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### Photoelectron spectroscopy: a strategy for the study of reactions at solid surfaces

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## Photoelectron spectroscopy: a strategy for the study of reactions at solid surfaces

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The development of X-ray photoelectron spectroscopy for the study of the nature of chemisorbed species and the mechanisms of surface reactions is described. The methodology of data analysis and the establishment of data banks which enable photoelectron spectra to be assigned to specific surface species is discussed by reference to examples from recent studies.

Although in the first instance the primary aim was to establish a qualitative logic in a well defined area of surface chemistry, this was then developed quantitatively and extended to studies of the mechanism of surface catalysed reactions. Emphasis is given here to the activation of molecules at metal surfaces either by surface modification or through chemical specificity which is associated with coadsorbed molecules. As illustration we discuss the activation of O-H and N-H bonds by 'oxygen' resulting in reaction pathways being followed which would not have been predicted on the basis of the known reactivities of the individual molecules. The examples chosen also illustrate the severe limitations of mechanistic studies in surface chemistry based (a) on the study of the individual reactants separately; (b) on a post-mortem type of analysis of the surface and (c) on just a gaseous product analysis. An important concept that has emerged is the dual role of surface 'oxygen'. It may either act as a promoter in activating an otherwise unreactive adsorbate molecule, or it may form an unreactive oxide overlayer.

Parallel studies of metal oxides *per se* provide information on the defect nature of both oxide overlayers at metal surfaces and also bulk oxide surfaces. Close similarities are shown to exist between the 'oxygen' activation of molecules at metal surfaces and the catalytic reactivity of defective bulk oxides. A common theme is that the dominant mechanism involves hydrogen abstraction by oxygen adatoms, which are assigned as O<sup>-</sup>(s) both at metal surfaces (by XPS) and at bulk oxide surfaces (by E.P.R. and XPS).

### 1. Introduction

The basic strategy of the chemist for unravelling the mechanisms of reactions has over the years been to obtain information on the concentrations of reactants and products over a wide range of conditions (temperature, pressure etc.). In surface, or two dimensional chemistry, there are severe problems which must be overcome if the development of quantitative mechanistic ideas is to succeed. They include the ability to detect surface species and to distinguish them from those present in the sub-surface; to define their chemical environment (what ligands are associated with them); the nature of the surface bonding (structure); to ascertain if the species are present in an ordered or disordered overlayer; the quantification of the concentrations of the species and, in particular, how these concentrations vary with temperature. With this information at our disposal surface chemistry would be at a comparable stage in development that the classical chemistry of both the gaseous and liquid states was at nearly fifty years ago.

Until about 1970 our understanding of surface chemistry and heterogeneous catalysis was based essentially on indirect experimental methods, that is, those methods

which relied solely on the analysis of the gas phase. There was direct evidence neither for the atomic nature of the surface of the solid catalyst nor of surface bonding involved in the adsorbed species. The one exception was carbon monoxide where its very favourable extinction coefficient in the infrared region of the spectrum enables the molecule to be investigated directly in the adsorbed state. Initially the adsorbant had to have a high surface to volume ratio but more recently with the advent of reflection infrared (rather than transmission) spectroscopy, spectra of carbon monoxide chemisorbed at single crystal surfaces became feasible (Pritchard 1978).

However, within the last 15 years there have occurred unprecedented advances in the development of surface-sensitive techniques which has led to two-dimensional chemistry emerging as one of the fastest growth areas of the physical sciences. It is on one of these techniques, photoelectron spectroscopy, that we wish to focus attention in this article, keeping very much in mind the kind of questions (outlined above) that the surface chemist regards as essential for the development of molecular mechanisms of surface processes. The development of photoelectron spectroscopy in surface science will be discussed from some of the early observations of its likely potential in surface studies, to the ability to distinguish qualitatively between different species involving the same element (e.g. O(a), OH(a), H<sub>2</sub>O(a); N(a), NH(a), NH<sub>3</sub>(a); CO(a), CO<sub>2</sub>(a), COOH(a) etc.) to estimating quantitatively the individual surface concentrations. It is information on how the latter vary with pressure (exposure), time and temperature that must be central to mechanistic aspects of surface chemistry and heterogeneous catalysis. It is this aspect that we will emphasize in this paper, at the same time providing a picture of how the photoelectron spectroscopic approach has matured over the last fifteen years into one of the most powerful quantitative surface-sensitive spectroscopic techniques.

The unpredictability of surface chemistry is well recognized; except in some limited examples detailed mechanisms, with intermediates delineated, are not available. The strategy of enquiry has therefore to be based initially on ensuring the availability of a data base which can lead to quantitative discussion; the present status of the subject is such that in the immediate future we can, at the best, anticipate the subject developing a logical consistency. The role of photoelectron spectroscopy in achieving this aim, we suggest, will be seen to be significant.

## 2. Development of photoelectron spectroscopy in surface chemistry

Photoelectron spectroscopy (PES) is by convention considered to embrace both core-level spectroscopy, where the impinging radiation is X-rays, (XPS), and valence-level spectroscopy, where the impinging radiation is in the ultraviolet region of the spectrum (UPS). The surface sensitivity of UV-induced spectra was clear from studies reported of the elemental semiconductor silicon over 20 years ago (Gobeli and Allen 1962). At about the same time it was recognized that the photoelectron escape depth ( $h\nu = 6.2$  eV) from an oxide overlayer at a nickel surface was less than 20 Å (Quinn and Roberts 1965) while the first attempt to use vacuum-UV radiation (He radiation) in surface chemistry was reported by Bordass and Linnett (1969). Nevertheless in 1969 the general consensus was that X-ray photoelectron spectroscopy was unlikely to exhibit sufficient surface sensitivity for it to become a significant experimental technique in surface chemistry. This was in spite of the spectrum reported by Siegbahn *et al.* (1967) for iodosteric acid monolayers. The pessimism was seen to be unwarranted when an O(1s) spectrum was reported by Thomas *et al.* (1971) for a graphite surface exposed to

'atomic oxygen', Delgass *et al.* (1970) reported XPS data for a variety of systems of catalytic interest while Eastman and Cashion (1971) reported the first UV-induced photoelectron spectrum of chemisorbed carbon monoxide at a metal (nickel) surface. The latter was of particular significance since it opened up the possibility of distinguishing between molecular and dissociative states of adsorption, crucial for mechanistic studies of the catalytic chemistry of carbon monoxide and a problem which had been given considerable attention by a variety of experimental methods—mainly kinetic in origin.

The possible potential of PES for surface chemistry, particularly the study of well defined atomically clean metal surfaces, could be explored only with a specially designed spectrometer, incorporating both X-ray and UV sources, and capable of an ultimate pressure  $10^{-10}$  torr (Brundle and Roberts 1972). This spectrometer had the distinct advantage of being able to monitor the valence orbitals concurrently with the core levels. It is the core-level spectra that provide definitive information for chemical identification of the surface species; without this facility UPS data are usually difficult to interpret. The surface sensitivity of both XPS and UPS for adsorbed molecules on clean metal surfaces was established by adsorbing  $\text{CO}_2$  and Hg at 80 K; assuming a sticking probability of unity it was possible to calibrate peak intensities and therefore estimate surface concentrations at different exposures (Brundle and Roberts 1972).

During the last decade one of the most important developments in PES relevant to surface chemistry has been the ability to obtain angle-resolved (rather than integrated) spectra, one of the first reports being by Lloyd *et al.* (1975). Although initially designed for use with helium radiation, with the advent of synchrotron sources its scope has been increased considerably. Although we shall not consider in any detail the application of synchrotron sources in surface studies there is no doubt that over the next five years we will witness extensive use of these radiation sources for the determination of absolute surface structures.

Methods of structure determination have been an important goal of photoelectron spectroscopy. One of the first to be explored was the photoelectron diffraction effect (Fadley 1984) where interference occurs between direct and ion-core-scattered photoelectron waves. This method has developed rather slowly but recently a new direct analysis approach, making use of photoelectron diffraction, has been developed (Barton *et al.* 1983). It has been shown that photoemission measurements can be analysed to give a Fourier spectrum with peaks which can be attributed in individual atoms. Peak positions give a scattering path length and peak area gives a scattering power, both the position and intensity providing clues to structure. The new approach is referred to as angle-resolved photoemission extended fine structure (ARPEFS). Although ARPEFS can elegantly solve simple surface structures such as that of  $p(2 \times 2)\text{S-Cu}(100)$ , surface EXAFS, first introduced by Brennan *et al.* (1981), would have been easier to analyse (Barton *et al.* 1983). The sulphur-copper distance was  $2.28(3) \text{ \AA}$ . The advantage of SEXAFS is that it provides direct structure analysis including accurate bond lengths without ordering of the overlayer being a prerequisite. A recent good example of surface structure determination is that reported by Puschmann *et al.* (1985) for the formate present at a  $\text{Cu}(110)$  surface where the advantages of combining SEXAFS with near-edge X-ray absorption fine structure (NEXAFS) are emphasized. The oxygen atoms almost bridge two copper atoms with an average Cu-O bond length of  $1.98 \pm 0.07 \text{ \AA}$  which is identical to that in bulk copper formate. For disordered systems the average bond distance may be the only useful parameter so that SEXAFS will be uniquely suitable. However, the ability to provide

direct information of average bond lengths to nearest neighbours is also the weakness of SEXAFS for complicated structures. A well characterized but complex adsorbate may have many similar bond lengths which SEXAFS may be unable to resolve (Barton *et al.* 1983).

### 3. Analysis and quantification of data

The usefulness of XPS in surface chemistry arises from its established surface and chemical sensitivity; the realization of its full potential depends upon the successful analysis and quantification of the experimental data. A quantitative knowledge of the distribution of the various species present on a surface during the course of or after the completion of a surface chemical process is essential to unravel reaction mechanisms. Similarly, the stoichiometry of an overlayer including evidence for any variable oxidation states during its development (for example, a thin film of oxide on a metal) is important for establishing the mechanism.

Data analysis is a prerequisite of quantification, and for this the development of the low-cost microcomputer has been most important. Although simple peak parameters (such as peak position, full-width at half-maximum (FWHM) and peak height and, with more effort, peak area) can be measured from analogue traces, the analysis can be achieved with much greater precision, reliability and speed using a microcomputer and digitized data. This is especially true when smoothing and background removal are performed. Since the magnitudes of typical FWHM values and binding energy chemical shifts are comparable, extraction of chemical information inherent in any X-ray photoelectron spectrum will depend on the detailed analysis of bands which may overlap. It is this spectral decomposition that is probably the most extensively used aspect of data analysis. Analogue methods for curve resolution do exist, and may provide useful information in the hands of an experienced user, but automatic curve-fitting on a digital computer scores heavily by comparison in terms of speed and lack of subjectivity. Decomposition via spectral subtraction has proved to be valuable and to offer advantages over curve-fitting approaches, particularly (but not uniquely) in the analysis of metal core-level peaks. These advantages reside mainly in the fact that the exact line shape is provided by the model experimental spectrum in the former case; in curve-fitting, a theoretical approximation must be used which may be a function of an undesirably large number of variable parameters. The subtraction procedure is discussed in more detail later.

Commercial data-systems offer complete computer control of the spectrometer functions, allowing the setting up and undertaking of an experiment entirely from the computer keyboard. Whilst such an approach may be desirable in an industrial laboratory where a large number of routine samples may be involved, it is less attractive in a research environment. Here the emphasis is more on suitable tailor-made analysis software, and one finds acceptable the minimum interfacing requirements—a means to initiate and terminate a spectral scan, and a signal input to the microcomputer. The signal may either be the output from a ratemeter, which must be digitized by the computer, or a direct pulse input; the latter gives a better quality signal, avoiding distortion introduced by the ratemeter filter circuits. The systems used in our laboratory are based around Apple II+ micros which, despite incorporating what is now old-fashioned technology, still provide probably the best, flexible low-cost solution.

A data-system in XPS must be built around a minimum software configuration of interactive display, smoothing, background removal and peak area calculation.

Figure 1 illustrates graphically the effect of these procedures on a typical spectrum. Desirable extensions include spectral comparison and subtraction, and curve-fitting and/or curve-synthesis. Deconvolution of instrumental broadening effects, although promising much, is usually let down by the quality (signal-to-noise) of the raw data.

Figures 2 and 3 demonstrate decomposition techniques (spectral subtraction and curve fitting) applied to O(1s) spectra obtained when a lead surface is exposed to oxygen at 80 K, followed by water at 80 K and then warmed slowly to room temperature (Carley *et al.* 1983). In both cases information about the interaction of physisorbed water molecules  $\text{H}_2\text{O}(\text{a})$  with weakly chemisorbed surface oxygen  $\text{O}^{\delta-}(\text{a})$  is obtained. In contrast, figure 4 shows substrate core-level spectra for oxygen interaction with titanium where the use of spectral subtraction avoids a very complex, and possibly insuperable, curve-fitting problem. Chemically shifted Ti(2p) peaks are observed in the difference spectra with binding energies intermediate between the  $\text{Ti}^0$  and  $\text{Ti}^{4+}$  values, and which we assign as  $\text{Ti}^{2+}$  and  $\text{Ti}^{3+}$  species (Au *et al.* 1985, Carley *et al.* 1985 b).

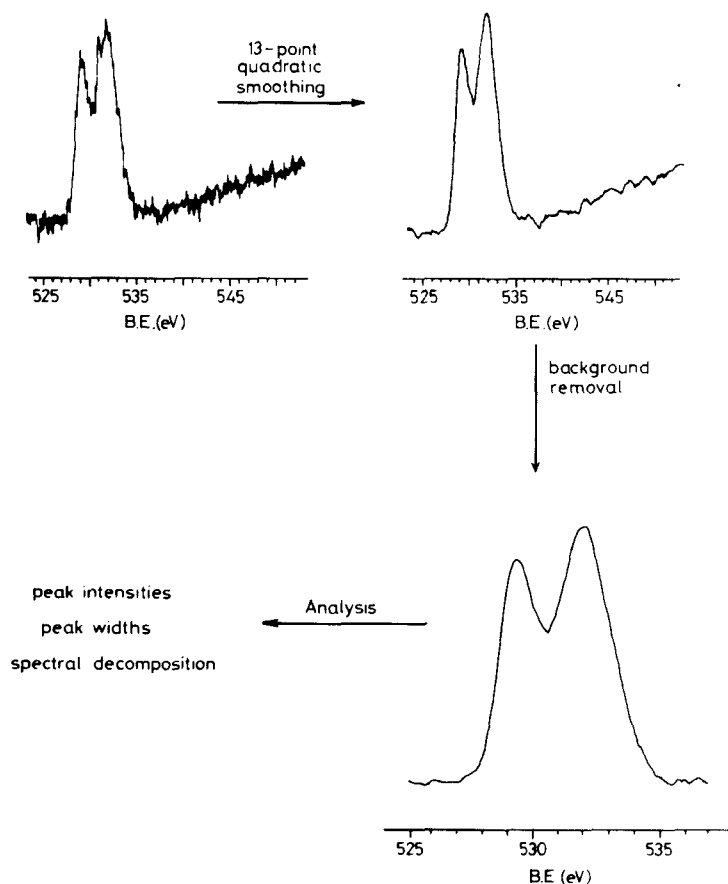


Figure 1. Data processing: the raw spectrum is smoothed according to the approach of Savitzky and Golay (1964), and the background due to inelastically scattered electrons removed using an iterative method (Shirley 1972). The resulting spectrum may then be integrated as a whole or resolved into separate components. The data used to illustrate the procedure is the O(1s) spectrum of Li-doped nickel oxide which is discussed later.

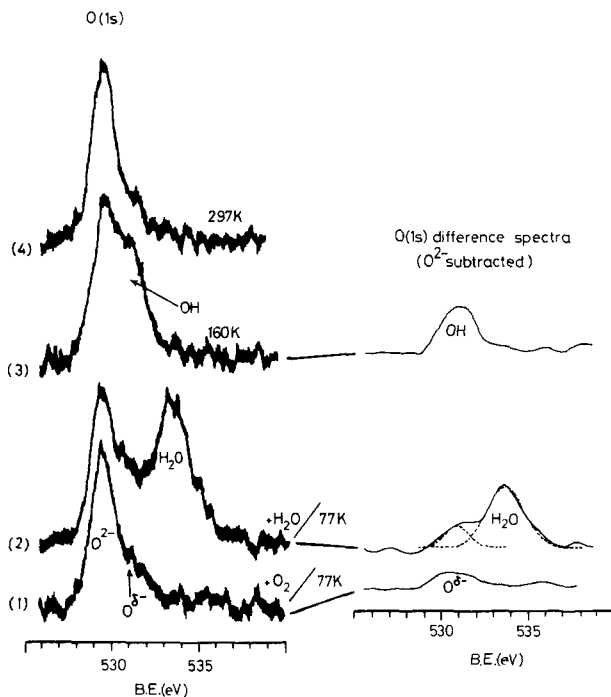


Figure 2. O(1s) spectra recorded for the physical adsorption of water vapour at 77 K at a lead surface pre-exposed to oxygen (150L) at 77 K, followed by warming to 297 K. Also shown are the O(1s) difference spectra, obtained from the raw data by subtraction of the O(1s) component of the oxide, O<sup>2-</sup>, species. The subtraction procedure shows that O<sup>δ-</sup>(a) species interact with H<sub>2</sub>O(a) to give OH(a) which is more stable than H<sub>2</sub>O(a) (Carley *et al.* 1983).

The basic approach used in the quantification of XPS data relevant to surface species is that based on equation (1) (Carley and Roberts 1978). It relates measured, normalized intensities from surface atoms to surface concentration

$$\sigma_m = (I_m \mu_s n_s \lambda_s \cos \phi) / I_s \mu_m \quad (1)$$

where  $\sigma_m$  is the surface concentration of the adspecies;

$\mu_m, \mu_s$  are the appropriate sub-shell photoionization cross-sections for the surface and substrate atoms respectively;

$n_s$  is the number density of the relevant atoms in the substrate;

$\lambda_s$  is the mean free path in the substrate material for photoelectrons from the substrate atoms;

$\phi$  is the angle between the surface normal and the direction of the entrance slit of the analyser;

$I_m, I_s$  are the detected intensities of the relevant core-level peaks from the surface species and clean substrate respectively, corrected for instrument transmission factors.

We have used this approach and have found that it gives consistently reliable values for surface concentrations. The accuracy of the method may be checked by applying it to a system where the surface concentrations are known from an independent technique. Thus, it is known that the physisorption of xenon at 80 K results in a

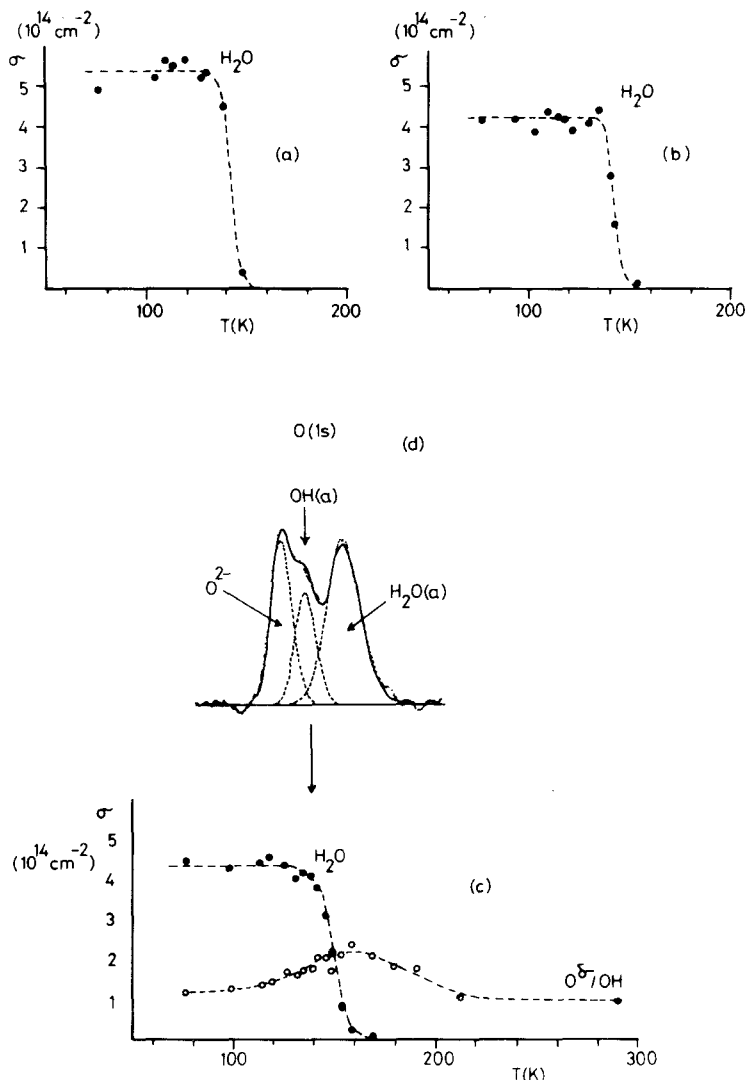


Figure 3. Surface concentrations of  $\text{H}_2\text{O(a)}$  and  $\text{OH(a)}$  species as a function of temperature for (a) clean Pb surface; (b) Pb surface exposed to oxygen at 295 K ( $\text{PbO}$  overlayer); (c) Pb surface exposed to oxygen at 77 K ( $\text{PbO-O}^{\delta-}$  (a)). In each case  $\text{H}_2\text{O(g)}$  was adsorbed at 77 K and the adlayer warmed to 295 K. The concentrations of  $\text{H}_2\text{O(a)}$  and  $\text{OH(a)}$  in (c) were obtained via a curve-fitting procedure: a typical curve-fitted  $\text{O}(1s)$  spectrum is also shown (d) (Carley *et al.* 1983).

hexagonal close-packed monolayer at saturation at a pressure of  $c. 10^{-6}$  torr. Knowing the cross-sectional area of the xenon adatom, the corresponding surface concentration may be deduced and compared with that calculated from equation (1) for data obtained from a xenon isotherm for Ni(210) at 80 K; the agreement is excellent (Rassias, unpublished work). For cases where an overlayer develops or penetration of the surface by adsorbed species occurs (as in metal oxidation), a correction for the attenuation for the emitted photoelectron must be made (Carley and Roberts 1978).



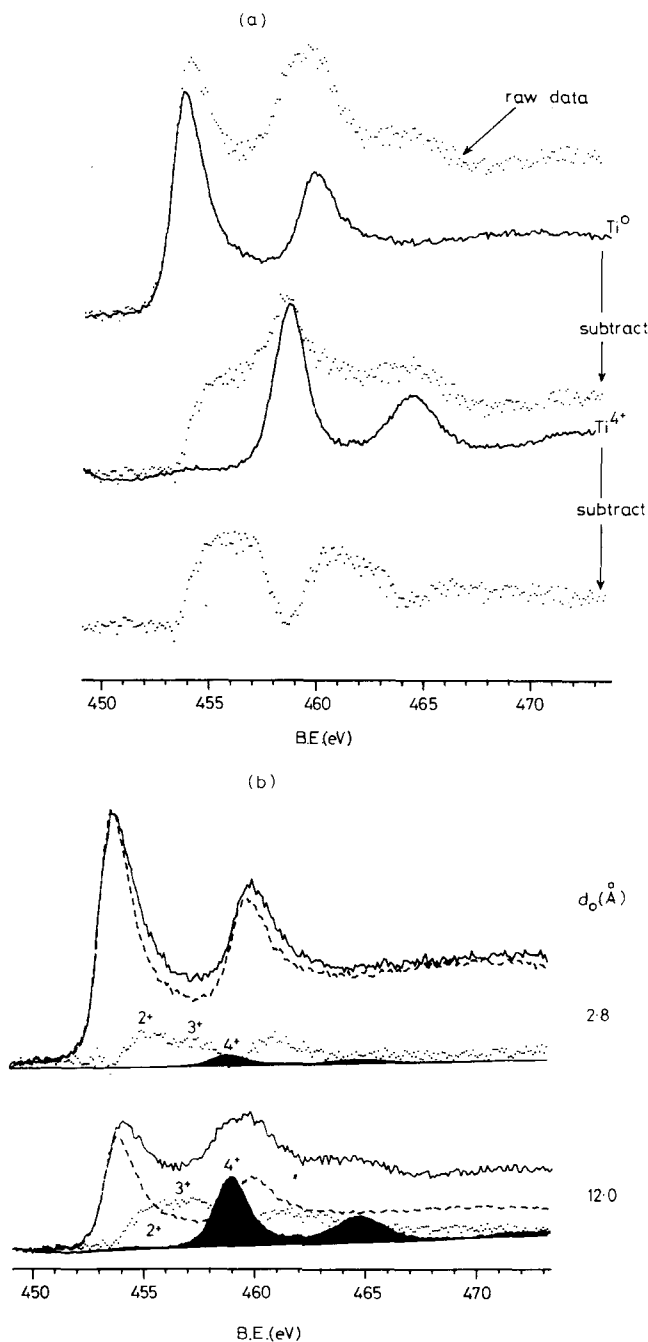


Figure 4. (a) An example of the spectral subtraction procedure. Model experimental Ti(2p) spectra for  $Ti^0$  and  $Ti^{4+}$  ( $TiO_2$ ) are subtracted sequentially, after suitable scaling and alignment, from the raw Ti(2p) spectrum observed when polycrystalline titanium is exposed to oxygen at 295 K. The resulting difference spectrum shows evidence for the two sub-oxides  $TiO$  and  $Ti_2O_3$ . (b) Decomposed Ti(2p) spectra for a titanium surface oxidized at 295 K to give an oxide thickness as indicated. The  $Ti^{2+}$  species dominates at low oxygen exposure but as the oxide thickens the  $Ti^{4+}$  becomes the majority species. Raw spectrum, —;  $Ti^0$  component, ---;  $Ti^{4+}$  component, shaded; derived difference spectrum, ... (Carley *et al.* 1985 a).

The various aspects of data analysis and quantification are best illustrated by considering a particular example. Some selected spectra from the lead–oxygen–water system were shown (figure 2) to illustrate spectral decomposition. A complete study of this system (Carley *et al.* 1983) involved the adsorption of water on clean lead, lead oxidized at 295 K when a PbO overlayer forms, and lead oxidized at 80 K; all water adsorptions occurred at 80 K. Subsequently the surface was warmed slowly to 295 K. The O(1s) spectrum for physisorbed water, peak at 533.5 eV, is sufficiently shifted from the O(1s) oxide peak at 529.4 eV for it to be easy to extract intensity data in those cases where there is no hydroxyl formation. The latter would result in intensity developing between these two species. Figures 3 (a) and (b) show the derived surface concentration of water molecules as a function of temperature for the adsorption of water on both a clean surface and in the presence of an oxide (PbO) overlayer. In both cases only physical adsorption occurs (at 80 K) and desorption is complete at 155 K.

By contrast, adsorption on lead oxidized at 80 K results in surface hydroxylation, and curve-fitting enables quantitative data to be extracted for the oxide, hydroxylated species and the molecular water (figure 3c). It should be noted that since the O(1s) spectra are quite noisy, individual curve-fits may be fairly inaccurate; however, the 'trend line' in the data plotted against temperature is very clear, illustrating the benefit of so-called 'dynamic' photoelectron spectroscopy where the quality of spectra is deliberately compromised in order to obtain extensive data as a function of other parameters such as temperature or exposure.

#### 4. Discrimination between surface species using XPS

The ability to assign components of an X-ray photoelectron spectrum unambiguously to particular adsorbed species is essential. Once the identifications have been made, the concentrations of the various adspecies may be quantified, ideally as a function of temperature, exposure and pressure. The fairly narrow range of binding energies exhibited by most core-level peaks leads frequently to degeneracy of assignments. The problem can sometimes be resolved by resorting to the difference in chemical reactivities of the various components of the adlayer. For example the O(1s) spectra of chemisorbed oxygen and surface hydroxyl species at a Cu(111) surface overlap (Au and Roberts 1980) but the species may be distinguished by their different reactivities to carbon monoxide, chemisorbed oxygen being reduced and desorbing as CO<sub>2</sub>(g) at 295 K. Another approach is to take advantage of differences in the heats of adsorption (strictly activation energies of desorption) and reflected in their thermal stability or ease of desorption. Although we have overwhelming evidence for the assignments of features in O(1s) spectra observed of water interaction with metal surfaces to the species O<sup>2-</sup>(a), OH(a) and H<sub>2</sub>O(a), recent studies with Mg(0001) surfaces have been supplemented by vibrational spectroscopy (Campbell *et al.* 1985), electron energy loss spectroscopy (HREELS) confirming the presence of OH(a) species and therefore removing any possible ambiguity between OH(a) and O<sup>-</sup>(a), based on XPS alone (figure 5). Analogous conclusions were reported (XPS and HREELS) for the activation of water by chemisorbed oxygen at platinum surfaces (Fisher and Sexton 1980).

Fingerprinting by XPS requires a data base of assignments, which can only be acquired by careful experimentation. We illustrate the experimental strategy for the development of an N(1s) data bank by discussing first some aspects of the interaction of nitric oxide with three different metals: aluminium (Carley and Roberts 1978), copper

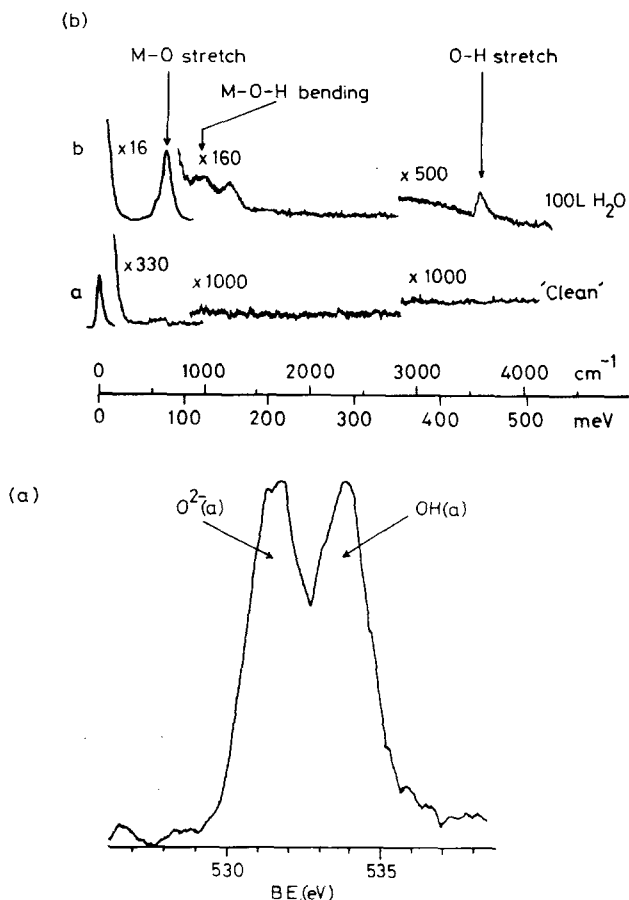


Figure 5. (a) O(1s) spectrum after exposing a Mg(0001) surface to water vapour (100L) at 295 K, showing peaks at 531.5 and 533.7 eV. From a study of the interaction of Mg(0001) with dry oxygen, the former is assigned to a surface oxide ( $O^{2-}$ ) species. The higher binding energy species is assigned to OH(a). (b) Analogous HREELS spectra show features due to adsorbed hydroxyl species. A peak indicative of an  $M-O^{2-}$  interaction is also present (Campbell *et al.* 1985).

(Johnson *et al.* 1979) and nickel (Carley *et al.* 1979). An aluminium surface chemisorbs nitric oxide at 295 K with the development of an O(1s) peak at 531.7 eV characteristic of surface oxide and an N(1s) peak at a binding energy of 397 eV (figure 6(a)). Dissociative chemisorption of NO occurs and the N(1s) feature is assigned to nitrogen adatoms, N(a). This is confirmed by studying the adsorption of atomic nitrogen at an aluminium surface which results in an N(1s) peak at the same binding energy, 397 eV. At 80 K the adsorption of nitric oxide is more complex, three N(1s) peaks being observed at binding energies of 397, 403 and 406.7 eV; the first peak is obviously due to the dissociation of nitric oxide which occurs even at 80 K. The other two peaks have binding energies similar to those of  $N_2O(a)$ , as observed in separate studies with a gold surface (figure 6(c)) but with an incorrect intensity ratio (i.e. not 1:1). In such a situation the way forward lies in perturbing the system and examining its response. This is achieved by warming the adlayer formed at 80 K and monitoring simultaneously the surface (with XPS) and gas-phase composition. Nitrous oxide was shown to be desorbed (mass

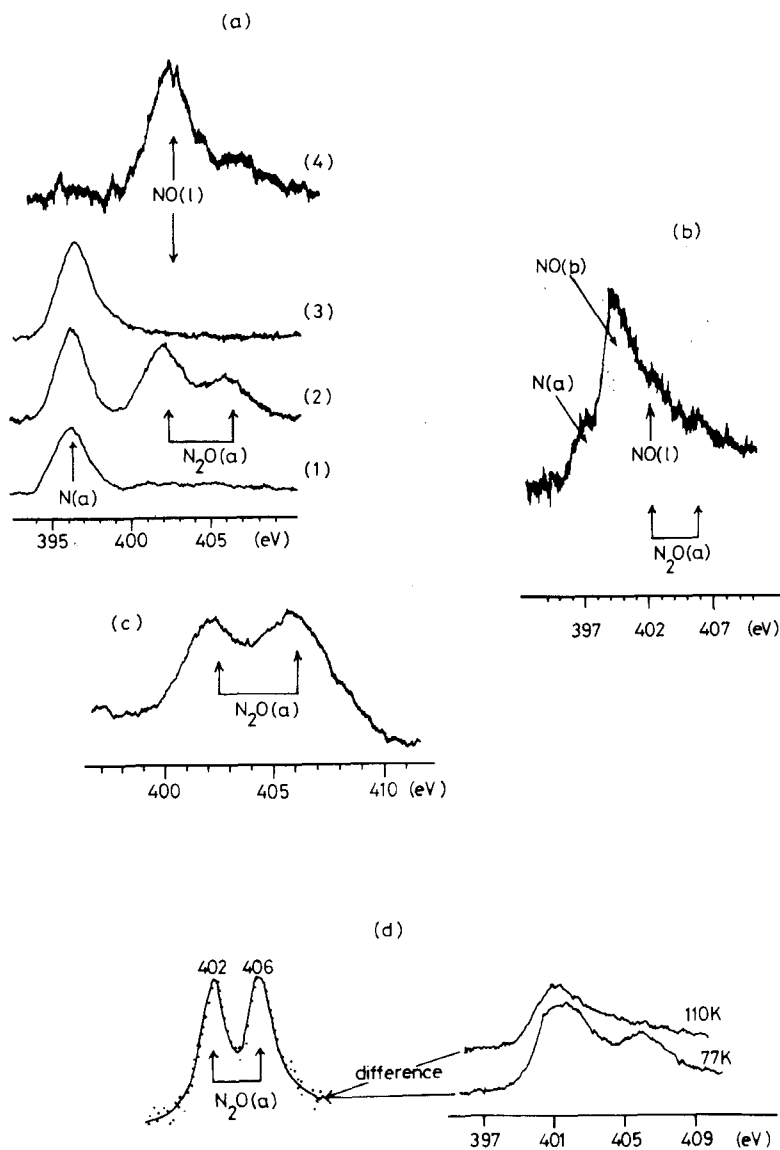


Figure 6. Representative N(1s) spectra for the chemisorption of nitric oxide at some metal surfaces illustrating the assignment of N(a), NO(l), NO(b) and N<sub>2</sub>O(a) species. (a) (1) Aluminium exposed to NO (25L) at 77 K showing dissociation of NO → N(a). (2) Aluminium exposed to NO (75L) at 77 K indicating the adsorption of NO(l) and the catalytic formation of N<sub>2</sub>O. (3) After warming (b) to 295 K; only N(a) remains. (4) Aluminium pre-exposed to H<sub>2</sub>O (240L) at 295 K, followed by exposure to NO ( $P=4 \times 10^{-6}$  Torr) at 77 K; only NO(l) is observed. (b) Nickel exposed to NO (1500L) at 77 K; the major surface species is NO(b), the strongly adsorbed precursor to dissociation N(a). (c) Physisorbed N<sub>2</sub>O on gold at 77 K. (d) (1) Cu(100) exposed to NO (24L) at 77 K. (2) After warming (1) to 110 K. (3) Spectral difference between (1) and (2), indicating the thermal desorption of N<sub>2</sub>O(g) between 77 and 110 K.

spectrometric analysis) at *c.* 85 K, and after warming to 295 K there is no trace of any spectral feature other than the peak at 397 eV due to N(a). We deduce that all of the 406.7 eV intensity and part of that at 403 eV is due to N<sub>2</sub>O(a): the remainder of the 403 eV peak is speculated to be due to a weakly bonded molecular species of nitric oxide. This is confirmed by exposing an aluminium surface, pre-treated with water vapour at 295 K, to nitric oxide at 80 K, when only the feature at 403 eV is observed (figure 6(a), spectrum 4). The pre-adsorption of water vapour inhibits all but the weakest of interactions. There are, therefore three states of nitric oxide present at the surface but most surprising is the catalytic generation of nitrous oxide within the adlayer at this temperature. Both kinetic and thermodynamic arguments would, at first sight, appear to be against the formation of N<sub>2</sub>O(a), the activation energy of the process being close to zero (occurs at 80 K) and its free energy of formation being more positive than NO(g).

Nitrous oxide was also generated at a Cu(111) surface exposed to nitric oxide at 80 K; in this case a spectral subtraction procedure was used to establish its formation (Johnson *et al.* 1978, 1979). After recording the N(1s) spectrum at 80 K the adlayer was warmed to 110 K and the N(1s) spectrum again recorded. The 'difference spectra', N(1s) and O(1s), indicated that warming the adlayer from 80 to 100 K resulted in the desorption of a molecule containing two distinguishable nitrogen atoms, and an oxygen 'atom'. Clearly, nitrous oxide had been generated catalytically at 80 K, the surface bonding was weak, and N<sub>2</sub>O desorbed between 80 and 110 K (figure 6(d)).

In the case of nickel, dissociative chemisorption of nitric oxide was inhibited at 80 K and a distinct molecular species with an N(1s) binding energy of 399.5 eV, a precursor to the dissociative state, was observed (figure 6(b)). This species dissociated on raising the temperature generating the N(1s) peak at 397 eV characteristic of nitrogen adatoms N(a). The 'precursor' is strongly chemisorbed and reactive, the activation energy for dissociation being no more than a few kilocalories. We assign it to a 'bent form' of chemisorbed nitric oxide, NO(b), to distinguish it from the more weakly adsorbed NO(l) state with an N(1s) binding energy of between 402 and 403 eV.

These observations provide, therefore, good evidence for the following N(1s) binding energy assignments:

	eV
N(a) ~	397
NO(b) ~	399.5
NO(l) ~	401–403
N <sub>2</sub> O(a) ~	402–403
	406–407

Independent evidence from XPS and IR studies of inorganic complexes, and theoretical estimates of N(1s) binding energies support the suggestion that NO(b) corresponds to a 'bent' configuration and that the NO(l) species is a linearly bonded molecule.

If XPS is to be useful for the study of surface reactions related to the mechanism of ammonia synthesis then a prerequisite is the ability to distinguish, through shifts in N(1s) binding energies, between the various chemisorbed hydrogenated nitrogen species, N, NH and NH<sub>2</sub>. The experimental approach is similar to that described for nitric oxide, and representative spectra are shown in figure 7. The binding energies are assigned as follows: N(a) ~ 396 eV; NH(a) ~ 398 eV; NH<sub>2</sub>(a) ~ 399 eV; and NH<sub>3</sub>(a) ~ 400 eV.

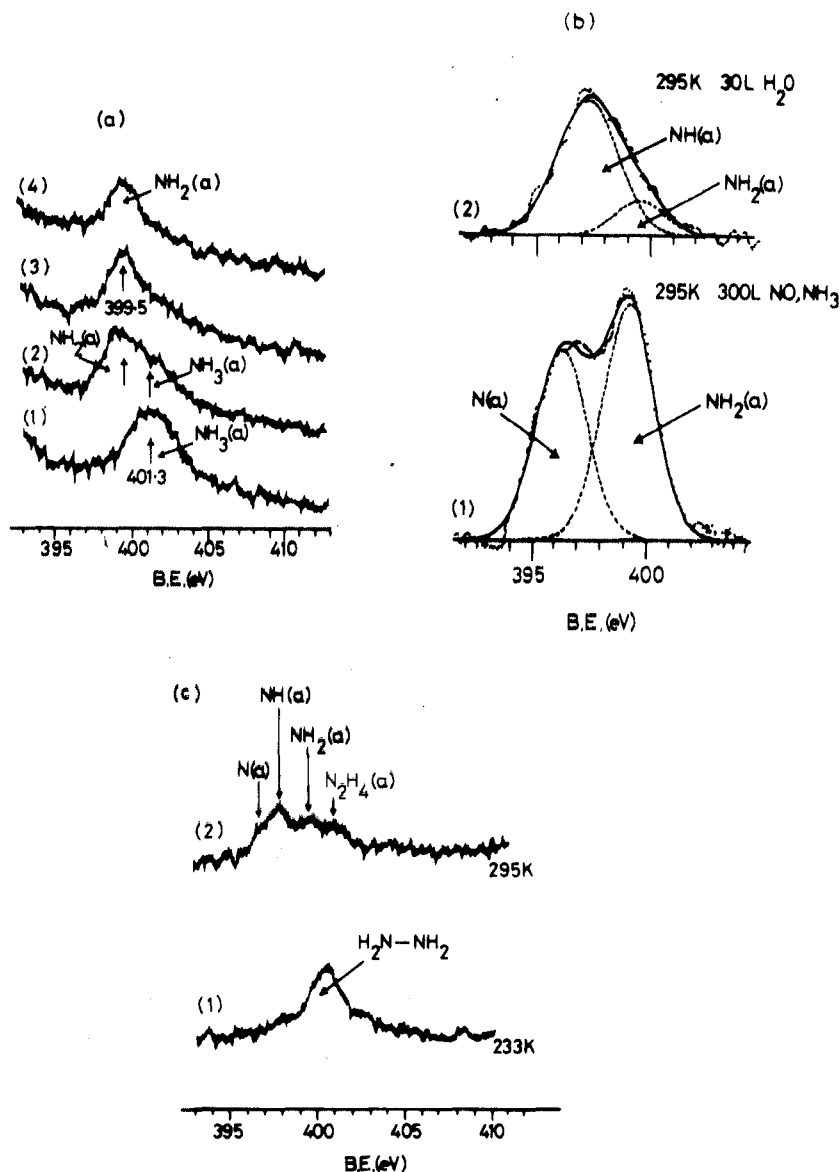
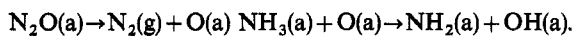
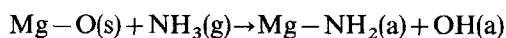
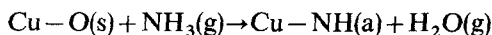


Figure 7. N(1s) spectra illustrating the assignment of  $\text{NH}_x$  species. (a) (1) Mg(0001) surface exposed to  $\text{NH}_3(\text{g})$  (30L) at 110 K. (2) Exposure of adlayer (1) to  $\text{N}_2\text{O}(\text{g})$  (60L) at 110 K, showing the development of intensity due to  $\text{NH}_2(\text{a})$  formed as follows:



(3), (4) After warming to 170 and 295 K respectively, showing the desorption of  $\text{NH}_3(\text{a})$ , and the presence of strongly chemisorbed  $\text{NH}_2(\text{a})$ . (See text for details.) (b) (1) Mg(0001) surface exposed to a mixture of  $\text{NO}(\text{g})$  and  $\text{NH}_3(\text{g})$  at 295 K; peaks due to  $\text{N}(\text{a})$  and  $\text{NH}_2(\text{a})$  are observed. (2) After exposure of (1) to water vapour at 295 K; hydrolysis of  $\text{NH}_2(\text{a})$  to  $\text{NH}_3(\text{g})$  and  $\text{N}(\text{a})$  to  $\text{NH}(\text{a})$  is observed (Au *et al.* 1985). (c) (1) Exposure of a polycrystalline iron film to hydrazine (90L) at 85 K followed by warming to 233 K; a single N(1s) peak due to  $\text{N}_2\text{H}_4(\text{a})$  is observed. (2) After exposure of (1) to 600L  $\text{N}_2\text{H}_4(\text{a})$  at 273 K followed by warming to 295 K; all the species  $\text{NH}_x(\text{a})$  for  $x=0, 1, 2$  and also  $\text{N}_2\text{H}_4(\text{a})$  are observed in this spectrum (Matloob and Roberts 1977).

An alternative strategy that has been successful for  $\text{NH}_x$  assignments for  $\text{N}(1s)$  spectra is to make use of chemisorption replacement reactions involving  $\text{NH}_3(\text{g})$  and chemisorbed oxygen at metal surfaces (Au and Roberts 1980). Specificity of the surface may result in either  $\text{NH}(\text{a})$  or  $\text{NH}_2(\text{a})$  being formed depending on the nature of the metal–oxygen interaction. For example with  $\text{Cu}(111)$  the preadsorbed oxygen is chemisorptively replaced with the formation of an imide species  $\text{NH}(\text{a})$  and water desorption while with  $\text{Mg}(0001)$  surfaces ammonia–oxygen coadsorption studies indicated the presence of surface amide  $\text{NH}_2(\text{a})$  and stable hydroxide species (Au *et al.* 1985). Aspects of this latter interaction are discussed in detail later.



Thus although fifteen years ago there was no data base available for the assignment of photoelectron spectra of surface species it is now possible, with some confidence, to recognize and differentiate between such closely related species as  $\text{OH}(\text{a})$  and  $\text{H}_2\text{O}$  and  $\text{N}(\text{a})$ ,  $\text{NH}(\text{a})$  and  $\text{NH}_2(\text{a})$ . It must be emphasized that in assigning peaks to specific surface species, use should be made of all possible experimental strategies; some of those used in this laboratory have been described. Furthermore the absolute binding energy of a given species may show small variations ( $\pm 0.2$  eV) depending on the nature of the substrate; it is, however, how the binding energies change in a progressive manner for related species with a given substrate that is more significant.

### 5. Molecular adsorbates: the control of incipient reactivity

It is not difficult to appreciate why contemporary thinking in heterogeneous catalysis is dominated by the chemistry of a few simple molecules: carbon monoxide, hydrogen, nitrogen, water, ammonia, nitric oxide and simple hydrocarbons. Each of these molecules has an obvious and key role in technologically significant processes: Fischer–Tropsch and methanol synthesis (carbon monoxide, hydrocarbons and water); ammonia (Haber–Bosch) synthesis (dinitrogen, hydrogen); and motor-exhaust catalysts and environmental chemistry (nitric oxide). If we are to understand the reactivity of these molecules ( $\text{N}_2$ ,  $\text{CO}$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ , and  $\text{C}_x\text{H}_y$ ), an essential prerequisite is to have precise information on possible chemisorbed states. Amongst the questions a surface chemist is likely to ask are the following: How is the carbon–oxygen bond perturbed when carbon monoxide is chemisorbed? Does the nitrogen–oxygen bond in chemisorbed nitric oxide behave in an analogous fashion? How facile is bond cleavage? What is the fate of the nitrogen and oxygen atomic fragments if and when the molecule dissociates? What trends are to be seen across the periodic table? How is the surface chemistry of the metal adsorbent perturbed as a consequence of dissociative chemisorption? Does the adsorption state of one molecule confer unique reactivity to the surface (promoter or poison) particularly when coadsorbed with a second different molecule?—in other words, How does the nature of the *reactants* control the reactivity of the surface?

Answers to these questions can be ascertained only by first making careful and detailed studies of the adsorption of the individual (inherently simple) molecules, followed by a logical progression to more complex systems involving both coadsorbed molecules and modified surfaces. We shall see that for many adsorbates bond cleavage at ‘clean’ metal surfaces is an energetically facile process, so that there are distinct

advantages in monitoring spectra over a range of temperatures starting at very low temperatures (80 K). Furthermore, in view of the longer lifetime of intermediates at low temperature, they have been observed by PES; at higher temperatures the intermediates would have been too reactive to be identified spectroscopically. In this way we have built up a picture of likely molecular events relevant to 'real catalysis'. The approach should be seen as complementary to the various kinetic approaches, such as temperature programmed desorption, used successfully by, for example, Madix (1980).

During the 1950s and 60s two particular molecules, carbon monoxide and dinitrogen, were accorded more attention than other by surface chemists. Elegant studies by Ehrlich (kinetic: flash desorption or temperature programmed desorption) backed up by various isotopic studies led to the view that carbon monoxide was molecularly adsorbed whereas dinitrogen was dissociatively chemisorbed at tungsten surfaces (Ehrlich 1964). That carbon monoxide was the archetype of molecular chemisorption received further support from the pioneering infrared studies of Eischens and Pliskin (1958) although these authors did add some notes of caution regarding this straightforward interpretation.

In designing an ultra-high vacuum photoelectron spectrometer, which had both valence and core-level spectroscopies, we had very much in mind the potential of photoelectron spectroscopy for being able to discriminate between associative and dissociative states of chemisorbed molecules. There were aspects of carbon monoxide chemistry (including mechanisms of Fischer-Tropsch catalysis) that relied on CO-dissociation as an essential step (Smutek and Cerny 1983). How did this fit in with the plethora of kinetic studies where the chemisorption of carbon monoxide was interpreted as molecular? Figure 8 shows the relationship between O(1s) electron binding energies observed when carbon monoxide was adsorbed on a number of metals in the temperature range 80–295 K as a function of their heats of adsorption (Joyner and Roberts 1974, Roberts 1980). The O(1s) binding energies decreased as the heat of adsorption increased. Furthermore to the left of the vertical line; the corresponding helium induced (valence level) spectrum exhibited peaks which could be assigned to the  $5\sigma$ ,  $1\pi$  (degenerate) and  $4\sigma$  orbitals. To the right of the vertical line evidence for these orbitals was absent and the O(1s) binding energy was close to, and invariant at, about  $530 \pm 0.2$  eV. C(1s) binding energies vary in a similar way with the heat of adsorption of carbon monoxide. Since there is a good correlation between electron binding energy and the electronic charge on the atom (the lower the binding energy the greater the charge) we have a direct measure of the electron density on the oxygen atom. As the metal-carbon monoxide bond becomes stronger, back bonding from the metal increases, the carbon-oxygen bond weakens until, for a heat of adsorption greater than about  $250 \text{ kJ mole}^{-1}$ , dissociation of the carbon monoxide occurs. Clearly this value is temperature dependent and the correlation should be seen as only a guide to the prediction of the state of chemisorbed carbon monoxide at metal surfaces (figure 8). Qualitatively one can, therefore, understand why dissociation of CO is more facile at step (higher heat of adsorption) rather than terrace sites and why surface additives (such as sulphur) inhibit the dissociation of CO by withdrawing electrons from the metal resulting in a lower heat of CO chemisorption and therefore weaker surface bond (Kishi and Roberts 1975). The detailed dynamics of the process of dissociation have yet to be delineated; presumably with increasing back bonding the CO molecule tilts over resulting in oxygen-metal interaction. In the case of nitric oxide, good evidence (figure 6) is available for the tilted NO being the precursor to dissociation (Carley *et al.* 1979).



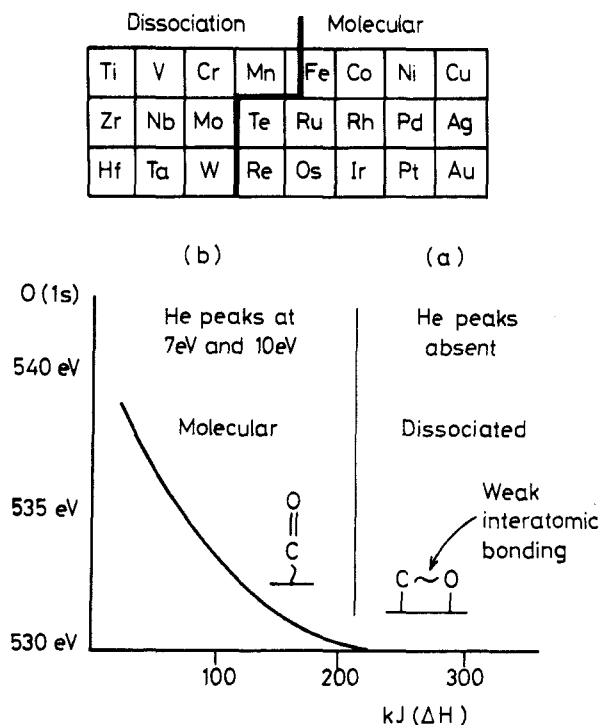


Figure 8. (a) Reactivity pattern for CO interaction with metal surfaces. (b) Correlation between the spectroscopic and thermodynamic properties of adsorbed CO. The binding energy of the O(1s) peak is invariant, at 530 eV, for heats of adsorption greater than 260 kJ mol<sup>-1</sup>. This value is typical ( $\pm 0.3$  eV) of chemisorbed oxygen adatoms on transition metals. He-induced peaks at about 7 and 10 eV below the Fermi level are characteristic of the ( $5\sigma + 1\pi$ ) and  $4\sigma$  orbitals respectively of chemisorbed CO in the molecular form (Roberts 1977).

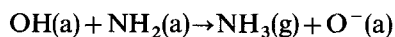
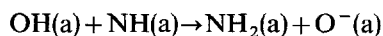
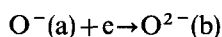
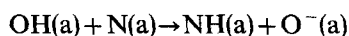
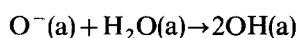
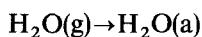
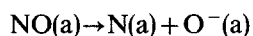
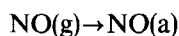
An alternative approach to monitoring O(1s) binding energies for predicting the chemistry associated with CO adsorption is that due to Rhodin *et al.* 1985, following Broden *et al.* (1976). They have used the separation in energy between the  $1\pi$  and  $4\sigma$  orbitals,  $\Delta E(1\pi-4\sigma)$ , as a guide to the stretching of the carbon-oxygen bond and therefore the susceptibility of the adsorbed CO to dissociation. A definite correlation exists (figure 8) between the chemisorption behaviour, i.e. whether or not CO chemisorption is dissociative, and the ability of metals to stretch or activate the carbon-oxygen bond as reflected by the O(1s) and the valence-level (helium-induced) spectra. In general the Blyholder model is useful and predictive but as emphasized by Rhodin *et al.* (1985) the possible significance of other electron interactions such as orbital relaxation, orbital interactions etc. need to be incorporated into the hypothesis of 'bond stretching' arising just from the donor-acceptor mechanism.

In heterogeneous catalysis it is important to understand the reasons for the activity and selectivity of the catalyst under 'working conditions'. The molecular events occurring when all the reactants are present must be delineated and with this in mind we investigated not only the influence of preadsorbed species (poisons and promoters) on chemical reactivity but also the possible synergistic chemistry associated with coadsorbed molecules (Au *et al.* 1985). Having established that activation of adsorbates by surface oxygen was a widespread phenomenon and with good background

knowledge of the surface chemistry of diatomics (nitric oxide, carbon monoxide etc.) studies of molecular events associated with coadsorption were initiated. The most thoroughly studied systems are those involving nitric oxide, ammonia and water vapour with substrates which, in the atomically clean state, and under the experimental conditions used, are relatively unreactive to one of the two different molecules in the coadsorption experiment. The aim of these studies is to explore to what extent the reaction pathway followed can be influenced by the presence of a second, different molecule. Thermodynamic calculations may indeed suggest that a particular reaction pathway is unlikely or it may well be that experimental studies have established that one of the reactant molecules is not chemisorbed (unreactive) at the surface of the catalyst so that its potential catalytic activity is low. However, both these conclusions may be misleading for systems involving coadsorbed molecules, reaction pathways being followed which may be both thermodynamically unlikely and also ruled out on the basis of knowledge of the kinetic reactivity of the individual molecules at the catalyst surface.

Although nitric oxide is dissociatively chemisorbed at Zn(0001) surfaces to give a stable Zn–N bond, in the presence of water vapour (itself unreactive at the Zn(0001) surface under the same conditions) hydrogenated nitrogen species  $\text{NH}_x$  are formed (Au and Roberts 1984 b). The activation energies of the steps involved (see below) are all relatively small since hydrogenation is rapid in the temperature range 200–300 K. The reactivity is induced by the chemisorbed oxygen (resulting from NO dissociation) activating the otherwise unreactive water molecule generating surface hydroxyl species which then participate in a hydrogen transfer reaction leading to hydrogenation of the Zn–N bond. The reaction is eventually poisoned when the concentration of surface oxide,  $\text{O}^{2-}(\text{b})$ , increases to the point at which nitric oxide dissociation is inhibited. The ‘oxygen’ has, therefore, a dual role acting as both a promotor and a poison.

The individual steps involved are as follows:



Confidence in the assignments of spectral features enabling distinctions to be made between, for example,  $\text{H}_2\text{O}(\text{a})$ ,  $\text{OH}(\text{a})$ ,  $\text{O}^-(\text{a})$  and  $\text{O}^{2-}(\text{b})$  or  $\text{NH}(\text{a})$ ,  $\text{NH}_2(\text{a})$  and  $\text{N}(\text{a})$  was possible only after detailed studies of other related systems e.g. Zn(0001)– $\text{H}_2\text{O}(\text{g})$ , Zn(0001)– $\text{O}_2(\text{g})$ ; Zn(0001)– $\text{NH}_3$ . XPS spectra were always supplemented by UPS data and appropriate difference spectra generated from both X-ray and UV-induced spectra (Au *et al.* 1982, Au and Roberts 1984 b). These conclusions are obviously of significance to the mechanism of motor-exhaust catalysts and draw attention to an alternative pathway for ammonia formation to that involving the isocyanate NCO intermediate (Unland 1973, Dalla Betta and Shelef 1976).

Analogous phenomena occur in the activation of N-H bonds in ammonia when coadsorbed with nitric oxide at Mg(0001) surfaces at 295 K (Au *et al.* 1985). Recently we have extended the studies of N-H bond activation in ammonia by nitric oxide to both oxygen and nitrous oxide over the temperature range 80 to 295 K. We report here the N(1s) and O(1s) spectra for the nitrous oxide induced activation of adsorbed (molecular) ammonia (figure 9). The interaction of  $N_2O(g)$  with a Mg(0001) surface involves the following steps, the evidence for

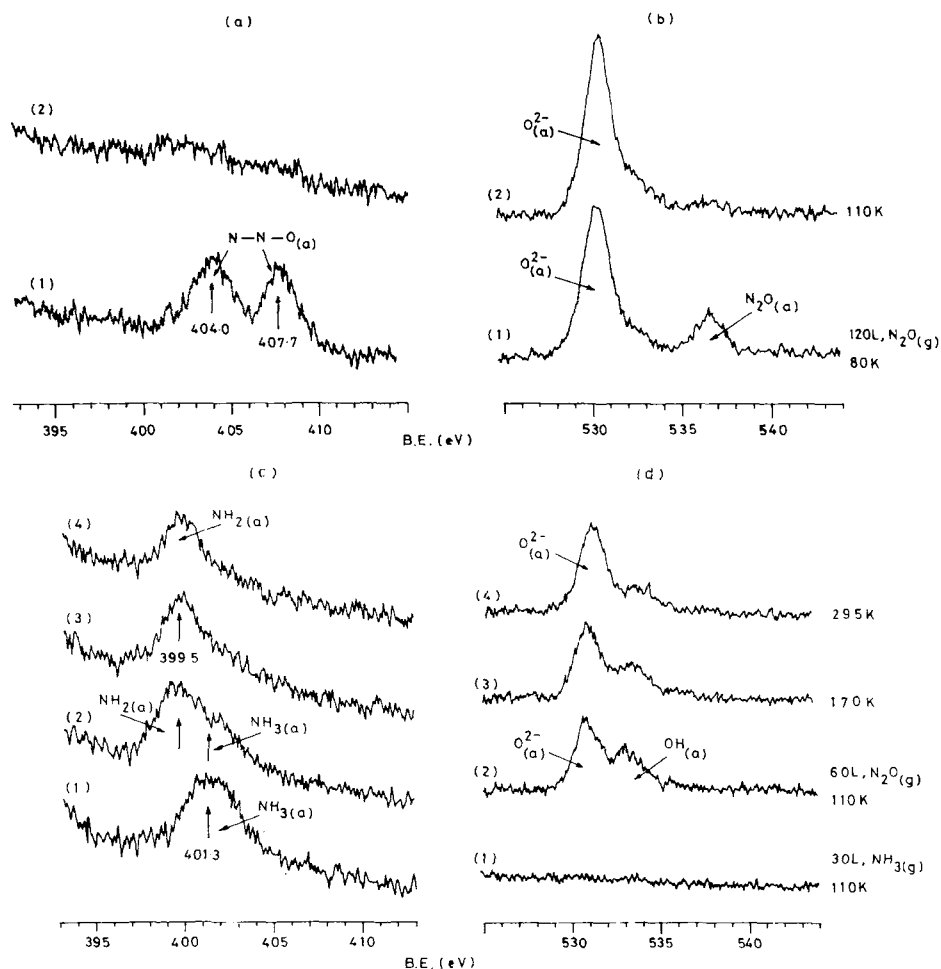
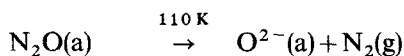
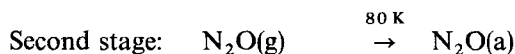
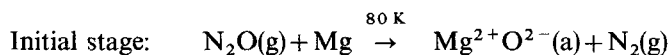
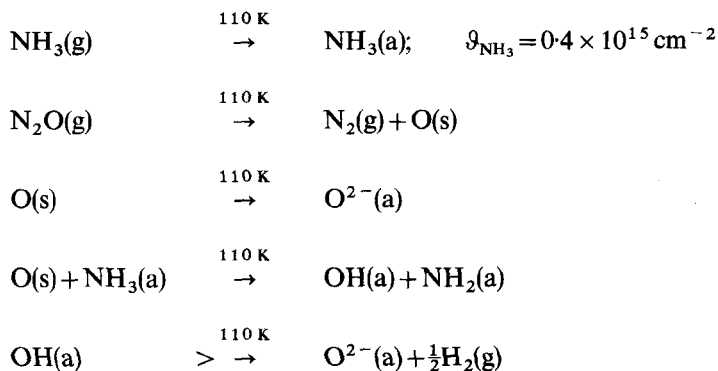


Figure 9(a), (b). N(1s) and O(1s) spectra for Mg(0001) surface exposed to  $N_2O(g)$  ( $10^{-6}$  torr) at 80 K followed by warming the adlayer to 110 K. (c), (d). N(1s) and O(1s) spectra for Mg(0001) surface exposed to  $NH_3(g)$  ( $10^{-6}$  Torr) at 110 K for 30 s (1) and then to  $N_2O(g)$  ( $10^{-6}$  Torr) for 60 s (2) followed by warming to 170 K (3) and 295 K (4).

which can be deduced from a study of the Mg(1s), O(1s) and N(1s) spectra (figure 9); in the Mg(1s) spectra (not shown) a distinct shift in the binding energy occurs corresponding to the generation of  $\text{Mg}^{2+}$ . The coadsorption study involved first the adsorption of ammonia at 110 K followed by nitrous oxide at the same temperature. Ammonia interacts only weakly with Mg(0001) surfaces at 100 K and desorbs at 170 K. It is obvious (figures 7 and 9) that the single N(1s) peak at 401.3 eV due to molecularly adsorbed ammonia splits into two components, a new peak emerging at 399.5 eV. The O(1s) spectrum indicates both oxide ( $\text{O}^{2-}$ ) and hydroxide species. At 170 K ammonia,  $\text{NH}_3(\text{a})$ , desorbs and only a single peak at a bonding energy of 399.5 eV is present. This is assigned to  $\text{NH}_2(\text{a})$ . Above 170 K dehydroxylation occurs with a simultaneous increase in the oxide concentration (figure 9, O(1s) spectrum). The following summarizes the individual steps:



Thus although studies of the reactivity of ammonia with both atomically clean Mg(0001), and in the presence of an oxide overlayer, would not suggest that surface amide species  $\text{NH}_2(\text{a})$  would be generated when ammonia and nitrous oxide were coadsorbed at low temperature (110 K), activation of N-H bonds is facile and the  $\text{NH}_2$  species is strongly chemisorbed. Ammonia may, therefore, be regarded as an 'interceptor molecule' in that it influences the particular reaction pathway chosen by the coadsorbed system. Rather than the oxygen formed in the dissociation of  $\text{N}_2\text{O}(\text{a})$  following pathway 1 (see scheme, figure 10), it can also follow a different channel, pathway 2. The efficiency of ammonia in rerouting the reaction along pathway 2 is clearly high, quantitative analysis of the spectra (Au and Roberts, to be published) indicating that 30% of the 'oxygen' participates in amide formation. The chemical specificity of the oxygen is emphasized in that the oxide ( $\text{O}^{2-}$ ) overlayer is unreactive to ammonia. Activation of  $\text{NH}_3(\text{a})$  by  $\text{N}_2\text{O}(\text{g})$  is similar in that they both generate  $\text{NH}_2(\text{a})$  provided they are coadsorbed, the 'active oxygen species' being generated during dissociative chemisorption. The 'active species' are certainly not in their thermodynamically stable oxide,  $\text{O}^{2-}(\text{a})$ , state and the reaction channel chosen is specific and dependent on the efficiency of ammonia 'intercepting' the active oxygen, O(s), species. There may of course be alternative methods of generating the 'active oxygen' species (lasers, discharges etc.) so that unlikely reaction pathways, with (relatively) unfavourable thermodynamics, can compete successfully with routes which at first sight, that is, with no knowledge of the molecular events involved, would be considered to be most probable. Quantitative analysis of the N(1s) and O(1s) spectra using equation (1) enables the surface concentrations of all the species  $\text{NH}_3(\text{a})$ ,  $\text{N}_2\text{O}(\text{a})$ ,  $\text{NH}_2(\text{a})$ ,  $\text{OH}(\text{a})$  and  $\text{O}^{2-}(\text{a})$  involved to be calculated. The concentrations of surface hydroxyls formed at

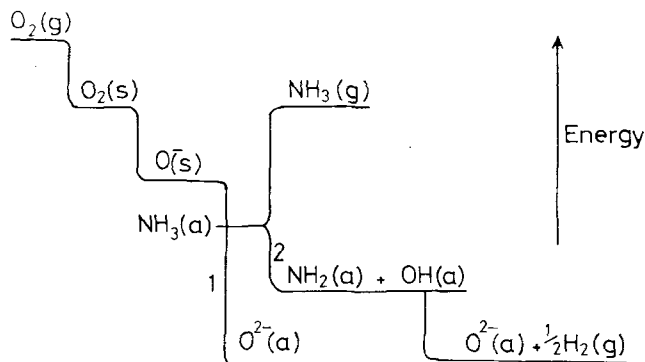
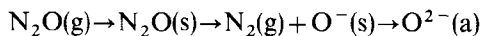
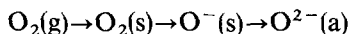


Figure 10. Schematic representation of reaction pathways in the coadsorption of 'oxygen' ( $N_2O$ ,  $NO$ , or  $O_2$ ) and ammonia: pathway 2 is an important route in spite of  $NH_3$  being only weakly adsorbed at a  $Mg(0001)$  surface (desorbs at 170 K). It is also of significance that an oxide overlayer at  $Mg(0001)$  is relatively unreactive to ammonia at 295 K. Bulk  $MgO$  samples are also unreactive to ammonia under these conditions (<10% of a monolayer) as indicated by infrared spectroscopy (Coluccia *et al.* 1983, Tench and Giles 1972, Zechina and Spoto 1985).

110 K is about  $0.3 \times 10^{15} \text{ cm}^{-2}$  which is identical with the  $NH_2(a)$  concentration, suggesting that the important step in the formation of surface amide species is  $O(s) + NH_3(a) \rightarrow OH(a) + NH_2(a)$ . Furthermore, there is good evidence to suggest that the active species is  $O^-(s)$  formed at the  $Mg(0001)$  surface in the sequence (see below),  $O^{2-}(a)$



being known to be inactive. However, since activation was also observed by dioxygen it is important to consider whether or not the species  $O^-(s)$  is also likely to exist as a surface intermediate in metal oxidation. We consider briefly the experimental evidence, mainly from our PES studies, for the sequence (see below)

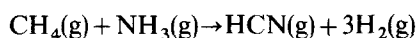


In the oxidation of  $Zn(0001)$ , although the formation of  $O^{2-}(a)$ , with an  $O(1s)$  value of 530 eV, is initially a fast process at 77 K, with increasing oxygen coverage evidence for a second oxygen species,  $O^-(s)$ , emerges with an  $O(1s)$  peak at 532 eV. Clearly, in this case the  $O^-(s)$  can be isolated due to the step  $O^-(s) \rightarrow O^{2-}(a)$  becoming activated. On increasing the temperature, further transformation to  $O^{2-}(a)$  occurs (Au and Roberts 1984 b, Au *et al.* 1982). That a weakly adsorbed oxygen precursor  $O_2(s)$  can participate in metal oxidation was evident from kinetic (XPS) studies with aluminium (Carley and Roberts 1978), oxidation being faster at 77 K than at 295 K. Furthermore, recent studies by Shayegan *et al.* (1984) have provided direct experimental evidence at 5 K for a molecular precursor state with an activation energy of 13 meV for dissociation at a  $Ni(111)$  surface. Each of the steps in the above sequence  $O_2(g) \rightarrow O^{2-}(a)$  has, therefore, been isolated although the energetics of the individual steps will vary with the metal. The evidence is, therefore, strongly in favour of  $O^-(s)$  as the active species in molecule activation at a  $Mg(0001)$  surface by both dioxygen and nitrous oxide.

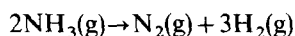
Although we have reported previously (Au *et al.* 1985) that surface amide species are generated by the coadsorption of ammonia and nitric oxide, the  $N(1s)$  and  $O(1s)$  spectra

were recorded after a 'single shot' exposure to a  $\text{NH}_3(\text{g})/\text{NO}(\text{g})$  mixture at one temperature (295 K). The present investigation is, by contrast, a dynamic study over a wide temperature range where the individual molecular events are delineated (figure 9). Activation is clearly not confined to nitric oxide but also occurs with dioxygen and nitrous oxide; furthermore, in contrast to the 'single shot' experiment, dynamic studies emphasize the difference in reactivity between  $\text{O}^{2-}(\text{a})$  and  $\text{O}^-(\text{s})$ . The advantages of spectral analysis, including the derivation of surface concentrations of *all the participating species*, is seen to be an important aspect of establishing reaction mechanisms. In this respect PES is unique.

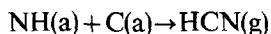
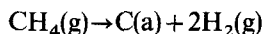
A particularly good example of the concepts discussed above, and illustrated by the coadsorption studies, is the industrially important Degussa process which occurs with 90% yield at a platinum surface at 1500 K. In the presence of



oxygen (the Andrussov reaction) the yield is about 70%. Now, the formation of HCN is obviously in competition with ammonia decomposition



and, in the presence of oxygen, with both ammonia and methane oxidations. Since methane is generally unreactive (very low sticking probabilities,  $\sim 10^{-4}$ ) at noble metal surfaces, its reaction with ammonia is, at first sight, unlikely. Furthermore both ammonia and methane decomposition ( $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ ) are more thermodynamically favoured than the HCN reaction. What, therefore, is the fundamental reason for the high yield of HCN in the Degussa process? Hasenberg and Schmidt (1985) have discussed this and concluded that although  $\text{CH}_4$  and  $\text{NH}_3$  must dissociate, neither  $\text{N}_2(\text{g})$  nor graphite must form to any appreciable extent. Carbon is therefore seen to be both a reactant and a poison; it inhibits ammonia adsorption (and therefore decomposition) but reacts with surface nitrogen to form HCN. Although no direct evidence is available the most likely important steps are suggested by Hasenberg and Schmidt (1985) to be:



The role of carbon is, therefore, seen to have very strong similarities to 'oxygen promoted' reactions discussed in the coadsorption experiments (figure 9) and also those involving ammonia, nitric oxide and water vapour (Au and Roberts 1984 b, Au *et al.* 1985). It is the coverages of the various species under synthesis conditions that are relevant and in the case of the Degussa process it is important to be able to reroute the 'carbon' along the HCN channel and prevent it increasing in surface concentration and becoming a poison for the dehydrogenation of ammonia and therefore of the reaction. The same arguments have been put forward (Au and Roberts 1985 b) for the role of water vapour in the hydrogenation of nitric oxide at  $\text{Zn}(0001)$  surfaces where surface 'oxygen' has been shown to act as both a promoter (of water dissociation) and also an inhibitor (of nitric oxide dissociation).

## 6. Metal oxidation, mixed-valence states and surface reactivity

### 6.1. Metal oxidation and mixed valence states

The transformation of chemisorbed oxygen at a metal surface to an oxide overlayer leading to subsequent growth has received considerable attention, the problem being first given an atomistic framework by the theory of Mott and Cabrera (1948). In addition to the intrinsic interest in obtaining information at the atomic level for the mechanism of metal oxidation there is a need to define precisely the nature of the species in an oxide overlayer, an aspect that has not yielded easily to experimental inquiry. We have particularly in mind direct experimental evidence for surface non-stoichiometry including mixed-valence states and also evidence for different oxygen species. In the context of surface reactivity, relating such evidence to chemical specificity, as for example in the selective oxidation of hydrocarbons, or the photoassociated catalytic decomposition of water at oxide surfaces, is the ultimate aim of any mechanism in heterogeneous catalysis. All too frequently the vital link is missing.

One of the most extensively studied oxide systems in the forms both of an oxide overlayer at a metal surface and as a bulk oxide is that of nickel. Wandelt (1982) has recently reviewed the topic of oxygen chemisorption and oxidation, while studies of the bulk defect character of nickel oxides have been well documented. By having recourse to the classical ideas of the defect chemistry of bulk nickel oxide and being intrigued by the interesting catalytic chemistry of some forms of nickel oxide, in particular nickel 'peroxide', a programme of research was initiated which aimed at bridging nickel single crystal and bulk nickel oxide surface chemistry (Moroney *et al.* 1983, Roberts and Smart 1981, 1984, Carley *et al.* 1985 a). Some of the important conclusions that emerged from these studies in relation to the possibility that nickel 'oxides' could exhibit both  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  species in the surface region are illustrated in figure 11. We conclude that  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  are characterized by intensities at 854.5 and 856 eV in the Ni(2p) spectral region; furthermore, angular-dependent data suggest that  $\text{Ni}^{3+}$  is at the surface relative to  $\text{Ni}^{2+}$ . The relative proportions of the two oxidation states depend on both the conditions used in oxide preparation and also its pre-treatment. Dynamic photoelectron spectroscopy was used whenever possible so that the changes observed in the spectra could be related to the chemistry taking place. In addition to monitoring the Ni(2p) spectra evidence was obtained from O(1s) studies of the presence of two oxygen species, one designated  $\text{O}^{2-}$ , with a binding energy usually at about 530 eV, and a second,  $\text{O}^-$ , which had a binding energy of about 531.5 eV. There is a strong correlation between the intensities at 856 eV ( $\text{Ni}^{3+}$ ) and 531.5 eV ( $\text{O}^-$ ). Although  $\text{Ni}^{3+}$  species were suggested some 20 years ago to be present in thin oxide overlayers at nickel surfaces, on the basis of work-function studies (Quinn and Roberts 1963), Ni(2p) spectra observed after exposure of nickel to oxygen did not reveal, in their raw form, any intensity which could be assigned uniquely to  $\text{Ni}^{3+}$ . It was only after recent developments in data processing that the question was reopened, although there was considerable circumstantial evidence that both  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  could be present at 'oxidized' nickel surfaces.

As to both bulk oxide surfaces and oxide overlayers ( $\sim 10 \text{ \AA}$ ) present at nickel single crystals, we suggest that they represent essentially redox systems with defect concentrations which have little, if any, relation to the defect concentrations in bulk oxides. Furthermore, their concentrations will depend on both the nature of the reactants in a catalytic reaction and on the temperature. Although in the case of nickel 'oxide' surfaces quantification of O(1s) and Ni(2p) spectra suggest that, in general, there is always excess oxygen present within the surface region (Carley *et al.* 1985 a), in the

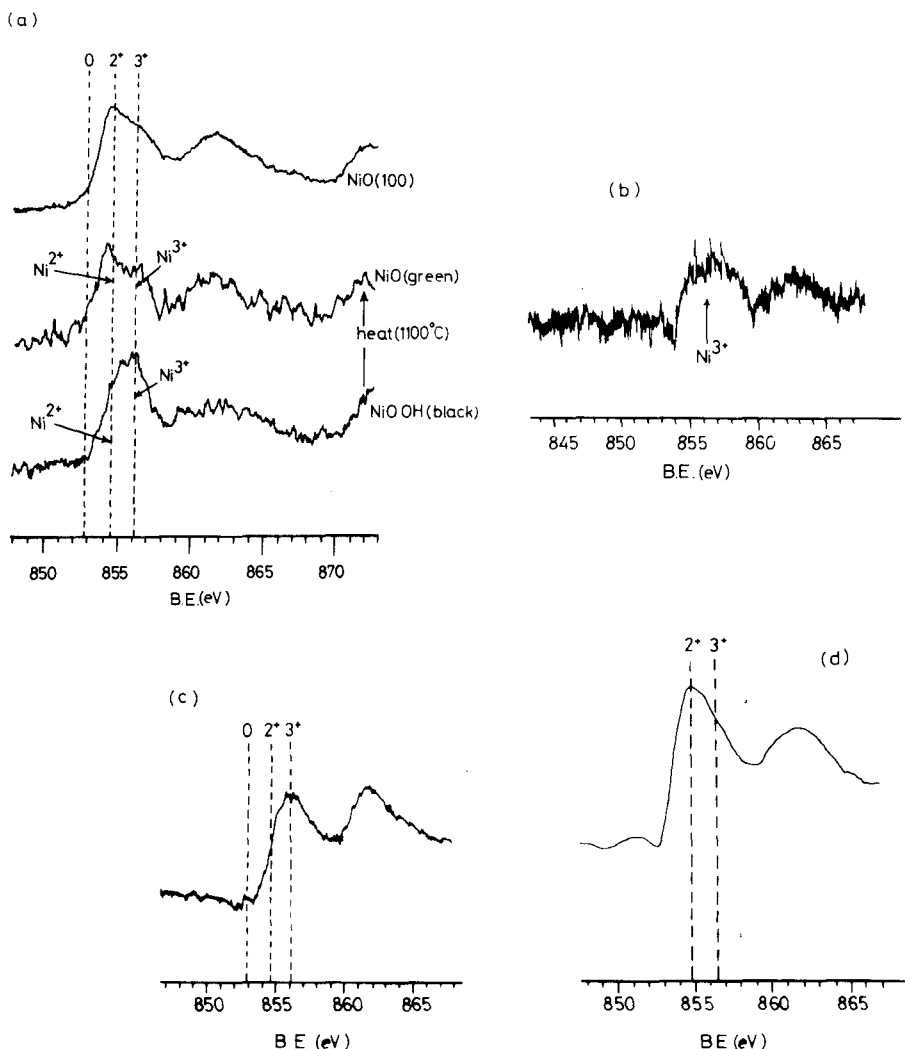


Figure 11. Ni(2p) spectra illustrating the assignment of features due to Ni<sup>2+</sup> and Ni<sup>3+</sup>. (a) (1) nickel oxyhydroxide, NiOOH (nickel 'peroxide'); (2) after heating (1) to 1100°C in air to give green 'NiO'; (3) single crystal NiO(100) after 'cleaning' and annealing *in vacuo*. (b) Ni(2p) difference spectrum showing the development of intensity due to Ni<sup>3+</sup> after warming to 295 K a Ni(100) surface exposed to oxygen and water vapour at 77 K. (c) Ni(2p) difference spectrum, after subtraction of the Ni<sup>0</sup> component, obtained after exposing a Ni(210) surface to oxygen at 80 K and warming the adlayer to 295 K; a 'pure Ni<sup>3+</sup> spectrum' is generated. (d) Ni(2p) difference spectrum (Ni<sup>0</sup> removed) for a Ni(100) surface exposed to oxygen at 295 K; note the dominant Ni<sup>2+</sup> component. The peak at ~6 eV higher binding energy than the parent photoelectron signal is a satellite peak (Carley *et al.* 1985a).

interaction of oxygen with aluminium the surface stoichiometry is close to AlO (Carley and Roberts, unpublished) and certainly oxygen deficient (or metal rich) compared with Al<sub>2</sub>O<sub>3</sub>. Detailed studies of oxygen interaction with titanium (figure 4) suggest that the early stages of oxide growth involve the suboxides TiO and Ti<sub>2</sub>O<sub>3</sub>, both metal rich relative to TiO<sub>2</sub>. These conclusions are based on the emergence of well defined Ti(2p) peaks in carefully obtained difference spectra (figure 4). They have binding energies of



455.5 and 457 eV, i.e. not only significantly different from  $\text{TiO}_2$  (458.5 eV), which becomes the predominant oxide species as the layer thickens, but also similar to the values reported for bulk  $\text{TiO}$  and  $\text{Ti}_2\text{O}_3$  (Simon *et al.* 1976). The spin-orbit splitting values observed were in good agreement with bulk oxide data (Rao *et al.* 1979). Good structural evidence for suboxides are available for a number of metal oxide systems including the alkali metals (Simon 1979) and the molybdenum oxide system (Gai 1981).

### 6.2. Catalytic selectivity and the role of surface oxygen

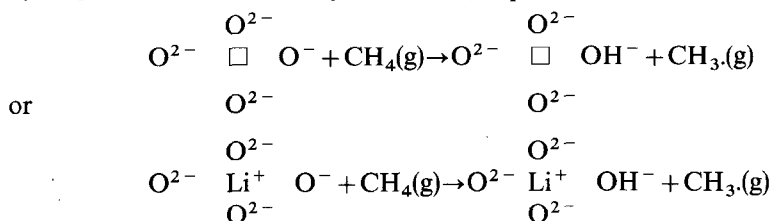
The important question of the role of surface oxygen in the activation of hydrocarbon molecules was reviewed recently by Haber (1984). A clear distinction was made between the bulk or lattice oxide ions,  $\text{O}^{2-}$ , and  $\text{O}^-$  or  $\text{O}_2^-$ ; the former exhibit selective oxidation characteristics whereas the latter, more electrophilic species, are responsible for total oxidation.

In view of our interest in metal oxidation *per se* we have approached the problem by studying the oxidation of a metal and monitoring the chemical reactivity of the surface both at the oxygen chemisorption stage and during growth of the oxide overlayer. The probe molecules have included water, hydrogen sulphide, ethylene and formic acid, the most extensively studied being water. An important conclusion which has a bearing on the question of selective oxidation is that in general (and the case study of lead oxide illustrates this unambiguously, figures 2 and 3) the 'bulk oxide', defined as an oxide overlayer of at least two or three unit cells, with a characteristic LEED pattern, is 'unreactive'. Activation of the oxide can, however, be induced if there are present chemisorbed oxygen adatoms,  $\text{O}^{\delta-}$  at the surface of the overlayer. In the case of nickel at low temperatures the chemically most reactive oxygen species (Carley *et al.* 1983) are those which are present in a state of incipient oxidation; they are characterized by large dipoles, are coordinatively unsaturated and would be readily incorporated into the sub-surface on slight thermal activation. These general ideas are shown to be valid for other metal-oxide systems, a further example being the  $\text{ZnO}(0001)\text{-O}^-$  surface (Au and Roberts 1984 a) where the chemisorbed  $\text{O}^-$  species can be distinguished by XPS from the lattice  $\text{O}^{2-}$  and also shown to have specific reactivity, which can be observed by PES, not only to water but also to formic acid (Au and Roberts, 1984 a, b).

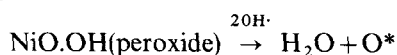
The  $\text{O}^{2-}$  (lattice) species behave in general as nucleophiles (Haber 1984) and are inserted into the reactant (hydrocarbon) molecule at electron-deficient sites. This process usually occurs at much higher temperatures than those where  $\text{O}^-$  reactivity is observed and depends on the 'activation' of the hydrocarbon molecule at the oxide surface. Although there is little known about the 'active centre' responsible for this activation there is good evidence that it is related to the possible redox nature of the oxide. Hence the importance of obtaining PES evidence, which can be quantified, for different oxidation states at oxide surfaces (figures 4 and 11).

Although some of the earlier work to elucidate the role of molecule activation by  $\text{O}^-$  (a) species present at bulk oxide surfaces, mainly  $\text{MgO}$ , was by Tench and his group using E.P.R. (reviewed by Che and Tench 1982), we draw attention here to a recent, and definitive study, of the role of  $\text{O}^-$  (s) species in hydrocarbon activation (Driscoll *et al.* 1985). These E.P.R. studies indicate unambiguously that the dominant process is hydrogen abstraction. With methane,  $\text{CH}_3$  radicals formed at a  $\text{MgO}$  surface at  $500^\circ\text{C}$ , desorbed, then trapped in a matrix-isolation system and characterized by E.P.R. With lithium-doped  $\text{MgO}$  a second type of  $\text{O}^-$  (s) site is present, assigned (Driscoll *et al.* 1985) as a  $[\text{Li}^+\text{O}^-]$  centre which is more active in hydrogen abstraction than  $\text{O}^-$  (s). These studies further support the general conclusion that adsorbate activation by

surface oxygen is highly specific to the nature of the oxygen, the most active being those species that are at the surface, are coordinatively unsaturated, carry a negative charge and are metastable with respect to the lattice oxygen. The following summarizes the Lunsford scheme for hydrocarbon activation which again emphasizes the high hydrogen-abstraction activity of the  $O^-(s)$  species.



Recently XPS studies in this laboratory (Symmonds, unpublished data) of lithium-doped nickel oxide (figure 12(b)) may well have some bearing on Lunsford's observations since they indicate the presence of very high intensity in the  $O(1s)$  spectral region associated with  $O^-(s)$  and possibly  $OH(a)$  species. Moreover, the oxygen : nickel atom ratio, within the photoelectron escape depth ( $20 \text{ \AA}$ ), is about 5 : 1 indicative of a highly defective oxygen-excess surface. Although speculative, we suggest these species may well be analogous to those responsible for the high reactivity associated with Lunsford's lithium-doped  $MgO$ . For comparison, figure 12 also shows  $O(1s)$  spectra observed with Cr-doped  $NiO$ ,  $NiO(100)$  and  $Ni(100)-O$ ; also given are the calculated  $O : Ni$  atom ratios; in the case of  $Ni(100)-O$  the ratio is for  $O : Ni^{2+, 3+}$  i.e. after removal of  $Ni^0$ . The contrast with Li-doped  $NiO$  is obvious. Although further work on lithium-doped oxides is planned it is perhaps, even at this stage, worth drawing attention to the formal similarities that exist between the photoelectron spectra of lithium-doped nickel oxide, highly defective (high surface area) nickel oxides (Roberts and Smart 1984) and nickel oxhydroxide (peroxide). Of equal significance is the similarity of the chemistry associated with such surfaces. In the case of the thermal decomposition of nickel peroxide, dioxygen and water are formed with the simultaneous reduction of  $Ni^{3+}$  to  $Ni^{2+}$  (Moroney *et al.* 1983). Now, nickel peroxide (in benzene) is a useful oxidizing agent for alcohols, phenols and amines (Konaka *et al.* 1969). The oxidizing characteristics involve hydrogen abstraction and  $OH$  radical donation, triphenylcarbinol being formed from triphenylmethane and benzhydrol oxidation, through hydrogen abstraction at the  $\alpha$ -position, to form benzophenone (Konaka *et al.* 1969). The mechanism is suggested to involve the generation of hydroxyl radicals which lead to the formation of oxygen atoms.



There are, therefore, obvious comparisons to be made between the oxidizing properties of nickel 'peroxide' in solution and its thermal decomposition. We speculate that the surface hydroxyl species in heterogeneously catalysed reactions may play an analogous role in generating  $O^-(a)$  species which then participate in hydrogen abstraction reactions of the kind observed by Lunsford. Water vapour is well known to have 'beneficial effects' in some heterogeneously catalysed reactions; it may well be that it is through the participation of surface  $OH$  and  $O^-$  species that its beneficent influence is manifested. The role of  $OH$  and  $O^-$  species in the chemistry of coadsorbed systems, one of the components being water, has already been illustrated by the water-induced hydrogenation of nitric oxide (Au and Roberts 1984 b).

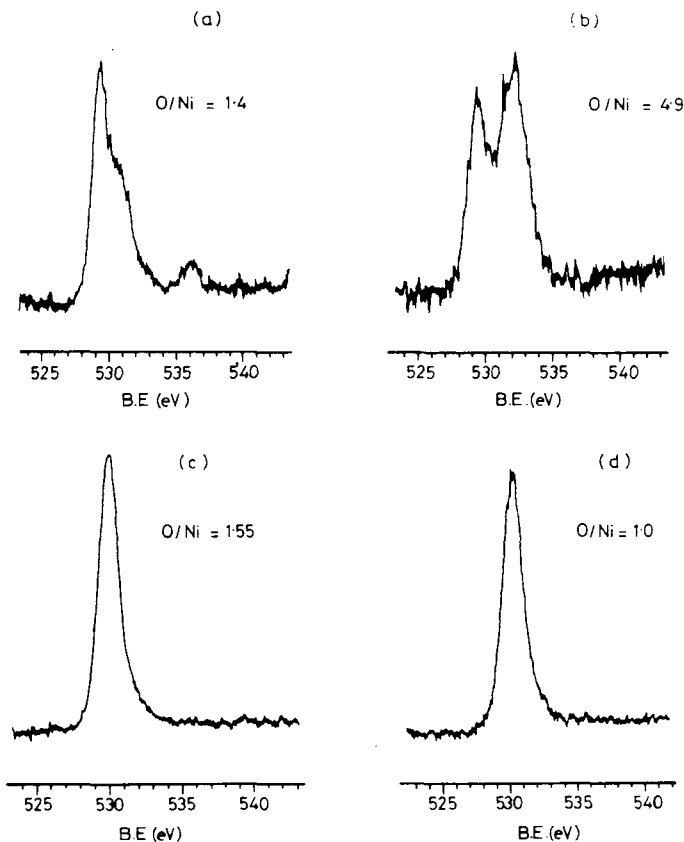
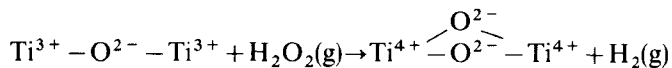
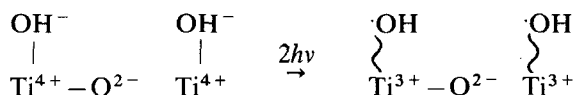


Figure 12. O(1s) spectra for various nickel oxides: (a) Cr-doped NiO; (b) Li-doped NiO; (c) Ni(100)-O surface generated by exposure of Ni(100) to oxygen; (d) NiO(100) single crystal after cleaning and annealing *in vacuo*.

The confirmation that the thermal decomposition of nickel peroxide involves a redox reaction,  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$ , with the evolution of oxygen (Moroney *et al.* 1983) has also formal similarities with the more familiar photochemically induced decomposition of water vapour at a titanium oxide surface (Somorjai *et al.* 1984). Both are redox reactions, and both involve hydroxyl species. Our interest in



obtaining quantitative data on the variable oxidation states (figure 4) present at titanium oxide overlayer and how they depend on the nature of gaseous reactants is obviously important for understanding its chemical and photochemical reactivity.

By contrast, and in keeping with the above discussion, Quinlan *et al.* (1985) have shown using EELS that the  $c(2 \times 2)$  Ni(100)-O surface, formed by oxygen exposure to Ni(100) at 575 K, interacts with methane at about 200 K to form a hydroformyl species

(CH<sub>2</sub>O). The surface hydroformyl species are suggested to be precursors to the formation of CO(g) and H<sub>2</sub>(g) which are also observed in temperature-programmed desorption studies of methane oxidation. Furthermore, methoxy (CH<sub>3</sub>O) species were absent and no evidence for bands assignable to C–H vibrations were observed. The reason for the latter is not known but similar observations were made with methanol (Baudais *et al.* 1980). On the other hand methoxy species were reported by Sexton *et al.* (1985) for CH<sub>3</sub>OH interaction at a Cu(110)–O surface. We believe the reason for these apparently diverse observations lies in the nature of the surface oxygen and in particular whether it has more nucleophilic than electrophilic character. In this context the acid–base properties of the surface (Kishi and Ikeda 1980, Barbeau and Madix 1982) are important; a good recent discussion of this aspect is that of Henry *et al.* (1985).

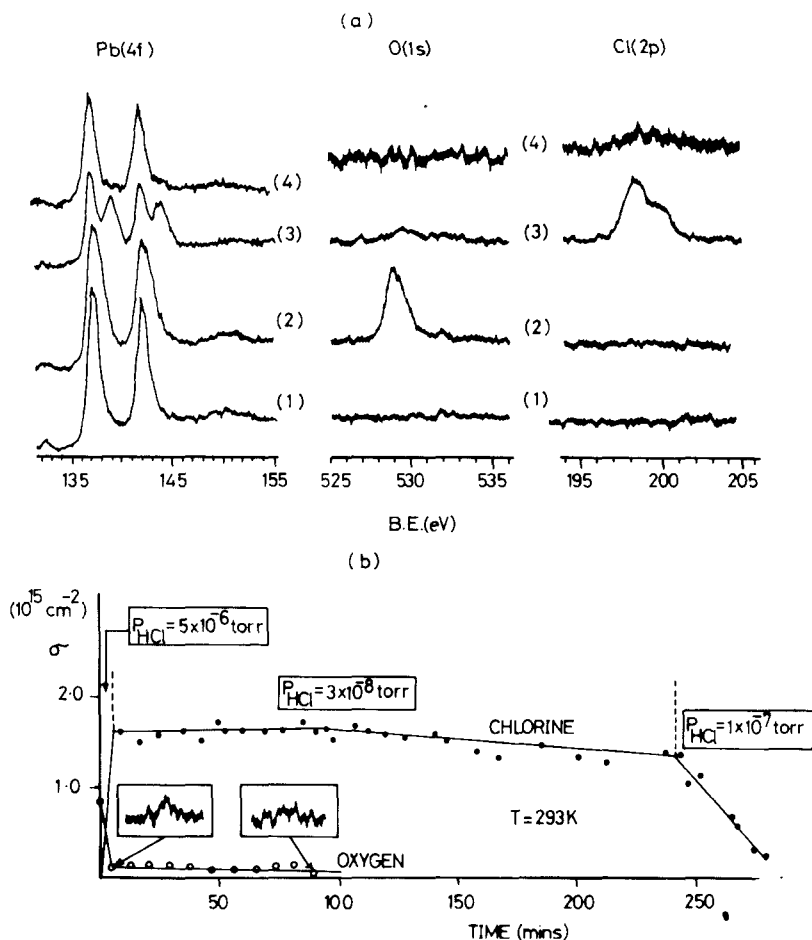


Figure 13. (a) Pb(4f), O(1s) and Cl(2p) spectra illustrating the chemisorptive replacement of surface oxygen by chlorine at a Pb(110)–O surface, followed by removal of the chloride overlayer to regenerate the clean surface. The Pb(110)–O surface (spectra (2)) is generated by exposing the clean surface (1) to oxygen (3000L) at 295 K. Exposure to HCl(g) (1200L, 295 K) leads to the formation of a chloride overlayer (3) at the expense of the surface oxide. Further exposure causes regeneration of the clean surface (4). (b) Variation of oxygen and chlorine surface concentrations during the exposure of a Pb(110) surface to HCl(g) at 295 K. The removal of the chloride overlayer is sensitive to both the presence of oxygen ( $1 \times 10^{14} \text{ cm}^{-2}$ ) and the HCl(g) pressure.



overlayer which, in the presence of HCl(g), reverts to the clean Pb(110) surface (figure 13). Kinetic data indicate a first-order dependence on HCl pressure and an activation energy for desorption of the overlayer, step (3), of about  $11 \text{ kJ mole}^{-1}$ .

This is a further example of where coadsorption studies reveal chemical reactivities which could not have been anticipated on the basis of studies of the individual molecules. Furthermore, the reactivity is specific to a chloride overlayer, the analogous bromide, formed by chemisorptive replacement of the surface oxide, being unreactive.

### 8. Summarizing comments

Having established that PES had the potential not only to detect surface species present at the sub-monolayer level but also to discriminate, through chemical shifts in electron binding energies, between a particular species in different bonding states, the way was open to apply PES in a quantitative way to mechanistic problems. The chemistries associated with the adsorption of such diatomic molecules as carbon monoxide and nitric oxide at metal surface illustrated very early on in their development the potential of both XPS and UPS. The advantages of low-temperature studies, involving dynamic PES, for observing intermediates in surface reactions have been illustrated by the novel chemistry associated with coadsorbed molecules. A coadsorbed system may follow a reaction pathway which would not have been easy to predict on the basis of the known reactivities of the individual molecules. For coadsorbed ammonia and 'oxygen' ( $\text{N}_2\text{O}$ , NO and dioxygen) at a Mg(0001) surface, a strongly chemisorbed amide ( $\text{NH}_2$ ) species forms under conditions where ammonia is unreactive with the atomically clean metal, the oxide overlayer and bulk oxide.

The selectivity along the amide route clearly depends on the efficiency of the ammonia molecule in intercepting the 'active oxygen' species  $\text{O}^-(s)$  and rerouting it away from the 'stable oxide'. As the surface concentration of the stable oxide ( $\text{O}^{2-}$ ) increases, the supply of 'active oxygen' decreases and the reaction poisons. The same arguments apply in the water-assisted hydrogenation of nitric oxide at Zn(0001) surfaces (Au and Roberts 1974 b). We draw attention to the analogies that appear to exist between models we have developed for some coadsorbed systems involving oxygen and metal oxide overlayers and the poisoning of hydrocarbon reactions at metal surfaces by carbide build-up.

One of our early objectives was to understand the role of surface modifiers (of which oxygen was one); this led to a search for spectroscopic evidence for different oxygen species and variable (defect) oxidation states. We have, by making comparisons with other studies, including those of Lunsford's group who used E.P.R. to probe the active surface site in hydrocarbon oxidation, drawn attention to the formal similarities that exist between oxygen-induced activation of molecules at metal surfaces and the reactivity and nature of various bulk oxide surfaces. There is good experimental evidence for  $\text{O}^-(s)$  being the active oxygen species in the chemistry of the coadsorbed molecules but in view of their short surface lifetimes further detailed studies will require alternative experimental strategies to be developed.

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