Clarke, I. D. Gay, B. Law, and R. Mason, *Chem. Phys. Letters*, 1975, **31**, 29.

Figure 3 shows O(1*s*) values as a function of the heat of adsorption of carbon monoxide on a number of metals.[11] Furthermore we include information from u.v. photoelectron spectroscopy using He (I and II) radiation. The vertical line divides these situations where peaks in the He spectra at about 7 eV and 10 eV were observed from those where they were absent. It is evident that there is a correlation between the molecular state of CO (dissociatively or associatively adsorbed), the heat of adsorption, and the O(1*s*) binding energy. It should be noted that when CO is chemisorbed at 295 K with a heat of adsorption greater than about 260 kJ mol^{-1} the O(1*s*) binding energy is invariant at 530 eV, a value typical of dissociatively chemisorbed oxygen on transition metals. What else can we deduce from this correlation? If we think of the decrease in the O(1*s*) value (Figure 3) as reflecting an increase in the electron density in the vicinity of the oxygen of the carbon monoxide molecule, then this increase can be associated with the accompanying increase in the heat of adsorption. Clearly it is attractive to think of the increased heat of adsorption as arising largely from back-bonding into the antibonding orbitals of CO. Support for this view is also inherent in the conclusions of Grimley's[12,13] theoretical work. As the extent of back-bonding increases, the heat of adsorption increases, the O(1*s*) value decreases, and the C—O bond strength decreases until ultimately no orbital structure is observed in the He spectra. At this stage we consider the molecule to be 'dissociated' but whether the carbon and oxygen exist as separate adatoms is another matter. The threshold for dissociation of CO at 295 K is therefore reached when the extent of back-bonding results in the heat of chemisorption exceeding about 260 kJ mol^{-1}. It should be noted that the threshold will vary with the substrate temperature. Now any correlation of this kind is only worthwhile if it is successful in predicting molecular processes and the system we chose to consider was the adsorption of CO on iron.

The heat of adsorption of CO on iron[14] is close to the 'threshold heat'; furthermore isotope exchange data[15] had suggested that the molecule was in an incipient state of dissociation at 190 K. In spite of this observation which was made some 20 years ago, and occasional reports of CO adsorption being infrared inactive,[16] it should be emphasized that the consensus of opinion was wholly in favour of the adsorption of CO on metals being molecular at room temperature. Figure 4 shows the C(1*s*) spectrum for the CO adlayer formed on polycrystalline iron[17] at 85 K and during the warming of the adlayer to 295 K. A new C(1*s*) peak, reflecting 'carbidic' carbon emerges at 295 K; this is accompanied by a diminution in the intensity of the (5σ and 1π) and 4σ orbitals. This diminution occurs slowly at

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[11] R. W. Joyner and M. W. Roberts, *Chem. Phys. Letters*, 1974, **29**, 447.
[12] T. B. Grimley, 'Batelle Colloq. Mol. Processes on Solid Surfaces', 1968.
[13] See also ref. 6*a*.
[14] D. Brennan and F. H. Hayes, *Phil. Trans. Roy. Soc.* 1965, **A258**, 347.
[15] A. N. Webb and R. P. Eischens, *J. Amer. Chem. Soc.*, 1955, **77**, 4710.
[16] A. M. Bradshaw and J. Pritchard. *Proc. Roy. Soc.*, 1970, **A316**, 169.
[17] K. Kishi and M. W. Roberts, *J.C.S. Faraday I*, 1975, **71**, 1715.

295 K but is accelerated by warming to 350 K. On recooling to 295 K the 'reacted' surface, which can be considered to be essentially a 'carbidic/oxide' adlayer, is active in further adsorption of CO and the C(1*s*) spectra (Figure 4), the O(1*s*) spectra, and the He (I and II) data indicate molecular adsorption. Menzel and his colleagues[18] have reviewed the present position regarding CO adsorption on metals and also reported data for the adsorption of carbon monoxide on W(110). The evidence is unambiguous regarding the ready cleavage of the C—O bond on metals and as a rule the ease of dissociation follows the correlation shown in Figure 3.

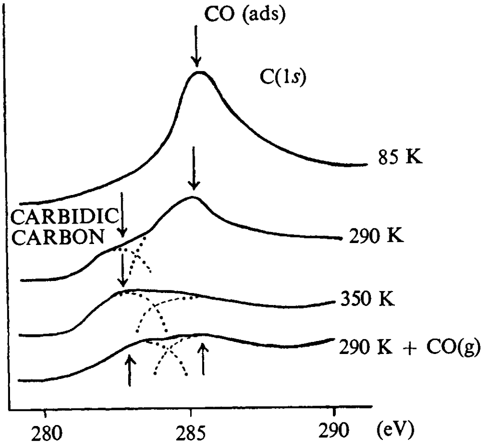

Figure 4 *Thermally induced dissociation of carbon monoxide adsorbed on iron at* 85 K. C(1*s*) *data*

Carbon monoxide adsorption on copper[19] has been studied extensively and, in general, there is good agreement between different studies. At low temperature there is unanimity of view that adsorption is relatively weak, with a heat of adsorption of about 60 kJ mol^{-1}, the adlayer exhibits a $(\sqrt{2} \times \sqrt{2})$ R45° symmetry but at higher coverage the symmetry is hexagonal which is attributed to a 'compression structure'. The adlayer formed at 85 K desorbs on warming to 295 K under a dynamic vacuum. At 295 K there has been some ambiguity as to whether or not copper adsorbs carbon monoxide, but by combining photoelectron spectroscopy with LEED we have recently reconsidered the question, the stimulus for this having come from observations we made on the (NO + Cu) system which we discuss later. Table 1 summarizes the data observed with Cu(100) at 85 K and 295 K. There is no doubt that if exposed to a relatively high pressure of CO ($\gtrsim 10^{-2}$ Torr), Cu(100) will adsorb CO in the molecular state[20] at 295 K. The electron spectroscopic characteristics of the two states (85 K and 295 K) are,

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[18] E. Umbach, J. C. Fuggle, and D. Menzel, *J. Electron. Spectroscopy*, 1977, **10**, 15.
[19] J. Pritchard, T. Gatterick, and R. K. Gupta, *Surface Sci.*, 1975, **53**, 1.
[20] S. Isa, R. W. Joyner, and M. W. Roberts, *J.C.S. Chem. Comm.*, 1977, 377.

Table 1 *Characteristics of* CO *adsorption on* Cu(100) *at* 80 K *and* 295 K (*XPS, UPS, LEED*)

	80 K	295 K
O(1*s*)	534 eV	532.8 eV
He-II/eV	8.6, 11.8, 13.7	8.1, 11.1
S (sticking probability)	~unity	$\sim 10^{-6}$
LEED (symmetry of adlayer)	$(\sqrt{2} \times \sqrt{2})$ R45° Sharp diffraction features $\theta \simeq 0.5$	$(\sqrt{2} \times \sqrt{2})$ R45° Diffuse diffraction features $\theta \simeq 0.3$
Desorption temp. (K)	~180	~380
Bonding	σ-bonding dominant: $CO^{\delta+}$	d-π^*-bonding dominant: $CO^{\delta-}$

however, very different, as also are their heats of adsorption and sticking probabilities. We designate the low-temperature state as $CO^{\delta+}$, implying that σ-bonding to the metal is dominant whereas we designate adsorption at 295 K as $CO^{\delta-}$. Back-bonding into the antibonding CO molecular orbital is suggested to be most significant at room temperature; this is compatible with our correlation of O(1*s*) binding energy values *versus* heat of adsorption (Figure 3). The estimated coverage at 295 K is only about 0.3 and the symmetry of the adlayer $(\sqrt{2} \times \sqrt{2})$ R45°; the LEED pattern is, however, rather diffuse implying appreciable disorder within the layer. The question that is immediately raised is why has *irreversible* adsorption of CO on copper at room temperature not been observed by infrared spectroscopy? One possibility is that $CO_{ads}{}^{\delta-}$ is infrared inactive, either because of its particular molecular orientation with respect to the surface and the incident radiation (this is critical in the reflection–absorption technique) or because the C—O bond has been appreciably weakened by back-bonding.*

A pattern is therefore emerging for CO adsorption on metals where the following sequence of events has been recognized:

$$CO(g) \rightarrow CO_{ads}{}^{\delta+} \rightarrow CO_{ads}{}^{\delta-} \rightarrow C_{ads} + O_{ads}$$

In the case of molybdenum we observe largely $CO_{ads}{}^{\delta-}$ at 85 K but we go through to $C_{ads} + O_{ads}$ at room temperature, whereas in the case of nickel we stop at $CO_{ads}{}^{\delta-}$ at 295 K. With iron, dissociation occurs slowly at 295 K but can be completely arrested[17] by preadsorbing submonolayer quantities of sulphur. With copper we see almost exclusively $CO_{ads}{}^{\delta+}$ at 85 K; this desorbs on warming to 295 K, but $CO_{ads}{}^{\delta-}$ forms only slowly from CO(g) at room temperature, possibly because $CO_{ads}{}^{\delta+}$ is an essential precursor and its concentration at 295 K is, in view of its low heat of adsorption, very small. Alternatively (or in addition) it is electron redistribution leading to bonding that is rate-determining. In this discussion we have emphasized the relationship between charge, electron

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*Note added in proof: For CO adsorbed on Ni(100) recent calculations suggest that the molecule is tipped over at an angle of about 34° with respect to the surface normal (Dr. J. B. Pendry, personal communication).

spectroscopy, and the chemical reactivity of adsorbed carbon monoxide. The interdependence of charge and stretching frequency has of course been established in transition-metal chemistry where the stretching frequency of CO is not only related to the number of *d*-electrons but also to the presence of a total net charge. In the following complexes, for example, all have d^6 electron configurations and the same co-ordination sphere but different formal charges:

$[Mn(CO)_6]^+$	$[Cr(CO)_6]$	$[V(CO)_6]^-$
$\nu_{CO} = 2095\ cm^{-1}$	$\nu_{CO} = 2000\ cm^{-1}$	$\nu_{CO} = 1860\ cm^{-1}$

The surface chemistry of carbon monoxide on atomically clean metal surfaces may therefore be considered in terms of the two-way electron transfer process, the molecule behaving as either an electron acceptor, $CO^{\delta-}$, or an electron donor, $CO^{\delta+}$. This is a point central to a number of infrared studies,[21a] to recent theoretical calculations of CO chemisorption and bonding in transition-metal complexes,[21b] and to certain homogeneous catalytic reactions. A particular example of the latter would be the carboxylation of alcohols where CO appears to behave as an electron acceptor.

3 Adsorption of Nitric Oxide on Metals

Our interest in nitric oxide was stimulated by the conclusions we reached with carbon monoxide. The bond energy of NO (600 kJ) is appreciably smaller than that of CO (1000 kJ) and if the model we used (Figure 3) to rationalize the molecular state of adsorbed CO is also valid for NO then we would anticipate analogous molecular events. There is an important difference between CO and NO and that is the inherent thermodynamic instability of NO, so that we will be exploring the conditions under which adsorbed molecular NO becomes kinetically unstable and dissociates. Although infrared studies[22] have shown that at high pressures (several Torr) NO interacts with iron and other surfaces to give oxide, there is no information on the possible molecular subtleties of the interaction. Furthermore the data have been interpreted over the years in different ways so that it is difficult to obtain a satisfactory model for the interaction. Figure 5(a) shows that the molecule, in fact, dissociates at low coverage on a clean iron surface at 85 K but at higher coverage molecular adsorption predominates.[23] If, however, the adlayer is thermally activated, by warming to 295 K, dissociation occurs to give a surface which is incipient oxide/nitride. Exposure to NO(g) at higher pressure (10^{-4} Torr) gave evidence for further molecular adsorption. Although we only report here the N(1*s*) data, similar conclusions are reached from an examination of the O(1*s*) spectra. One further point to note is that when the N(1*s*) and O(1*s*) intensities are compared, making use of known ionization cross-section data, we find that at low coverage at 85 K some recombination of

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[21] (*a*) G. Blyholder, *J. Phys. Chem.*, 1964, **68**, 2773; (*b*) I. H. Hillier and V. R. Saunders, *Mol. Phys*,. 1971, **22**, 1025.

[22] (*a*) A. N. Terenin and L. M. Roev, *Actes du Deuxieme Congres International de Catalyse*, 1961, **2**, 2183; (*b*) A. Alekseev and A. N. Terenin, *J. Catalysis*, 1965, **4**, 440.

[23] K. Kishi and M. W. Roberts, *Proc. Roy. Soc.*, 1976, **A352**, 289.

nitrogen adatoms leading to desorption of N_2 occurs. By examining the surface species using He (I and II) radiation [Figure 5(b)] the conclusions from core-level spectroscopy regarding the nature of the adsorption, dissociative or associative,

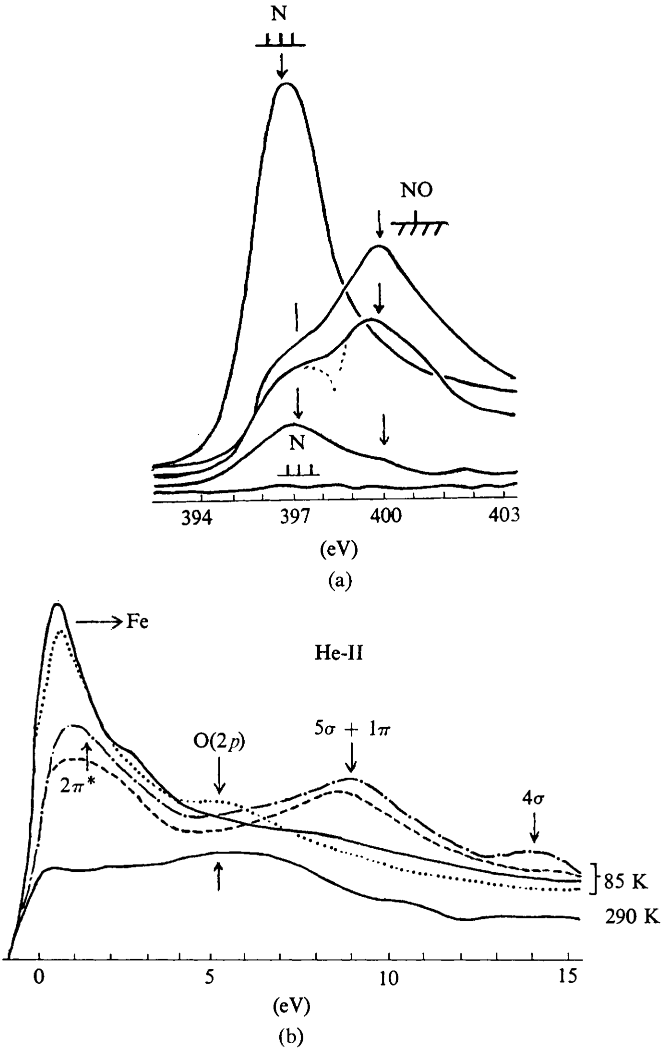


Figure 5 (*a*) *Adsorption of* NO *on* Fe *at* 85 K *followed by warming the adlayer to* 295 K, N(1*s*) *spectra are recorded with increasing exposure* (*Curve* 2:2 × 10^{-7} Torr, 80 s; 4 (*total*):2 × 10^{-7} Torr, 480 s) (*b*) He-II *spectra for* NO *adsorbed on* Fe *at* 85 K *followed by warming the adlayer to* 295 K [*details of exposure as in* (*a*)]

are confirmed. Peaks in the u.v. spectrum at high coverage at 85 K can be assigned to the $2\pi^*$, 1π and 5σ, and 4σ orbitals. These are absent at 295 K and the density of states curve has similarities to 'oxidized' iron.

Clearly it is necessary to explore in more detail the high binding N(1*s*) (Figure 5) and O(1*s*) regions, *i.e.* that part of the spectrum assigned to molecular NO adsorption. The comparatively large FWHM value (*ca.* 6 eV) suggests contributions from more than one type of NO bonding. With this end in mind we investigated the interaction of nitric oxide with copper and, by analogy with carbon monoxide, adsorption was anticipated to be weak and molecular in nature. Figure 6 shows the O(1*s*) spectrum for the adlayer formed on copper[24] at 80 K; there are two distinct peaks. We assign the peak at 531.6 eV to $NO_{ads}^{\delta-}$ and that at 535 eV to $NO_{ads}^{\delta+}$. He (I and II) spectra confirm the molecular nature of these species. Furthermore, intensity data suggest that the molecule is linearly bonded to a single copper surface atom. We believe that in the case of iron (Figure 5) these two species are not resolved and the broad envelope at high binding energy probably incorporates them.

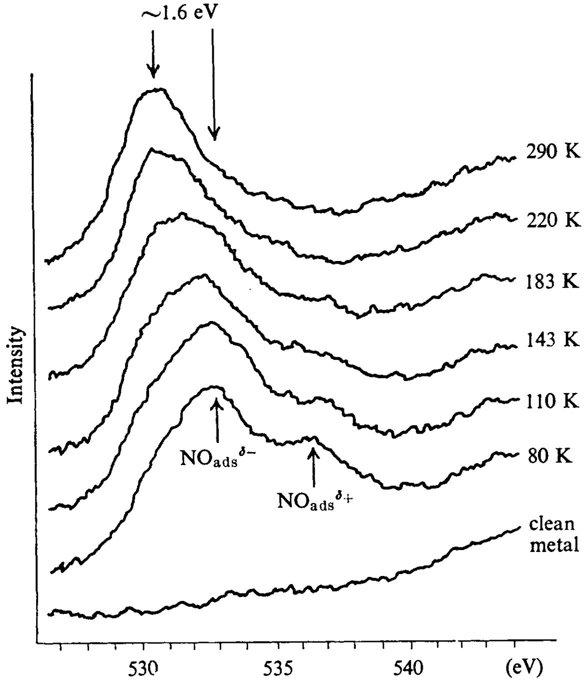
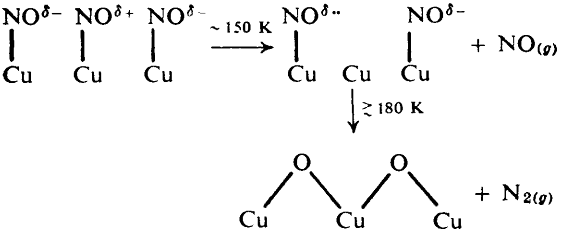


Figure 6 O(1*s*) *spectra for* NO *adsorption on copper at* 80 K *followed by warming of the adlayer, in stages, to* 290 K

[24] M. Matloob and M. W. Roberts, *J.C.S. Faraday I*, (in press); *Physica Scipta*, (to be published).

This molecular adlayer on thermal activation transforms into a layer which has no surface nitrogen present (Scheme 1). The nitrosonium-like species desorb at about 150 K and we estimate their heat of adsorption to be about 60 kJ mol^{-1}. The $NO_{ads}{}^{\delta-}$ or nitrosyl-like species dissociate above about 180 K, giving exclusively chemisorbed oxygen which is bridge-bonded to copper. The nitrogen adatoms recombine and desorb as molecular nitrogen, above about 180 K.



Scheme 1

On the other hand, when copper is exposed to NO at 295 K, dissociation occurs and both the nitrogen and oxygen are retained at the surface in what we believe is a bridge-bonded configuration.[24] Clearly there is a small activation energy for nitrogen adatoms to be chemisorbed by copper and in the temperature range 150—200 K recombination and desorption is faster than chemisorption. By making use of recent ionization cross-section and electron escape depth data it has also been possible to calculate from the photoelectron intensity data [N(1*s*), O(1*s*), and Cu($2p_{3/2}$)] the surface concentrations of nitrogen and oxygen adatoms. It is on this basis that we conclude that bridge-bonding occurs at 295 K whereas at 85 K each surface copper atom is linearly bonded to an NO molecule. We are currently investigating the structural aspects of these processes using Cu single crystals and combining photoelectron spectroscopy with LEED.

In the case of NO adsorption on aluminium,[25] dissociation to give nitrogen adatoms $N^{\delta-}$ occurs [N(1*s*) = 397 eV] at 85 K followed at higher exposure by the emergence of two further N(1*s*) peaks at 403 eV and 406 eV. The former, as with copper, we designate $NO_{ads}{}^{\delta-}$ and the latter $NO_{ads}{}^{\delta+}$. Evidence for these assignments was obtained by exposing the adlayer at 85 K to water vapour, a strong electron donor, when the $NO^{\delta+}$ species was desorbed entirely and the $N^{\delta-}$ and the $NO^{\delta-}$ species remained substantially unaltered.

We can, in a sense, therefore think of the nitric oxide molecule as probing the electronic nature of the adlayer formed on aluminium (and also copper and iron) when it is but a few ångströms thick, $NO^{\delta-}$ providing information on electron-excess sites and $NO^{\delta+}$ being bonded at Lewis acid or electron-deficient sites such as Al^{3+}. That $NO_{ads}{}^{\delta-}$ is the precursor to dissociation is in keeping with these

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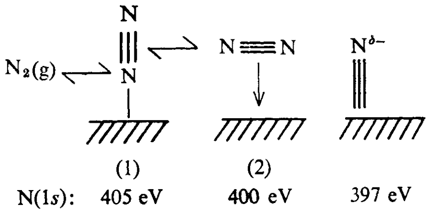
[25] A. Carley and M. W. Roberts, (to be published).

assignments since the N—O bond will have been considerably weakened. It also follows that we might anticipate (as we observe with copper) that $NO^{\delta+}$, where the N—O bond is effectively strengthened on adsorption, would desorb on thermal activation of the adlayer. The occurrence of nitrosonium-and nitrosyl-like species is entirely compatible with the chemistry of nitric oxide but what is perhaps significant from the present work is that it is possible to isolate their analogues at metal surfaces and that monitoring their behaviour during thermal activation provides a better understanding of surface reactivity.

Stimulated by our results for nitric oxide and carbon monoxide interaction with, in particular, iron, we explored[26] the dinitrogen + iron system by *X*-ray photoelectron spectroscopy. The data and conclusions are summarized in Scheme 2.



Scheme 2

Species (1) and (2), observed only at 85 K, are in equilibrium with $N_2(g)$ and are weakly adsorbed [Figure 7(a)]. We suggest that these two species are precursors to the formation of nitrogen adatoms characterized by an N(1*s*) value of 397 eV [Figure 7(b)]. The low concentration of the two molecular species that would obviously be present at 295 K would account for the observed low rate of formation of nitrogen adatoms; we estimate its overall sticking probability to be less than 10^{-6}. Studies of other nitrogen molecules[27] (N_2H_4, NH_3) and nitrogen complexes offer supporting evidence for the molecular processes suggested and assignments made for the N(1*s*) peaks observed. An interesting feature of this study[26] and relevant to the catalytic activity of nitrogen was that XPS indicated that the electronic environment of a nitrogen adatom was perturbed by surface impurities such as chemisorbed oxygen. This work was carried out on polycrystalline iron, but Mason[28a] and his colleagues have recently reported similar results for dinitrogen chemisorption on Fe(111) at 295 K.

Mössbauer spectra have recently been reported for ^{57}Fe in a solid nitrogen matrix where at 4.2 K molecular nitrogen is considered to bond to an iron dimer. In fact Barrett and Montano[28b] suggest that molecular nitrogen only bonds to iron when the latter is present as a dimer. If this is correct then our assignment of

[26] K. Kishi and M. W. Roberts, *Surface Sci.*, 1977, 62, 252.

[27] M. Matloob and M. W. Roberts, see ref. 24.

[28] (*a*) I. D. Gay, M. Textor, R. Mason, and Y. Iwasawa, (to be published); (*b*) P. H. Barrett and P. A. Montano, *J.C.S. Faraday II*, 1977, 73, 378.

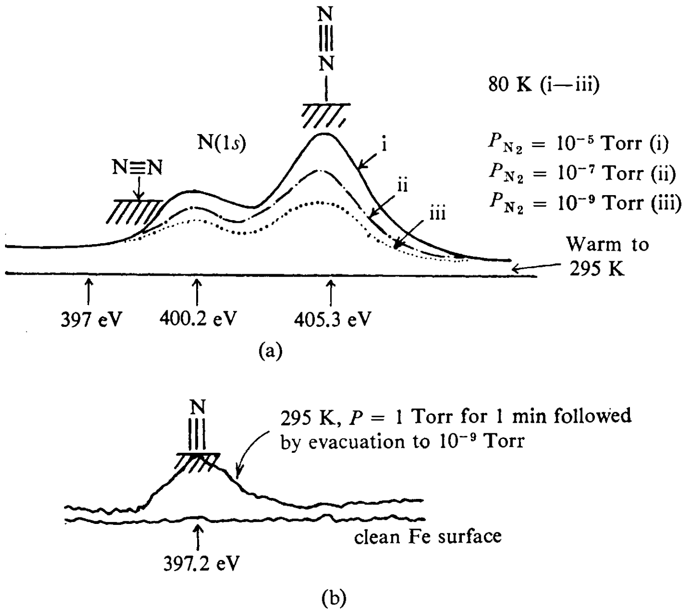


Figure 7 N(1*s*) *and assignments for the adsorption of nitrogen on iron at* (*a*) 80 K *and* (*b*) 295 K

the N(1*s*) peak at 405 eV will require further investigation. It is apposite to enquire as to why N_2 dissociates less easily than CO on, for example, iron. The clue may well lie in the observation that σ-donation and π-back-bonding is considerably less in metal–dinitrogen ligands than in metal–carbonyl ligands. This would certainly fit in with the general ideas proposed here to account for the reactivity of simple diatomic molecules on 'clean' metal surfaces.

4 Metal Oxidation

I have, as yet, not mentioned any example where information has been extracted from core-level spectra of the metal, and the explanation for this is that substrate core-level binding energies are generally rather insensitive to adsorption. However, in the interaction of oxygen[29] with aluminium the Al(2*p*) spectra have provided useful information on the mechanism of oxidation. Figure 8 shows the emergence of a peak at about 2.4 eV higher binding energy than the 'metal' Al(2*p*) value. The variation of the FWHM of this second 'oxide component' peak with oxygen exposure and temperature, in the range 85—295 K, was complex and indicated quite clearly that it was composite. By deconvolution, removing both instrumental and *X*-ray broadening from the experimental data, two distinct

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[29] A. Carley and M. W. Roberts, (to be published).

components α and β are solved. Furthermore, we suggest that the α-component is a precursor of the β-form. This is compatible with the observation that the 'oxide component' peak develops more rapidly at 85 K than at 295 K. If the β-form, which we believe is analogous to Al_2O_3, can only develop *via* the α, and since the formation of the α is faster at the lower temperature, then the overall kinetic characteristics of the oxidation may be understood. It is important to note that the O(1*s*) data, although compatible with the behaviour of the Al(2*p*) peak during oxygen interaction, are not in themselves revealing.

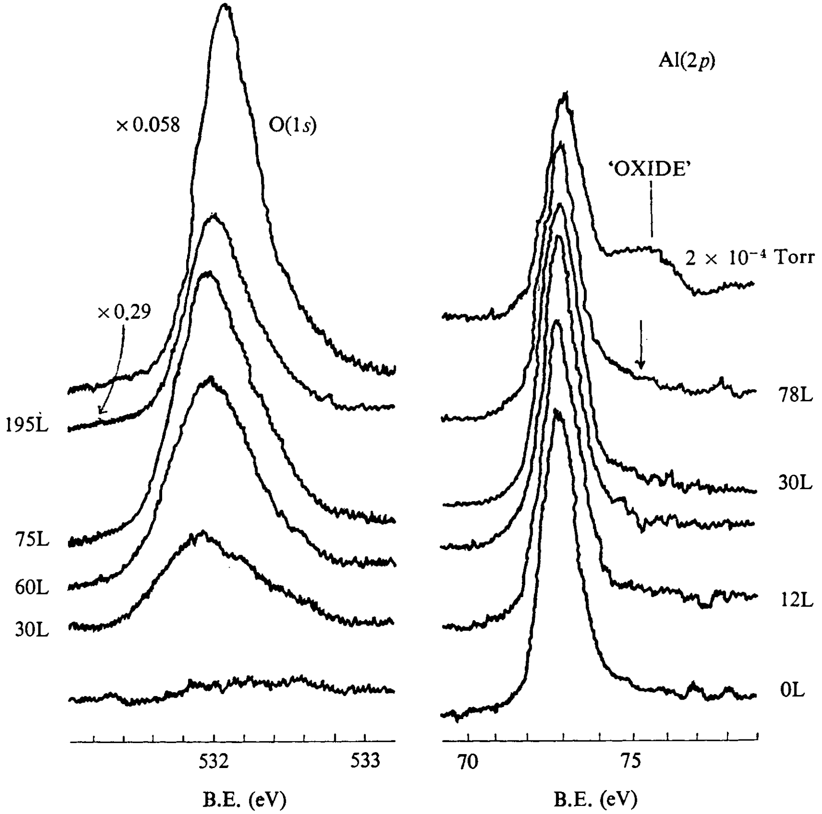

Figure 8 O(1*s*) *and* Al(2*p*) *spectra during oxygen interaction with aluminium at* 290 K (1 L ≡ 10^{-6} Torr sec)

One of the consequences of the emergence of such new and powerful techniques as electron spectroscopy is that one can reflect critically on the information obtained from more traditional techniques. The aluminium–oxygen system is one of them. A decade or so ago we investigated[30] the interaction of oxygen with

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[30] M. W. Roberts and B. R. Wells, *Surface Sci.*, 1969, **15**, 325.

aluminium by monitoring the change in work function. There is one aspect of that work which I would like to recall, namely the observation that oxygen incorporation occurred with an activation energy of no more than a few kJ mol^{-1} and that a transitory low work function oxide was observed before the formation of the oxide of higher work function. These particular studies were made in the same temperature range (85—295 K) and at about the same oxygen pressure (*ca.* 10^{-6} Torr). It is, therefore, tempting to attribute the low work function 'oxide' to the α-component, and the higher work function 'oxide' to the β-component which we believe is probably the ionic-spinel Al_2O_3. Furthermore, this would be compatible with the $NO^{\delta+}$ and $NO^{\delta-}$ species observed when aluminium, oxidized to an estimated thickness of 9 Å, is exposed to nitric oxide at 85 K.

In contrast to the above, the electron spectroscopy of the interaction of oxygen with Pb(100) and Pb(110) single crystals was not as revealing[31] as the information we obtained from LEED. The data were unusual in that from the lowest oxygen exposures used the extra diffraction spots which were observed remained unaltered during the continuous growth of the oxide (up to about 9 Å, at 295 K). It is much more common during 'oxidation' at low temperature for the adlayer to appear either highly disordered or for facet structures to develop. We interpret the present data as reflecting the growth of four domains of orthorhomobic PbO with $\alpha = 89°$ and that growth is continuous from the lowest oxygen exposure used. A nucleation model is proposed for oxide growth for both Pb(100) and Pb(110). Epitaxial behaviour was, however, only observed above 120 K indicating that although thermal activation is essential it need not be more than a few kilojoules per mole. There has been a tendency to study metal–oxygen systems in the hope that something new will emerge from electron spectroscopy, and generally speaking the outcome has been disappointing, previous ideas being merely confirmed. However, a few examples do exist where particular problems related to oxidation have been probed, and two of these, the oxidation of copper[32] and cobalt,[33] have relied on monitoring the shake-up satellites to decide on whether Cu^{II} or Cu^{I} (and Co^{II} or Co^{III}) are present. In the case of cobalt oxidation both oxygen pressure and temperature determine whether the surface, when no more than three or four oxide layers thick, is CoO or Co_3O_4 and recourse is made to the detailed studies of McDowell *et al.*[34c] who had established the relationship between shake-up satellites and the valence state of cobalt with a range of different metal complexes. In the case of oxygen interaction with Cu(100)[32a] in addition to core-level spectroscopy and associated satellite peaks LEED has provided important complementary structural data giving convincing evidence on, for example, the interplay between the two surface oxides involving the Cu^{II} and Cu^{I} valence states.

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[31] K. Kishi, R. W. Joyner, and M. W. Roberts. (to be published).

[32] (*a*) S. Evans and J. M. Thomas, *Faraday Disc. Chem. Soc.*, 1974, No. 58, p. 97; (*b*) M. J. Braithwaite, R. W. Joyner and M. W. Roberts, *Faraday Disc. Chem. Soc.*, 1975, No. 60, p. 89.

[33] R. B. Moyes and M. W. Roberts, *J. Catalysis*, 1977, (in press).

5 Molecular Nature of Solids and the Role of the Reactants

Finally, I want to discuss briefly some examples (Table 2) we have come across where new surface sites are created under conditions which illustrate the facile nature of many surface processes. Mechanistic aspects are not considered here. We see that the reactant molecules can control the molecular nature of the surface sites thus emphasizing the need to know more about the catalyst surface under reaction conditions when it may bear little relationship to the 'unused' catalyst. The temperature region in which the processes are observed (85—295 K) indicates that the activation energies of the molecular processes occurring can not be more than about 15 or 20 kJ mol^{-1}. Perhaps the only example (Table 2) which needs any amplification is the iron–water interaction,[37] the implications from the others being self-evident. After the formation of only a monolayer or so of what we suggest is the hydroxide FeO·OH, reaction becomes very slow. Furthermore the surface becomes passive to subsequent oxidation by molecular oxygen even though in the absence of the water vapour pre-treatment the oxide thickness would have been some four or five times greater at the oxygen pressure used. The role of water vapour in metal oxidation is far from understood and more work of this kind should be useful to extract some generalizations which may also be helpful in understanding some aspects of catalytic reactions.

Table 2 *Examples of facile surface processes and the creation of new 'surface sites'*

		Ref.
$PbO(s) + H_2S(g) \xrightarrow[10^{-6}\ \text{Torr}]{100\ \text{K}} PbS(s) + H_2O(g)$	XPS/LEED	34 *a,b*
$PbO(s) + HCOOH(g) \xrightarrow[10^{-5}\ \text{Torr}]{295\ \text{K}} Pb(s) + H_2O(g) + CO_2(g)$	XPS/LEED	35
$Cu_2O(s) + NH_3(g) \xrightarrow[10^{-4}\ \text{Torr}]{295\ \text{K}} CuNH(s) + H_2O(g)$	XPS	36
$Fe(s) + H_2O(g) \xrightarrow[10^{-6}\ \text{Torr}]{295\ \text{K}} FeO{\cdot}OH$	XPS	37

One obvious point that emerges from the examples I have chosen is the dynamic nature of a catalyst surface. It seems, for example, rather futile to carry out a detailed experimental or theoretical study of an oxide catalyst with a view to understanding its catalytic behaviour if it is not recognized that under catalytic conditions its surface is not an oxide at all, but a chemisorbed sulphide layer on an underlying oxide, or an overlayer of imide-like species on an oxide (Table 2). In this general context it is apposite to mention that studies at high coverages are more likely to be relevant to heterogeneous catalysis while experimental studies

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[34] (*a*) K. Kishi and M. W. Roberts, *J.C.S. Faraday I*, 1975, **71**, 1721; (*b*) R. W. Joyner, K. Kishi, and M. W. Roberts. (submitted for publication); (*c*) D. C. Frost, C. A. McDowell, and I. S. Woolsey, *Mol. Phys.*, 1974, **27**, 1473.

[35] S. A. Isa, R. W. Joyner, and M. W. Roberts, (to be published).

[36] M. H. Matloob and M. W. Roberts, *J.C.S. Faraday I*, 1977, (in press).

[37] M. W. Roberts and P. R. Wood, *J. Electron Spectroscopy*, 1977, (in press).

at low coverage, with possibly single crystals, are more relevant to theoretical calculations. These are not tight compartments, however, and the recent interest in cluster calculations may be one area where one can get close to the 'real situation'. One particular cluster complex, $Fe_6(CO)_{16}C^{2-}$, iron carbonyl carbide, is the molecular analogue of carbon monoxide chemisorbed on iron carbide, the central carbon atom being co-ordinated octahedrally by iron atoms at almost the precise Fe—C distance characteristic of bulk iron carbide. Is this relevant to the fact that iron carbide is a good Fischer–Tropsch catalyst for the conversion of carbon monoxide into hydrocarbons? Are the carbon atoms formed during CO dissociation (Figure 3) relevant? It is questions such as these that are providing much of the impetus to current research in surface chemistry.

6 Conclusions

What I have attempted to do in this lecture is to discuss some of our recent work, and in this sense it is a rather narrow viewpoint. But I hope it at least illustrates the very dramatic change that has taken place in the approach to tackling problems in interfacial chemistry. The contribution made by electron spectroscopy, and to a lesser extent LEED, to a better understanding of the surface chemistry of some diatomic molecules (nitrogen, carbon monoxide, nitric oxide, and oxygen) has been considered, the interplay between associative and dissociative modes of adsorption emphasized, and the relative stabilities of molecular states on different metal surfaces discussed. A recurrent theme is the significance of the two-way electron transfer process (σ-donation and π-back-bonding) and how this can account for the spectroscopic data as well as the overall surface chemistry. The role of the metal catalyst can be seen as a vehicle for pumping electrons into antibonding orbitals, thereby inducing potential reactivity in otherwise unreactive bonds. Although there has been a general tendency to overemphasize the 'surface physics' that has emerged from the more recently developed experimental methods we must not lose sight, however, of the relevance the new data have for those of us more interested in the chemical reactivity of solids, and in this context Mason and Textor[38] showed how information from organometallic chemistry can facilitate a better understanding of the two-dimensional chemistry emerging from LEED and electron spectroscopy. The 'new approach' (see also, for example Spicer *et al.*[39] and Baron, Blakely, and Somorjai[40]) will provide insights hitherto inaccessible to the surface chemist, and although the development of a new catalyst will remain the prerogative of the catalytic chemist, its genesis may well be accelerated by an efficient flow of ideas across the 'interface'. For example, the simple nature of the molecular events referred to in Table 2 is a timely reminder of the difficulties of defining the surface of a 'working' catalyst. It is already

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[38] R. Mason and M. Textor, in 'Surface and Defect Properties of Solids', (Specialist Periodical Reports), ed. M. W. Roberts and J. M. Thomas, The Chemical Society, London, 1976, vol. 5, p. 189.

[39] W. E. Spicer, K. Y. Yu, I. Lindau, P. Pianetta, and D. M. Collins, in 'Surface and Defect Properties of Solids', (Specialist Periodical Reports), ed. M. W. Roberts and J. M. Thomas, The Chemical Society, London, 1976, vol. 5, p. 103.

[40] K. Baron, D. W. Blakely, and G. A. Somorjai, *Surface Sci.*, 1974, **41**, 45.

obvious that the ‘new’ data have provided a stimulus to the theoretician, and I am thinking here particularly of the cluster-type calculations of Johnson and Slater which are bringing the experimentalists and theoreticians closer together. Both groups, however, have a long way to go to satisfy the industrialist but I believe we are on the right road, with the three milestones I mentioned earlier in my talk well behind us.

It is a pleasure to express my gratitude to those many collaborators who have played an essential part in our surface chemistry studies.