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SATYENDRA NATH BOSE MEDAL LECTURE—1980*

STUDIES OF SURFACES BY ELECTRON SPECTROSCOPY

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Techniques of electron spectroscopy have made a great impact on modern surface science. Some of the techniques employed in the study of surfaces are briefly presented in this article. Applications of these techniques to study surfaces of solids and adsorbed species are discussed in some detail.

Keywords: Surfaces; Surface Science; Electron and Energy Loss Spectroscopy; Gas-Solid Interaction; Auger and Photoelectron Spectroscopy

INTRODUCTION

MAJOR strides in the study of surfaces have become possible in recent years due to the advent of sophisticated techniques like electron spectroscopy and low energy electron diffraction which provide extremely sensitive probes to investigate the first few atomic layers on surfaces of solids. These techniques are not only powerful in characterizing surface states of solids but also in studying adsorbed species. In this lecture, we shall concern ourselves with the study of surfaces by techniques of electron spectroscopy. Some of the important electron spectroscopic methods are photoelectron spectroscopy employing UV and X-radiation (UVPS and XPS), Auger electron spectroscopy (AES), energy loss spectroscopy (ELS) and inelastic electron tunnelling spectroscopy (IETS). Applications of these techniques to study surface phenomena constitute the frontiers of modern surface science and there is still much to be explored. These techniques have become possible due to the ready availability of ultra-high vacuum ($\sim 10^{-10}$ Torr or better) and sophisticated instrumentation, both undergoing constant improvement. There seems to be little doubt that in the near future these surface characterization techniques will provide a better understanding of complex surface phenomena like catalysis and corrosion.

In this lecture, I shall first discuss results obtained from electron spectroscopic studies of surfaces of metals, oxides and other materials with some attention to surface states. Then I shall examine at some length investigations of molecules adsorbed on surfaces including some aspects of oxidation of metals, catalysis and other surface phenomena.

TECHNIQUES

In photoelectron spectroscopy, a monochromatic photon beam impinges on a solid and the resulting photoelectrons are energy analysed. The binding energy of electrons, E_B, originating from a particular state is obtained by the energy balance equation,

$$h\nu = E_B + E_K + \Phi \qquad ..(1)$$

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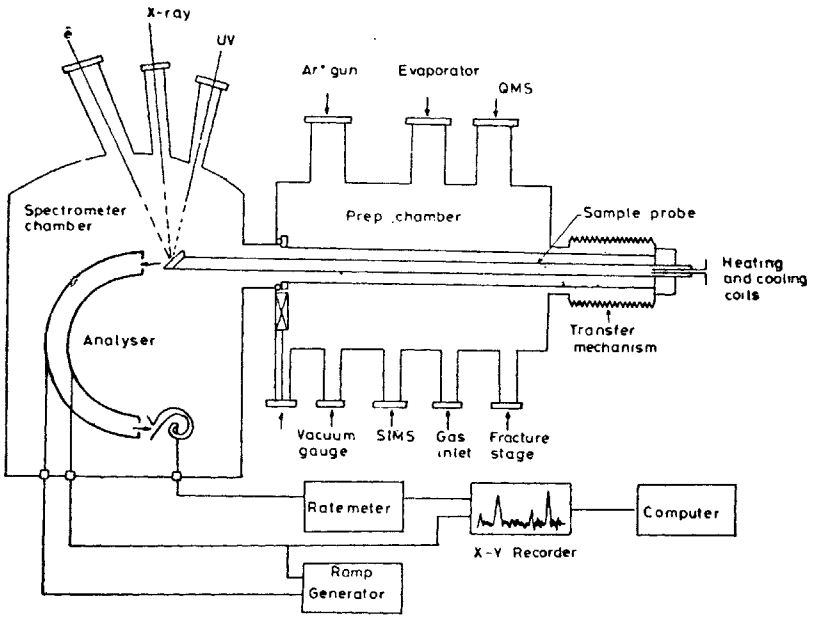


FIG. 1. A schematic diagram of an electron spectrometer (Rao & Hegde, 1981).

where E_k is the kinetic energy of the electron and Φ is the work function of the solid. A schematic diagram of an electron spectrometer is shown in Fig. 1. In UV photoelectron spectroscopy, He I (21.22 eV) and He II (40.8 eV) are the most common radiations employed. Al K_α (1486.6 eV) and Mg K_α (1253.6 eV) are the common X-radiations used in XPS. While UVPS is useful to study valence bands (Green, 1977), XPS provides detailed information about the core electron levels as well (Carlson, 1975). Angular dependence of photoelectrons is particularly useful in the study of surface species (Lloyd *et al.*, 1977). The advent of synchrotron radiation has further increased the potential of photoelectron spectroscopy to study surface phenomena.

In Auger spectroscopy, an impinging electron beam causes the ionisation of a core electron and this core level vacancy is filled by a non-radiative electron jump from a higher energy level with the simultaneous ejection of an Auger electron from a higher level. Thus, the energy of a KL_1L_{23} Auger transition in the case of an atom with an effective atomic number Z is given by the equation

$$E_{KL_1L_{23}}(Z) = E_K(Z) - E_{L_1}(Z) - E_{L_{23}}(Z + \Delta) - \Phi \qquad \ldots(2)$$

Here the final state is left with two core holes with reference to the neutral atom and the L_{23} level will have an effective atomic number higher than the singly ionized atom by Δ. The Auger transition energy is independent of the primary electron energy. Auger spectroscopy is particularly useful in the determination of oxidation states of elements and characterization of elements on solid surfaces in presence and absence of gas adsorption (Joyner & Roberts, 1975).

In energy loss spectroscopy, one measures the loss in energy of incident electrons due to impact with matter. Depending on the primary beam energy, one can obtain information regarding vibrational and electronic transitions involving adsorbed species; valuable information on surface electronic states of the adsorbent (substrate) can also be obtained. The information obtained from ELS on adsorbed molecules is similar to that obtained from reflection-absorption infrared spectroscopy (Ibach, 1977). In Fig. 2, a schematic diagram of an energy loss spectrometer is shown.

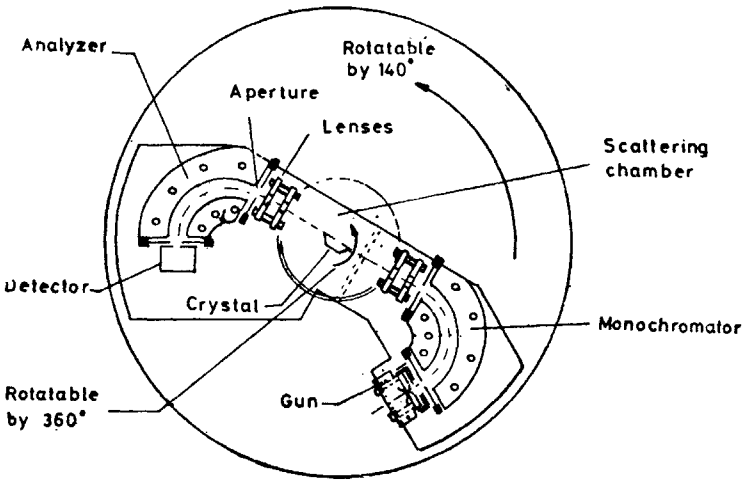


FIG. 2. A schematic diagram of an energy loss spectrometer.

In inelastic electron tunnelling spectroscopy, tunnelling of electrons through an insulating barrier formed between two conducting electrodes in a planar or diode geometry with a bias voltage applied across the two conductors is measured. Commonly, IETS measurements are made using metal-oxide-metal tunnel junctions. There are several possible mechanisms for inelastic electron tunnelling of which the vibrionic excitation of molecular species adsorbed on the surface of the insulating barrier is exploited to probe the vibrational structure of the adsorbed reactants (Weinberg, 1978). The inelastic electron tunnelling process is shown in Fig. 3. The second derivative of the current with respect to voltage for a tunnelling junction represents the IETS spectrum.

STUDY OF SOLIDS

Since the outgoing electrons in XPS can essentially be considered as free, XPS valence band spectra faithfully reproduce the density of occupied valence states of solids. Where He I radiation is used, the photoelectron energy is about 15 eV and the spectrum represents initial as well as final unoccupied states. For photons of $h\nu >$ 30 eV, photoionisation can be described by a single step process as in XPS and the valence bands represent the occupied density of valence states. By employing He II radiation, fine structure of valence bands can be obtained from photoemission studies.

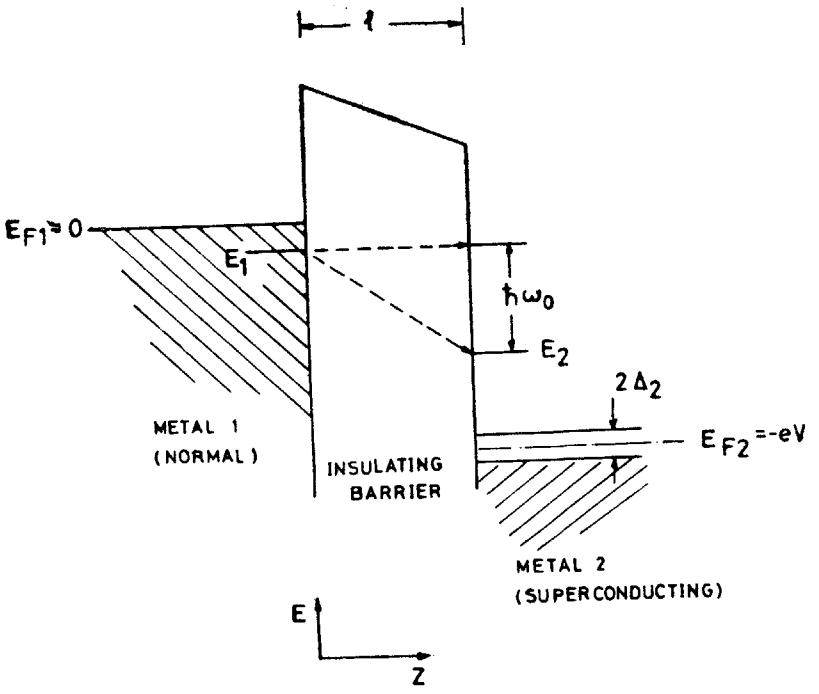


FIG. 3. Tunneling process in inelastic electron tunneling spectroscopy.

There are a number of reports in the literature on the study of valence bands of metals, semi-conductors and insulators (Green, 1977). Valence bands of metals are comparatively simple to understand because relaxations and screening are relatively unimportant for delocalised band electrons. The valence band, therefore, is a true representation of occupied density of states. Excellent agreement between band structure calculations and XPS data has been repeatedly demonstrated.

A good illustration of the use of UVPS in the study of surface states is provided by silicon. Photoemission studies show the full extent of surface states near the band gap (Wagner & Spicer, 1972; and Eastman & Grobman, 1972). In Fig. 4*a* the energy distribution curves of doped (n^{++}, n^- and p^{++}) silicon taken with a $h\nu$ of 11.8 eV are given to show how the relative energy of the surface states and bulk bands depends on doping (Spicer *et al.*, 1976). The band bending for heavy n^- and p doping are also shown in the figure. Band bending occurs to enforce a common Fermi level throughout the semiconductor. Fig. 4*a* clearly shows how the bulk and surface states are affected by band bending. Since the surface position of the Fermi level is pinned by the surface states, these states move very little due to doping compared to bulk states. Fig. 4*a* also provides information on the spatial extent of the surface state electrons. The data suggest that the electrons must b eessentially localized in the first atomic layers. Surface states are also readily identified by exposing them to reactive gases like oxygen. Since surface states are due to unsatisfied chemical bonds, they are extremely sensitive to oxygen exposure (due to for mation of Si-O bonds).

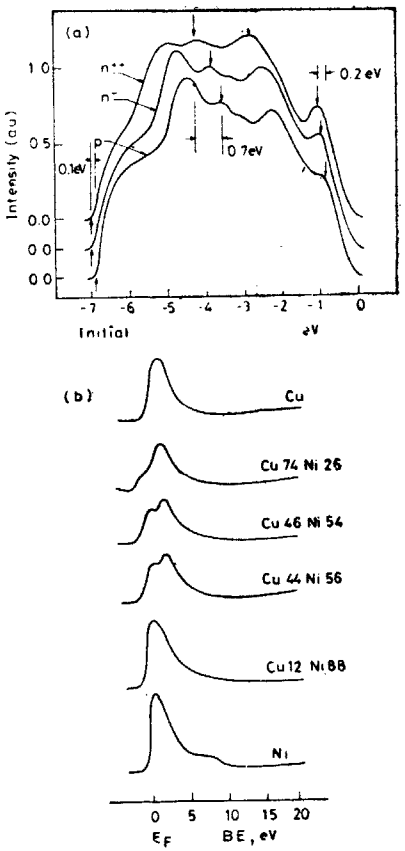


FIG. 4(*a*). Photoemission spectra of doped Si employing 11.8 eV radiation (from Spicer *et al.*, 1976).
FIG. 4(*b*). XPS valence bands of Cu-Ni alloys.

Although empty surface states cannot be detected by photoemission techniques they can be used to locate the bottom of the empty surface state band by measuring the position of the surface Fermi level as a function of doping (Wagner & Spicer, 1972; and Spicer, 1976). Yield techniques can be fruitfully used to study empty surface states (Eastman & Freeouf, 1974). The process involves a transition into empty surface states (say, from Ga(3d) of Ga As emoloying $h\nu$ of 20 eV), followed by recombination of an electron with the *d*-hole releasing energy through an Auger process to a valence electron (which is then emitted and whose energy is measured).

XPS and UVPS studies of various metallic alloy systems, in particular those containing transition metals, have led to a better understanding of the valence band structure in these systems (Watson & Perlmann, 1975). Studies on the valence bands of $Cu_{1-x}Ni_x$, $Ag_{1-x}Pd_x$ and so on have shown that each constituent in these alloys contributes its *d*-band spectra to the valence band of the alloy, relatively unaffected by the presence of other atoms over the entire range of composition. These observations indicate that the rigid band model is not sufficient to explain the valence

band of alloys, as this model proposes the existence of a common band in the alloy. Though the band positions are relatively unaffected, it has been found that the shape and structure of the individual *d*-bands of the constituents in the alloy are somewhat affected due to alloying. These changes can be explained by hybridization of the individual *d*-levels and are all well described by the coherent potential approximation. The valence band spectra of the Cu-Ni alloy system is shown in Fig. 4(*b*) for purpose of illustration.

Band structures of oxides and other compounds of metals have been investigated where the final state effects have been analysed. In oxides like MnO, FeO and NiO, bands due to metal (3*d*) and oxygen (2*p*) can be separated (see e.g., Madhusudan *et al.*, 1979). Typical XP spectra of V_2O_3, VO_2, V_2O_5 and TiO_2 are shown in Fig. 5 where we can clearly see the separation of metal (3*d*) and 0(2*p*) bands. No 3*d* band is present in V_2O_5 and TiO_2 as expected. The (2*p*) band of oxygen shows a doublet structure due to σ and π bonding. To illustrate final state effects, we have shown the valence band spectra of the three iron oxides in Fig. 6; the observed spectrum of Fe_3O_4 agrees with that predicted theoretically (Vasudevan *et al.*, 1979).

One of the problems often faced is the identification of surface oxidation states of metals in oxides and other surfaces. This is readily done by examining the core levels (in XPS) as well as valence bands of these materials. It has been shown that metal core level binding energies increase with increase in the oxidation number of the metal (Rao *et al.*, 1979). Presence of multiple valencies in compounds like Fe_3O_4 and Ti_nO_{2n-1} are clearly seen in core levels where distinct bands are found due to each of the oxidation states. This is particularly important because in systems like Fe_3O_4, other techniques like Mössbauer spectroscopy would not show the two valence states due to the problem of time scale. Valence bands would also show differences in suitable instances as in the case of iron oxides (see Fig. 6).

Core level spectra of metals show asymmetry arising from the collective response of valence electrons to the creation of core holes. Surface plasmon peaks are observed towards the higher binding energy side of core levels in addition to bulk plasmon peaks. It would be out of scope of this lecture to discuss other features of XPS such as shake-down and shake-up satellites, exchange and spin-orbit splittings of bands and so on (Carlson, 1975; Rao *et al.*, 1979 ; and Sarma & Rao, 1980).

Valence Fluctuation

A number of materials particularly lanthanides exhibit inter-configurational or valence fluctuations by promoting a valence electron to the conduction band. This has to be distinguished from the mixed valent systems of the type Fe_3O_4 wherein two distinct ions are present. The systems which show valence fluctuation are generally metallic. XPS is ideally suited to study valence fluctuation in solids (Rao & Sarma, 1980). Theoretical considerations show that the energy separation between the different valence states in valence fluctuating rare earth systems is greater than 7 eV for 3*d* and 4*d* levels and two distinct peaks are therefore expected to appear due to the two different valences in XPS. Rare earth metals capable of showing valence fluctuations are Ce, Sm, Eu, Tm and Tb as they satisfy the conditions,

$$E_{exc} = E_n - (E_{n-1} + E_e) \simeq 0 \qquad \ldots(3)$$

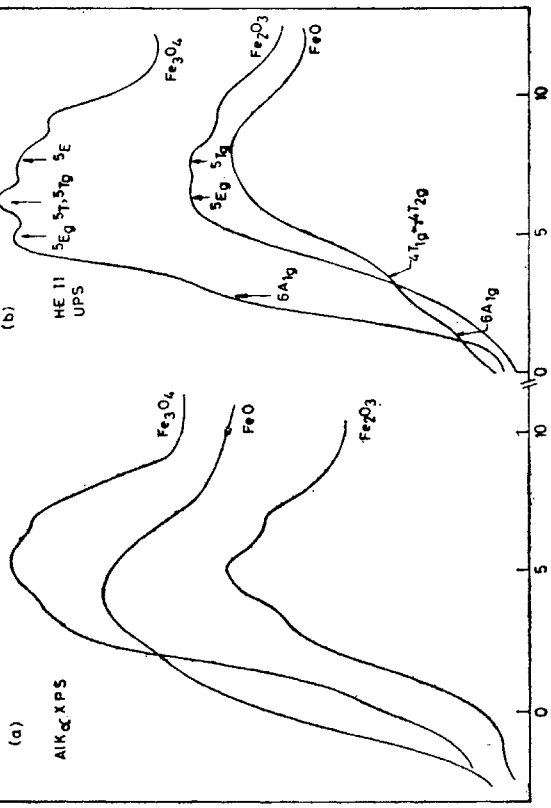


FIG. 6. Valence bands of three iron oxides employing (*a*) XPS and (*b*) UVPS.

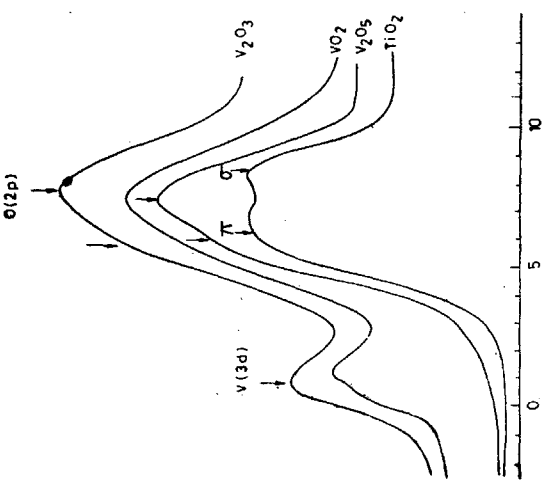


FIG. 5. XPS valence bands of a few oxides showing metal (3*d*) and O (2*p*) bands.

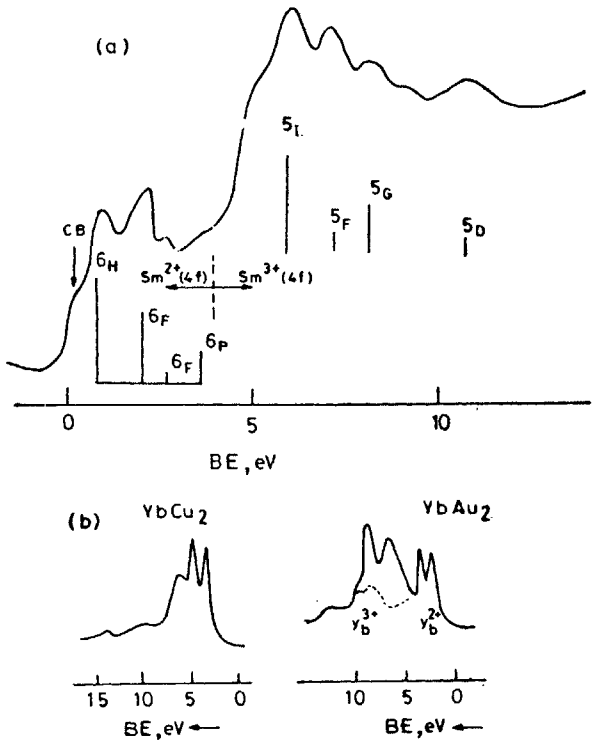


FIG. 7(*a*). Valence band of Sm metal showing Sm^{+2} and Sm^{+3}. FIG. 7(*b*). Valence bands of $YbCu_2$ and $YbAu_2$, the latter showing mixed valence (from Wertheim, 1979).

where $(E_n—E_{n-1})$ is the energy difference between the $4f^n$ and $4f^{n-1}$ states and E_e is the energy of the promoted electron. Extensive XPS studies have been carried out on systems like SmB_6, SmS and allied compounds and also on CeN, $CeYAl_2$, $CePd_3$, $EuCu_2Si_2$ and thulium chalcogenides. A brief review of XPS studies of valence fluctuation in rare earth systems has been recently published (Rao & Sarma, 1980).

In Fig. 7*a* the valence band of Sm metal is shown to illustrate the presence of valence fluctuation. Special mention must be made of SmS which shows valence fluctuating property in the chemically collapsed state by suitably substituting Sm by smaller ions like Gd. It is interesting that in many such valence fluctuating systems a lower oxidation state is often stabilized at the surface compared to the bulk, typical examples being $YbCu_2$ and $YbAu_2$ (see Fig. 7*b*). In these cases the +2 state is more stabilised at the surface compared to the bulk because of the large lattice parameters near the surface.

Catalysts

An important application of the study of surface oxidation states by XPS is in the area of catalyst characterisation (Minachev *et al.*, 1978). XPS studies of surfaces of chromia-alumina catalysts (Jagannathan *et al.*, 1980) with different

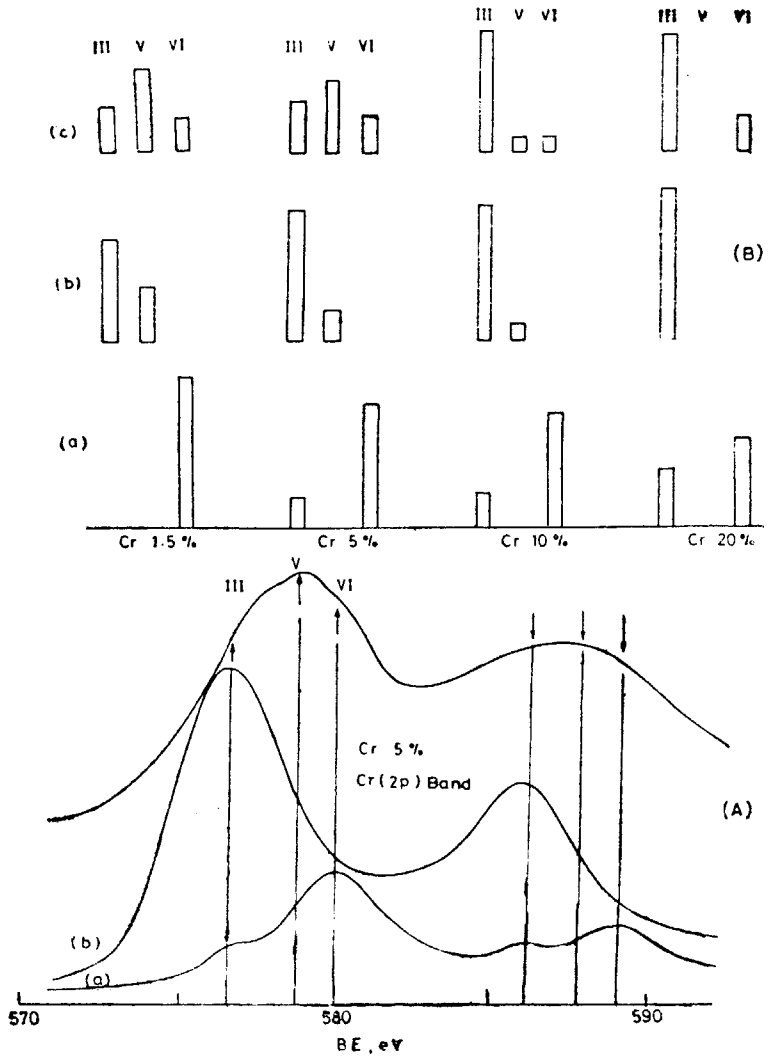


FIG. 8. Cr(2*p*) bands of Cr 5 per cent—alumina catalysts alongwith bar diagrams showing the proportions of different Cr species on the surface: (*a*) calcined at 720 K; (*b*) reduced in H_2 at 720 K for 1 hr, and (*c*) treated with cyclohexane at 720 K for 1 hr.

chromia contents subjected to (*a*) calcination at 720 K for 24 hrs, (*b*) reduction in H_2 at 720 K for 1 hr and (*c*) cyclohexane treatment at 720 K for 1 hr show the presence of three species, namely, Cr(III), Cr(V) and Cr(VI). The relative proportions of these species on the catalyst surfaces are shown in Fig. 8. It can be clearly seen that Cr(V) appears on the reduced catalyst surface and its concentration increases after the dehydrogenation reaction; the proportion of Cr(V) is maximum when the chromia content is < 10 per cent.

XPS studies of the bismuth molybdate catalyst (Jagannathan *et al.*, 1980) show

that Mo(V) is an important species in determining the activity of bismuth molybdate catalyst. The Mo(3*d*) band of this catalyst clearly shows that Mo(VI) is the only species on the surface. Heating the catalyst to 670 K under ultra-high vacuum seems to result in only Mo(V); cooling to 300 K under ultra-high vacuum shows evidence for the formation of both Mo(IV) and Mo(VI) species (see Fig. 9).

UVPS and XPS studies of O_2, H_2 and H_2O adsorbed on surfaces of reduced and stoichiometric $SrTiO_3$ (Ferrer & Somorjai, 1980), an active material for water photolysis, reveal the presence of Ti^{3+} on reduced $SrTiO_3$ (111) surface whose concentration decreases with O_2, H_2 and H_2O adsorption. Subsequent band gap

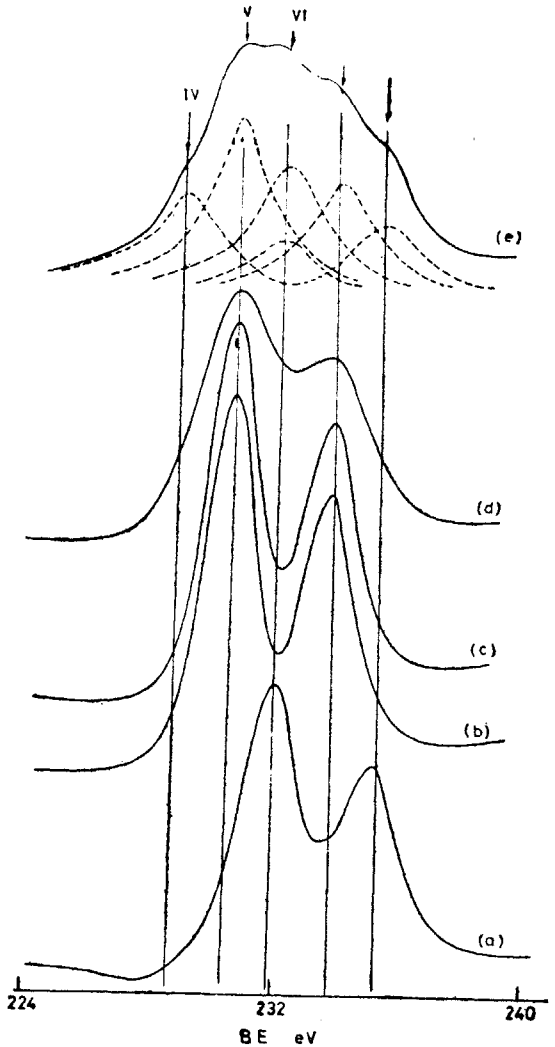


FIG. 9. Mo(3*d*) bands of bismuth molybdate showing different types of Mo species : (*a*) as prepared; (*b*) heated to 670 K under UHV; (*c*) *b* cooled to 570 K; (*d*) *b* cooled to 300 K and maintained to 1 hr, and (*e*) after maintaining for 20 hrs at 300 K.

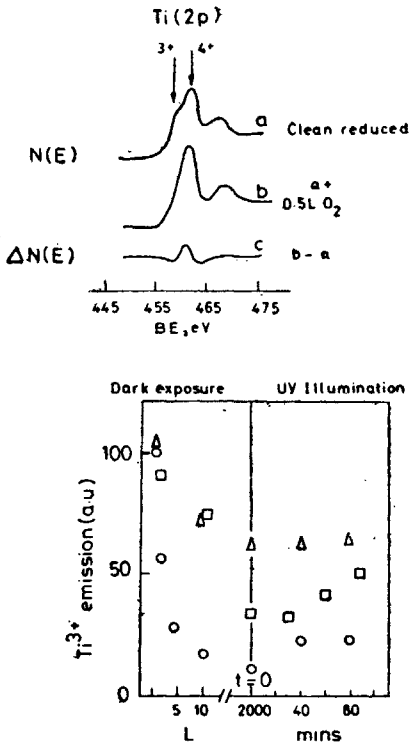


FIG. 10. Ti(2*p*) bands of $SrTiO_3$(111) alongwith Ti^{3+} emission as a function of exposure: Triangles exposed to H_2O; Squares, exposed to H_2 and circles, exposed to oxygen (from Ferrer & Somorjai, 1980). Here *L* stands for Langmuir ($1L = 10^{-6}$ Torr. sec).

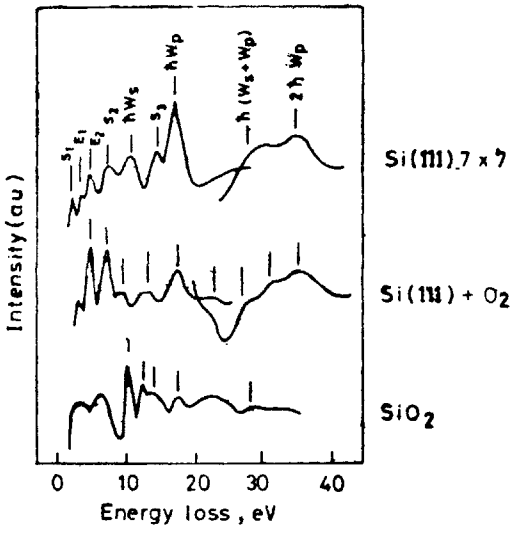
illumination is found to partially restore the Ti^{3+} initial concentration for O_2 and H_2 exposures but not for H_2O exposures. The above results are illustrated in Fig. 10.

CdS Solar Cell

XPS studies of the solar cell system Cu_2S/CdS prepared at 2 *p*H reveal some interesting features about this system (unpublished results of colloborative work of this laboratory with Dr V. G. Bhide of National Physical Laboratory). The surface composition of this solar cell system when monitored at different etching periods using Ar^+ ion sputtering reveal that while the surface layers are richer in Cu the bulk layers are richer in Cd.

ELS Study of Surface States

ELS is very useful in providing direct information on electron states of clean surfaces. ELS shows loss peaks due to surface and bulk plasmons as well as inter-band transitions. In Fig. 11, we have shown the energy loss spectra of Si(111) 7×7 surface before and after oxygen exposure (Ibach & Rowe, 1974). One can easily observe the changes in the surface state transitions and the surface plasmon loss peak. An ELS spectrum of SiO_2 is also shown for purpose of comparison.



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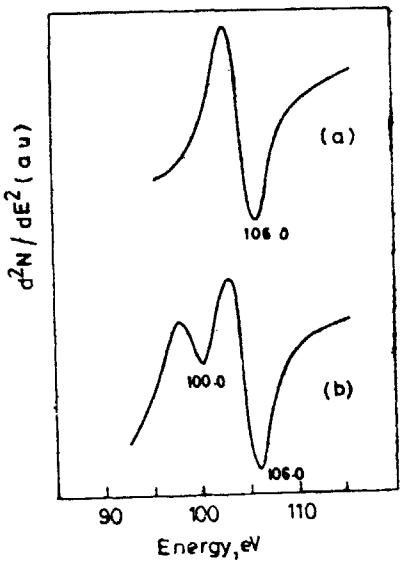


(12)

FIG. 11. Electronic states of Si(111) 7 × 7 surface: clean and exposed to oxygen obtained from ELS with E_P = 70 eV (from Ibach & Rowe, 1974).

FIG. 12. 50% Cu-50% Ni alloy as seen by Auger spectroscopy (*a*) annealed sample showing only Cu on the surface; (*b*) sputtered sample showing both Cu and Ni (from Spicer *et al.*, 1976).

Metal Surface States

Angularly resolved photoemission spectra are extremely useful in the study of surface states. Surface states on a metal like Al has been recently studied (Gartland *et al.*, 1978) by employing this technique. In Al(100), the surface states appear at the band gap of the bulk density of states. The intensity dependence of the surface sensitive peak on excitation energy and the emission angle are made use of to assign the surface state. Exposure to O_2 causes a decrease in the peak intensity of the surface state as one would expect.

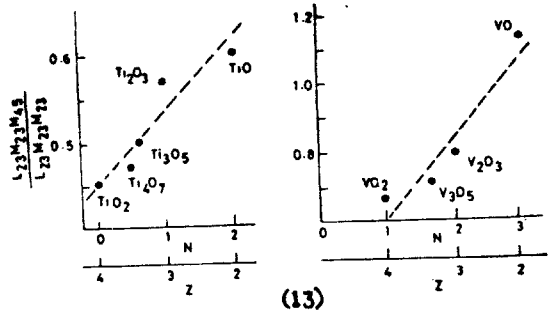
Auger electron spectroscopy has been used widely for the elemental analysis of surfaces. Particularly in situations where surface composition is different from bulk composition, the technique is very useful. To illustrate how the surface composition is different from bulk composition in an alloy, Auger spectra of a 50 per cent Cu-50 per cent Ni sample (Spicer *et al.*, 1976) is shown in Fig. 12. We see that an annealed sample shows only Cu on the surface. Only on sputtering or depth profiling one sees Ni; bulk composition can be found only after a certain depth.

Auger energies of metals and their compounds are often quite close. Only in some cases like Zn or Sn, the oxides show appreciable shifts relative to the metals. When shifts are appreciable one can relate the shifts to the oxidation state of the metal, a typical example being the case of vanadium oxides (Szalkowski & Somorjai, 1974). Surface oxidation has also been studied by some workers by examining the

relative intensities of the O_{KLL} and metal Auger lines (Rao *et al.*, 1980). Recently, a major contribution has been made from this laboratory (Rao *et al.*, 1980) to the study of surface oxidation states of metals by AES. The technique is based on the observation that the relative intensities of metal Auger lines themselves are related to the number of valence electrons or the oxidation state of the metal as given by the following equations;

$$\begin{aligned} &I\ (L_{23}M_{23}M_{45})/\ I\ (L_{23}M_{23}M_{23}) \propto N \\ &I\ (L_{23}M_{45}M_{45})/\ I\ (L_{23}M_{23}M_{45}) \propto (N-1) \\ &I\ (L_{23}M_{45}M_{45})/\ I\ (L_{23}M_{23}M_{23}) \propto N(N-1) \qquad \ldots(4) \end{aligned}$$

In the above equations N stands for the number of valence electrons; in the case of first-row transition metals one has to take into account both the ($3d$) and ($4s$) electrons. These metal intensity ratios are found to vary systematically with the



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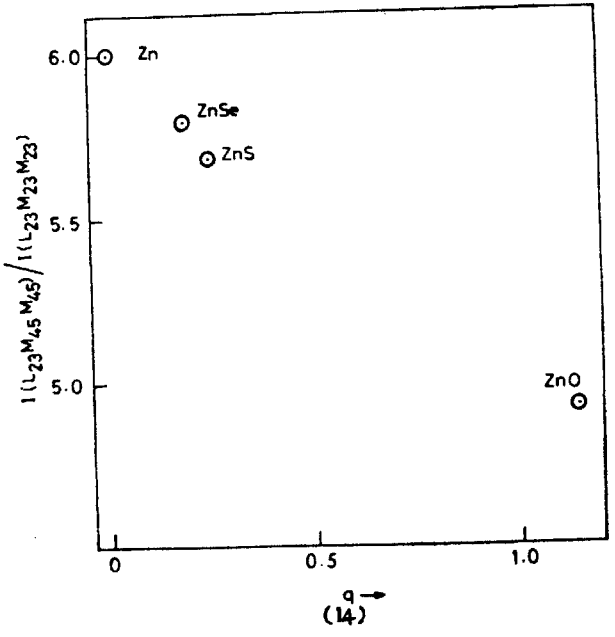


(14)

FIG. 13. Variation of metal Auger intensity ratios in Ti and V oxides with number of valence electrons N and the oxidation number Z.

FIG. 14. Variation of metal Auger intensity ratios in compounds of Zn with the charge q on Zn.

number of valence electrons as shown in Fig. 13. These relations have been employed to study surface oxidation of metals (Rao *et al.*, 1980; Sarma *et al.*, 1980). By a study of the intensities in a related series of compounds like ZnO, ZnS, ZnSe and ZnTe, it has been possible to show that the metal Auger intensity ratios are actually related to the charge on the metal (see Fig. 14).

Interaction of Molecules with Surfaces

Study of adsorbed molecular species by infrared spectroscopy and such techniques have been known for some years. The different techniques of electron spectroscopy provide much more information on adsorbed molecules than other forms of spectroscopy. Photoelectron spectroscopy directly probes what happens to the valence bands of solids and the molecular levels of the adsorbate (Spicer *et al.*, 1976). In addition, we can also monitor the development of core levels due to the adsorbed species (for example, C(1s) and O(1s) in the case of CO) and shifts in the core levels of the solid adsorbent due to adsorption of gases (for example, shift in metal core level peaks due to oxidation). Auger spectroscopy provides valuable information on adsorbate-adsorbent interactions (Joyner & Roberts, 1975). ELS provides information on the vibrational frequencies of adsorbed species when low energy primary electrons are used and about electronic levels of molecules when high energy electrons are used (Rao *et al.*, 1981). In addition, electronic transitions due to surface plasmon and bulk plasmon losses as well as interband transitions can be studied by ELS. We shall now examine a few illustrative electron spectroscopic studies of the interaction of molecules with solid surfaces.

Oxidation of Metals

Surface oxidation of metals can be studied at different temperatures and oxygen exposures by employing valence bands in UVPS and XPS as well as metal and oxygen core levels in XPS (see for example, Srinivasan *et al.*, 1979). In the case of iron, for example, we find evidence for the formation of both FeO and Fe_3O_4 at the surface, the proportions of which depend on temperature and oxygen exposure. In Fig. 15, we have shown the variations in the valence band of iron with oxygen exposures at 300 K and 500 K. The variations in the Fe($2p_{3/2}$) bands with oxygen exposure and temperature are shown in Fig. 16. A plot of oxygen uptake as a function of oxygen exposure is shown in Fig. 17. It can be seen from Fig. 17 that the oxygen uptake is appreciable even below 100 *L* at 500 K. The valence band at 300 K at high *L* is likely to consist of Fe^{2+} and Fe^{3+} alongwith $Fe^{(0)}$. The valence band at 500 K seems to indicate the formation of Fe_3O_4 probably admixed with FeO even at low to moderate oxygen exposures. This result is also supported by the variations in the Fe(2*p*) band (Fig. 16). The O(1*s*) band at 300 K shows the presence of two peaks at 529.8 eV and 531.7 eV at low exposures. With increase in exposure to 10^5 *L*, the main peak is found around 529.3 eV. At 500 K, the 529.3 eV peak is predominant throughout the range of exposures 10–10^3 *L* indicating that the species present at 300 K under high *L* is probably the same as that present at 500 K at low *L*. These features are illustrated in Fig. 18.

Surface oxidation of iron was also studied using metal Auger intensity ratios (Rao *et al.*, 1980). Typical Auger spectra are shown in Fig. 19. In Fig. 20, the

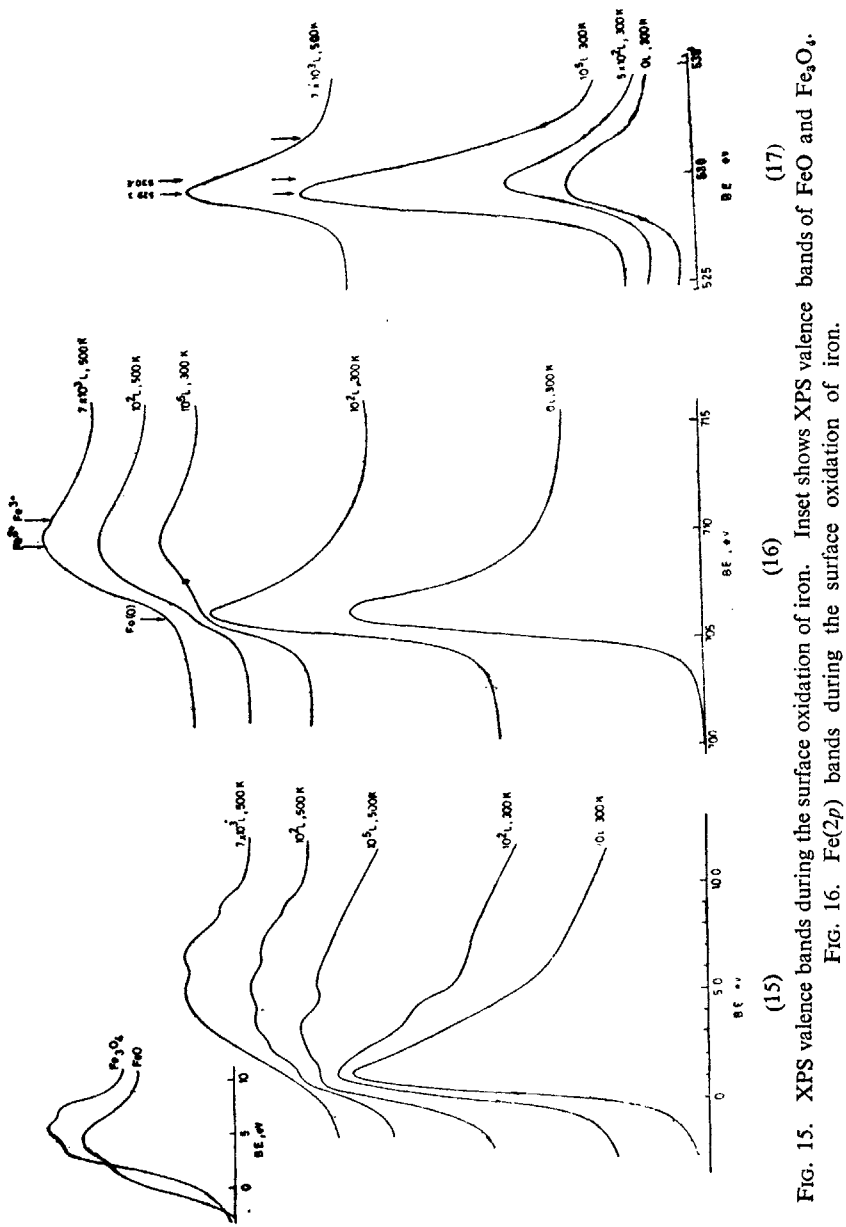


FIG. 15. XPS valence bands during the surface oxidation of iron. Inset shows XPS valence bands of FeO and Fe_3O_4.

FIG. 16. Fe(2*p*) bands during the surface oxidation of iron.

FIG. 17. O(1*s*) bands during the surface oxidation of iron.

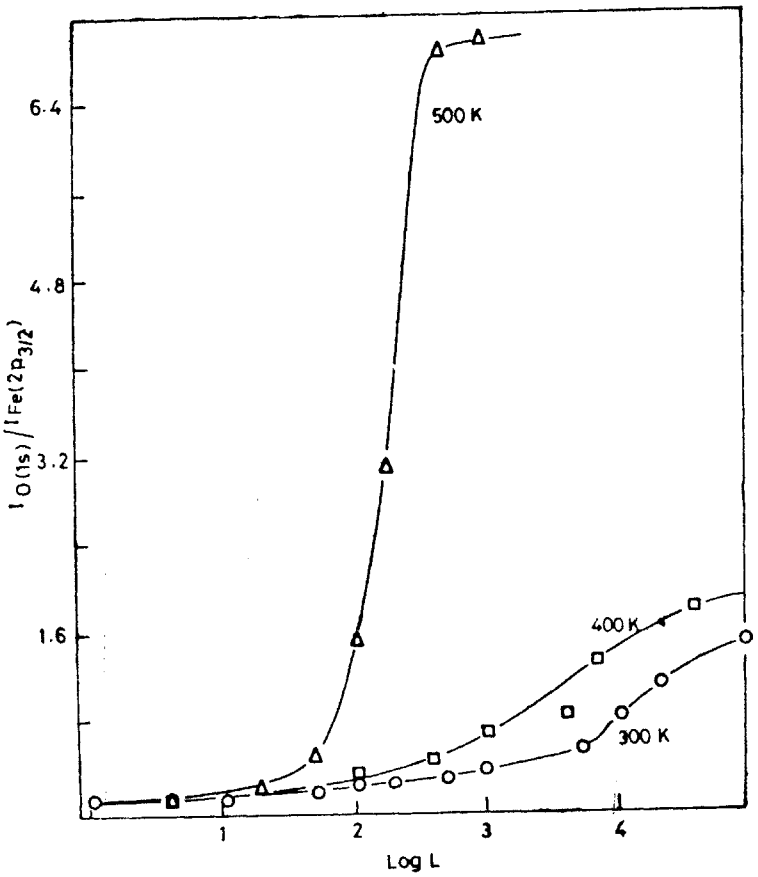


FIG. 18. Variation of O(1*s*)/Fe($2p_{3/2}$) band intensities ratio with amount of oxygen exposure during the surface oxidation of iron.

variation of $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ intensity ratio is shown as a function of oxygen exposure at different temperatures. We see three distinct regions of oxidation. The oxygen uptake as shown by the O(1*s*)/Fe($2p_{3/2}$) intensity ratio in Fig. 17 also indicates these three regions (*i*) a relatively flat region at low oxygen exposures; (*ii*) a region of rapid increase in intensity ratios at intermediate exposures and (*iii*) a saturation region at high oxygen exposures.

Adsorption of CO on Metals

When carbon monoxide is adsorbed on metals associatively, we see characteristic levels of the molecule in the valence band (Fig. 21). The two peaks at 8 and 11 eV below E_F are assigned (Page *et al.*, 1974) to the 5σ—1π and 4σ orbitals. Angular dispersion electron spectroscopic (ADES) studies (Lloyd *et al.*, 1977)have enabled to establish these assignments (see inset of Fig. 21). Adsorption of carbon mon-

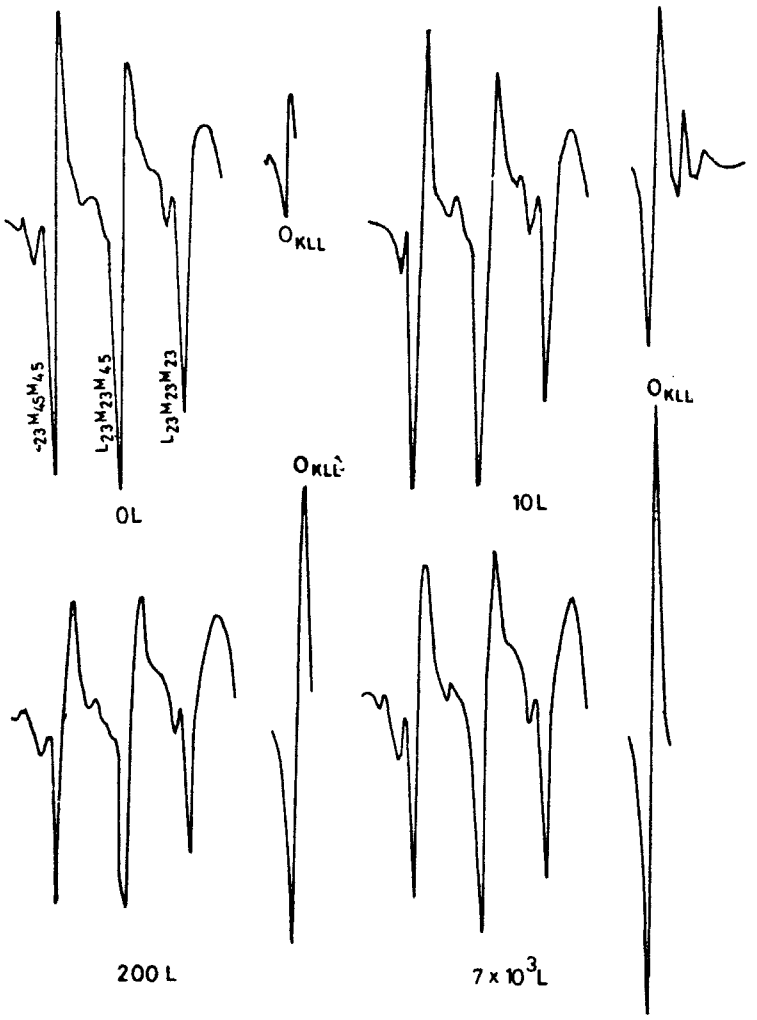


FIG. 19. Auger spectra of Fe exposed to oxygen showing the variation in O_{KLL} and Fe Auger peaks. Notice the variation in the metal Auger intensities with exposure to oxygen.

oxide on metals is accompanied by the development of C(1*s*) and O(1*s*) levels in core level spectra. On metal surfaces, CO shows two types of reactions:

$$CO \rightarrow C + O \quad \text{(dissociation)}$$
$$2\,CO \rightarrow CO_2 + C \quad \text{(disproportionation)}$$

The relative magnitudes of these reactions can be followed by the variation of the C(1*s*)/O(1*s*) intensity ratios as shown in Fig. 22. Any oxidation would also show variation in metal core levels and Auger intensity ratios. In our study of the interaction of CO with metals (Jagannathan *et al.*, 1980), we find an increase in the oxygen content on the surface with increase in exposure of carbon monoxide. We, however,

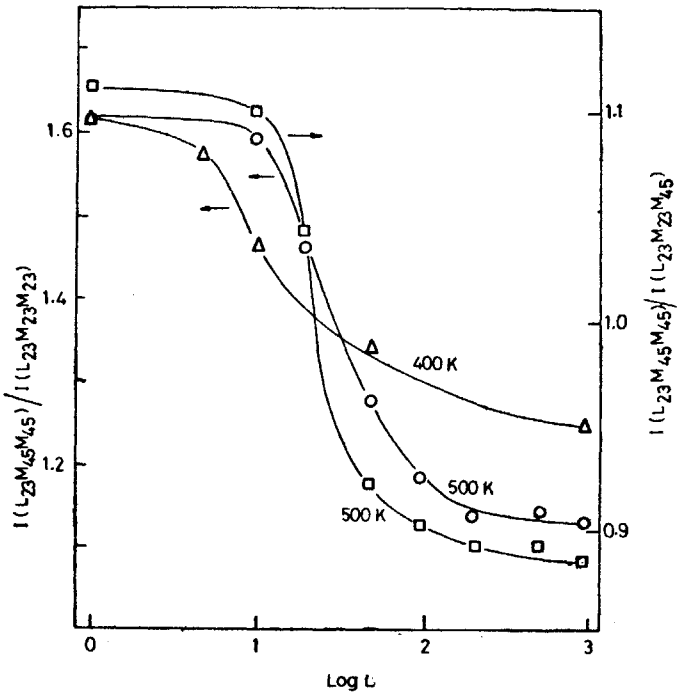


FIG. 20. Variation of Fe Auger intensity ratios with oxygen exposure.

do not see a corresponding increase in the carbon content on the surface. By subsequent heating and etching (the surface with Ar^+ ion), we find that some of the carbon has gone into the interior of the surface as made evident by Fig. 23.

ELS can be used effectively to study the adsorption of CO on metals. It gives information on the stretching frequencies of different types of adsorbed CO molecules and also metal-carbon stretching frequencies. A typical vibrational ELS spectrum of CO adsorbed on nickel (Andersson *et al.*, 1977) is shown in Fig. 24. The different models for the adsorption of CO on nickel (Anderson *et al.*, 1777) are shown in Fig. 25. One can readily assign the characteristic frequencies based on the scheme suggested by Sheppard and Nguyen (Sheppard & Nguyen, 1978).

	Frequencies vary in the order
1880–1650 cm^{-1}	B_3 (111) > B_4 (100) > B_5 (110)
2000–1880 cm^{-1}	B_2 (111) > B_2 (100) > B_2 (110)
2130–2000 cm^{-1}	C_6 (111) > C_8 (100)
> 2130 cm^{-1}	oxidised metal surface

In such studies, a combined use of LEED and ELS is very fruitful in that we can directly relate the spectra to the specific type of adsorbed species. The C-O vibrational stretching frequency of linearly adsorbed CO decreases with increase in the metal-carbon (M-C) stretching frequency as shown in Fig. 26(*a*). This implies that

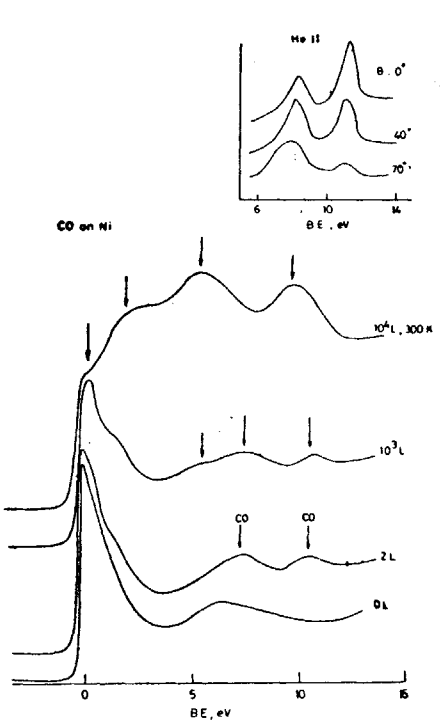


FIG 21

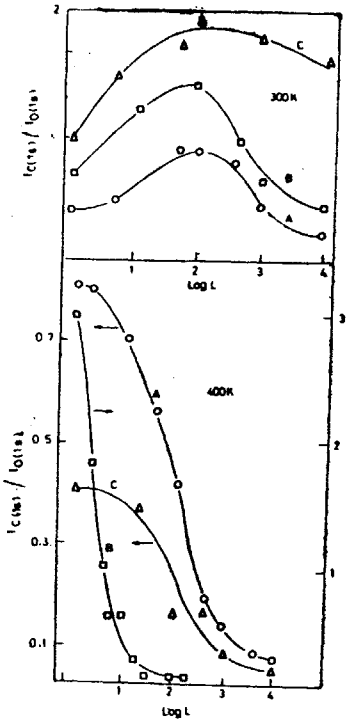


FIG.. 22

FIG. 21. Valence band of Ni exposed to carbon monoxide at 300 K. The spectrum shows peaks due to molecular as also dissociated CO. Inset shows angular dispersive UVPS of CO adsorbed on Pd(111) surface (inset from Lloyd *et al.*, 1971).

FIG. 22. Variation in the relative intensities of C(1*s*) and O(1*s*) peaks of CO adsorbed on (*A*) iron; (*B*) cobalt; and (*C*) nickel.

the C-O bond strength decreases as the M-C bond strength increases. Accordingly, we see that the C-O stretching frequency decreases with increase in heat of adsorption (Fig. 26*b*). The 5σ binding energy (from UVPS) of adsorbed CO also decreases with the heat of adsorption (see inset of Fig. 26*b*).

ELS using high primary beam energy gives information regarding electronic losses involving adsorbed species. Adsorption of CO on transition metals gives rise to two important losses (see Fig. 27) in the region 3-6 eV and 13.5–14 eV, the former assigned to metal *d*-CO (π*) charge-transfer (CT) transition and the latter to the 5σ, 1π-2π* intramolecular transition (E_T). From available ELS data of CO adsorbed on metals, we find that both the *CT* energy and the energy difference $\triangle(E_T-5\sigma)$ vary systematically with the heat of adsorption as shown in Fig. 28.

Other Adsorbed Molecules

Valence band studies of ethylene adsorbed on *W* clearly shows the presence of peaks due to ethylene at low temperature (Plummer *et al.*, 1974). At room tem-

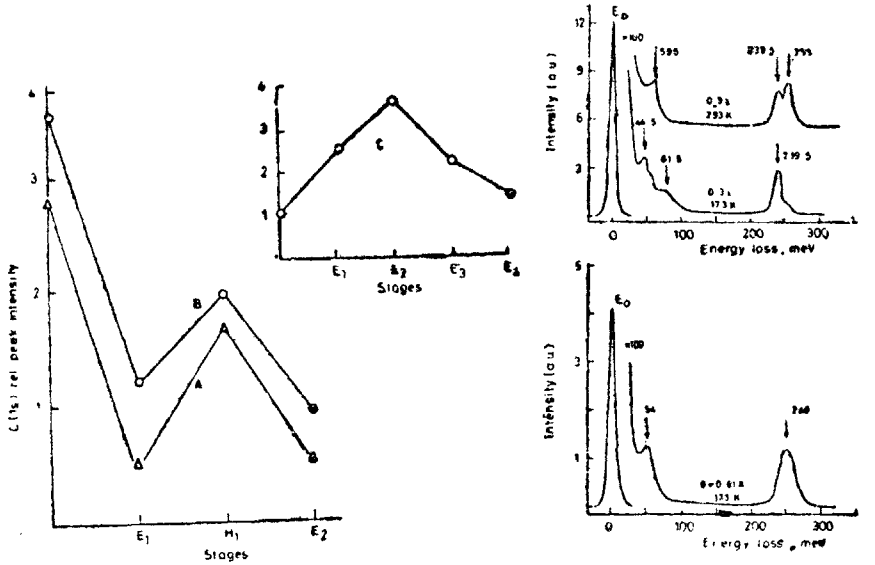


FIG. 23. Variation of the relative intensity of C(1s) band during the various heating (H_1) and etching (E_1, E_2, E_3....) treatments. (*A*) iron; (*B*) cobalt; and (*C*) nickel.

FIG. 24. Vibrational ELS spectra of CO adsorbed on Ni(100) with E_P = 1.4 eV (from Andersson, 1977). The peaks in the region 40–60 meV are due to Ni-C stretching and those around 240 meV are due to C-O stretching vibrations.

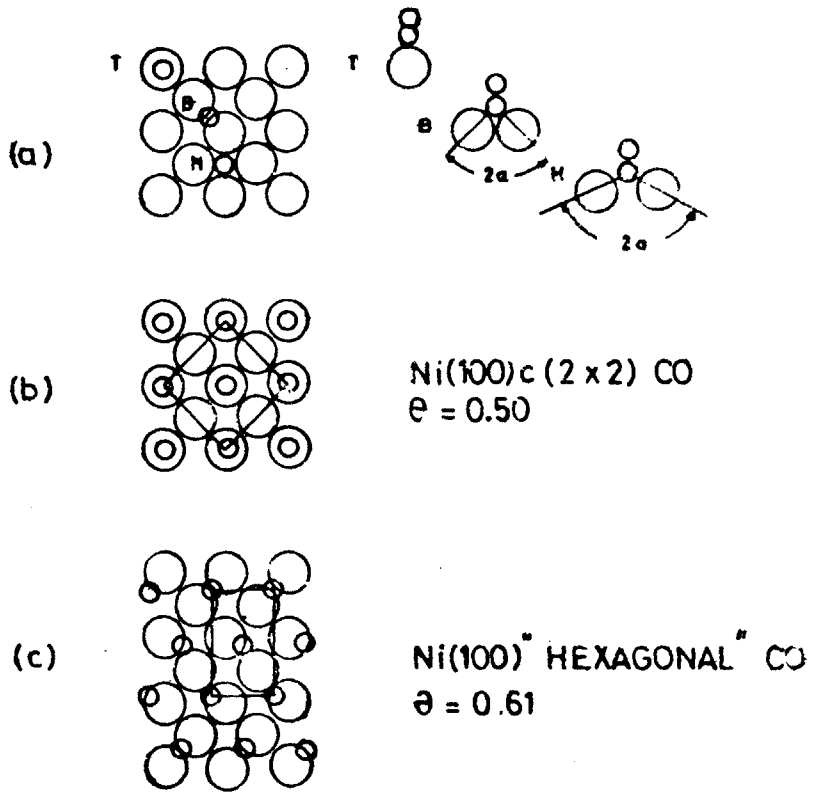


FIG. 25. Models for CO adsorption on Ni(100) surface (from Andersson, 1977).

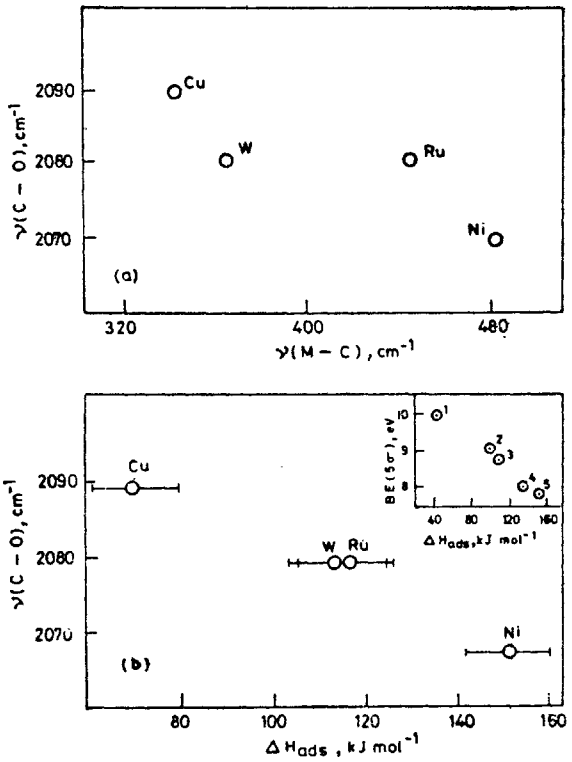


FIG. 26(*a*). Relation between C-O and metal—carbon (M-C) stretching frequencies for CO adsorbed on metal (100) surfaces.

FIG. 26(*b*). Relation between C-O stretching frequency and the heat of adsorption of CO on various metal (100) surfaces. Inset shows variation of the binding energy of 5σ (CO) orbital with heat of adsorption for CO adsorbed on: 1, Cu(311); 2, Pt(100); 3, W(100) and Ni(111); 4, Ni(110); and 5, Pd(100) and Ni(100).

perature, these peaks disappear due to dehydrogenation. ELS studies of adsorbed ethylene (Ibach & Lehwald, 1979) clearly show evidence for saturated species involving rehybridization of the molecule; thus, the C-H stretching frequency of adsorbed C_2H_4 is found around 2945 cm^{-1} (see Fig. 29). A model for the chemisorption of C_2H_4 on Pt(111) consistent with the presence of $—CH=CH_2$ species at room temperature has also been suggested (Demuth, 1980). All the energy loss data on the adsorption of C_2H_4 on Ni(111) seem to be consistent with a di-σ bonded molecule, with a C_s or C_1 symmetry at high coverages (Lehwald & Ibach, 1979). The estimated π-bond order of adsorbed C_2H_4 molecules are less than 0.5.

Adsorption of a number of hydrocarbons including acetylene and benzene have been studied by employing both UVPS and ELS techniques. From the available ELS data, we find that the C-H and C-C sretching frequencies linearly decrease with increase in the metal-carbon stretching frequencies (Fig. 30). One can also estimate the changes in the C-C π-bond order of these molecules on adsorption (Fig. 31).

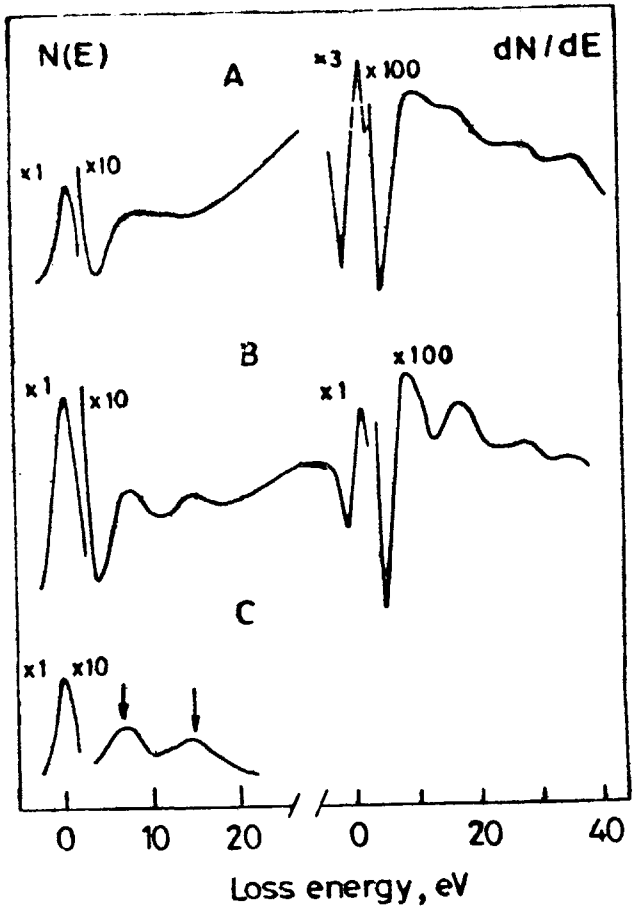


FIG. 27. Electronic excitations due to CO adsorbed on Pt(100) as seen by ELS with E_P = 70 eV (*a*) clean surface; (*b*) saturated with CO; and (*c*) difference spectra (from Netzer *et al.*, 1977).

Such plots can be employed to understand the nature of rehybridization of these molecules adsorbed on surfaces. It can be seen from Fig. 30 that the C-C π-bond orders of the various adsorbed molecules are lower than in free state.

Adsorption of different types of molecules on metals and other surfaces have been studied and I shall not be in a position to discuss them at length. We shall, however, briefly examine one or two instances to illustrate the nature of spectra obtained in these cases. UVPS studies in the valence region can clearly distinguish physical adsorption as distinct from chemisorption. As one would expect, molecules chemisorb on surfaces giving rise to selective shifts of peaks due to orbitals involved in bonding. UVPS peaks due to adsorbent are unaffected by condensed gases; physical adsorption only results in a small relaxation shifts of the peaks due to the adsorbate (Spicer *et al.*, 1976). Chemisorption, on the other hand, gives rise to

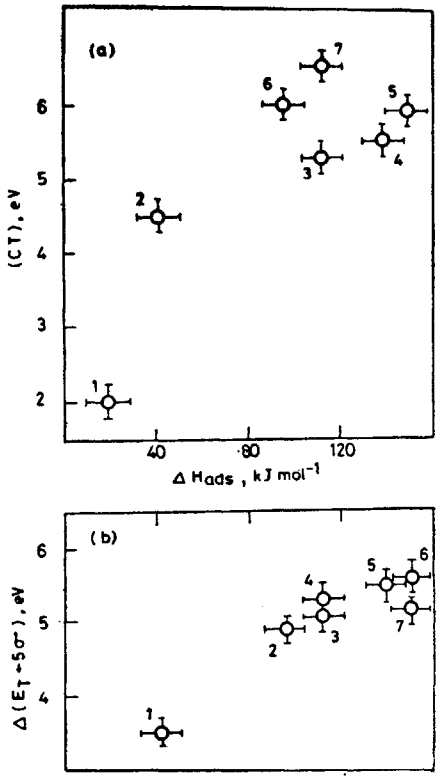


FIG. 28

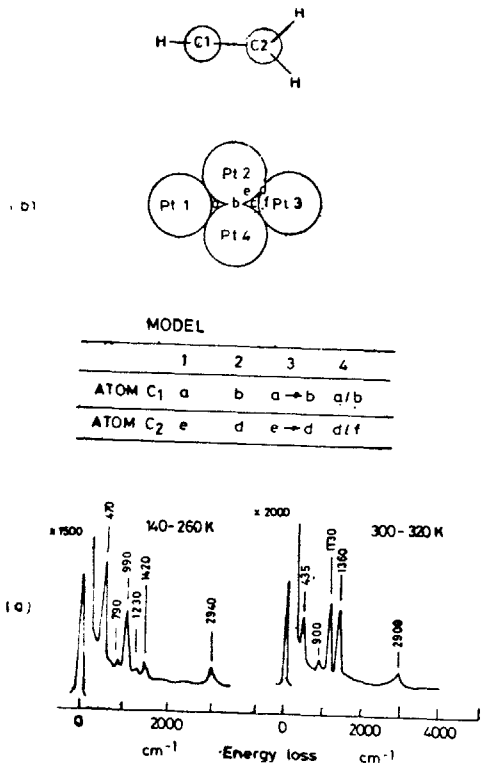


FIG. 29

FIG. 28(*a*). Relation between the metal d-π*(CO) charge-transfer energy and heat of adsorption for CO adsorbed on metals: (1) Ag(111); (2) Cu(311); (3) W(100); (4) Ni(110); (5) Ni(100); (6) Pt(111); and (7) Ni(111).

FIG. 28(*b*). Relation between the π* (CO) orbital energy and the heat of adsorption for CO adsorbed on metals: (1) Cu(311); (2) Pt(111) and Pt(100); (3) W(100); (4) Ni(111); (5) Ni(110); (6) Pd(100); and (7) Ni(100).

FIG. 29. Vibrational ELS of ethylene adsorbed on Pt(111) alongwith model for adsorption (from Ibach & Lehwald, 1979; and Demuth, 1980).

large shifts of peaks as illustrated by the spectrum of benzene on Ni (111) shown in Fig. 32.

Interaction of organic molecules with transition metal surfaces could be studied by both UVPS and XPS. In Fig. 33, we have shown the He II UVPS of methylamine adsorbed on polycrystalline iron. In the inset, X-ray photoelectron spectra of N (1*s*) bands under similar conditions are also shown. In Fig. 34, the C (1*s*) and O (1*s*) spectra of acetaldehyde adsorbed on iron is shown. New peaks due to adsorbed species develop with increasing exposures of the adsorbate. With increase in temperature of the substrate, some of the peaks disappear while some others get shifted.

Auger Spectra of Adsorbed Species

Auger spectra show interatomic transitions and relaxation effects due to adsorption of gases (Salmerón *et al.*, 1976). Spectra of a number of gases adsorbed

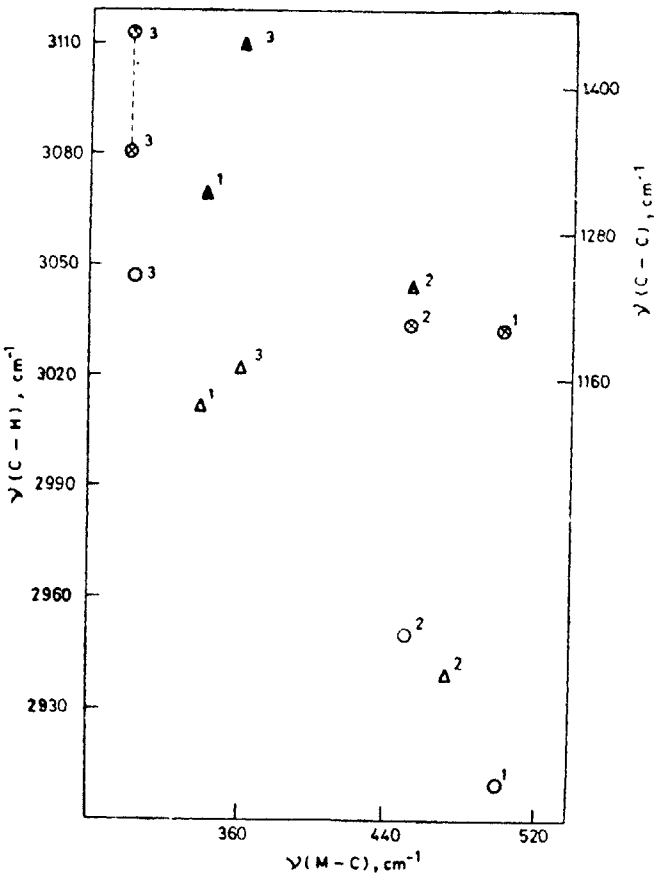


FIG. 30. Variation of C-H and C-C vibrational frequencies of adsorbed hydrocarbons with metal-carbon stretching frequencies : (1) acetylene; (2) ethylene; and (3) benzene; Circle refers to Ni(111) and triangle refers to Pt(111) surfaces; symbols with a cross refer to C-C vibrations and without a cross refer to C-H vibrations.

on transition metals show interatomic transitions involving deexcitation of the initial adsorbate core hole from electrons in the valence band of the adsorbent. These transitions are similar to those found in ion neutralization spectroscopy (INS) and are essentially unperturbed by final state effects. Intra-atomic transitions, however, show the same type of perturbation normally found in Auger spectra due to localised valence bands such as *d* electrons in transition metals. In Fig. 35, we have shown the KVV Auger spectrum of N_2 adsorbed on metals to illustrate inter-atomic transitions (X_1 and X_2). From a study on the adsorption of O_2 and CO on Al (Katayama *et al.*, 1979), the inter-atomic Auger transitions of the type Al(L) O(L) O(L) and Al(L) C(L) C(L) have been obtained indicating Al-O and Al-C bond formation respectively. In Fig. 36, we have shown typical Auger spectra of CO adsorbed on Al where P_1, P_2 and P_3 arise from Al(L) O(L) O(L) and Y_1 and Y_2 arise from Al(L) C(L) C(L) transitions.

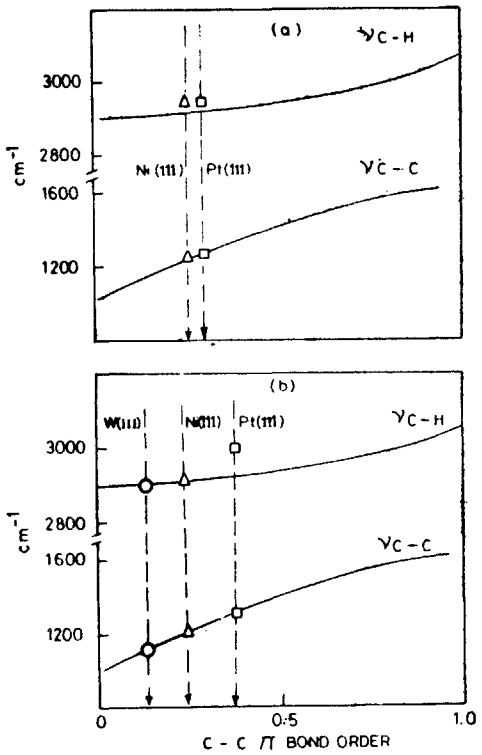


FIG. 31. Plot of C-C and C-H frequencies against C-C π bond order in gas molecules. From the plot, the change in C-C π-bond order of molecules on adsorption to metal surfaces could be determined.

The potential of Auger spectroscopy for chemical state analysis of adsorbed species has gained some recognition recently. The use of Auger line shapes to identify surface chemical species has been reported by several workers (Rye *et al.*, 1979). The unique chemical information that is contained in Auger spectra of molecular species derives mainly from the very localised character of the core hole. In a core-valence-valence Auger transition, the initial core hole probes the local valence electron distribution. The measured relative intensity and line shape are therefore sensitive to changes in this distribution. From the point of view of surface science, data for chemisorbed monolayer (submonolayer) coverages is of great interest in order to probe changes in intramolecular bonding on adsorption and to determine the coupling of electronic states of the substrate with those of the adsorbate. Experimentally, however, instrumental broadening and other factors distort Auger line shapes and an appropriate response function has to be employed to deconvolute the data. Such deconvoluted Auger spectra of monolayer coverages of NH_3 have been reported recently (Campbell *et al.*, 1980).

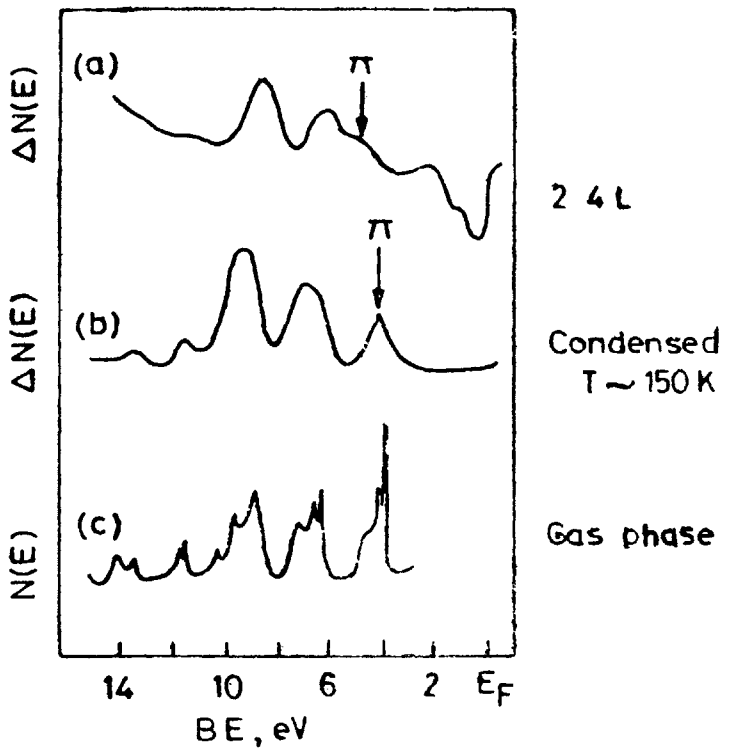


FIG. 32(*a*). Difference spectrum of benzene adsorbed on Ni(111) showing selective interaction of π-orbital with surface.
FIG. 32(*b*). Spectrum of benzene condensed on Ni(111); and
FIG. 32(*c*). Gas phase spectrum of benzene.

IETS

Inelastic electron tunnelling spectroscopy can be used to investigate chemisorption of gases on metallic atoms or clusters evaporated on to the oxide film. This experimental configuration serves to model industrially important supported metal catalysts. Thus, at a statistical coverage of Rh of ½ Å, CO chemisorbs (on Rh/Al_2O_3) with the appearance of a single Rh-CO mode at low frequency and a Rh C=O mode at higher frequency (Hansma *et al.*, 1976). At higher coverages (4Å) five modes are seen at 408, 454 and 580 cm^{-1} (Rh-C), 1730 and 1935 cm^{-1} (Rh-C=O). Evidently, at higher coverages, clustering of Rh occurs and CO may chemisorb both in 'linear' and 'bridged' configurations. The results are shown in Fig. 37.

Molecular Beam Scattering

Yet another method for the study of dynamics gas-surface interactions and the kinetics of elementary surface reactions is the molecular beam surface scattering technique. A well-collimated beam of molecules of known velocity impinges on the surface at variable angles of incidence. UHV is required to maintain surface cleanli-

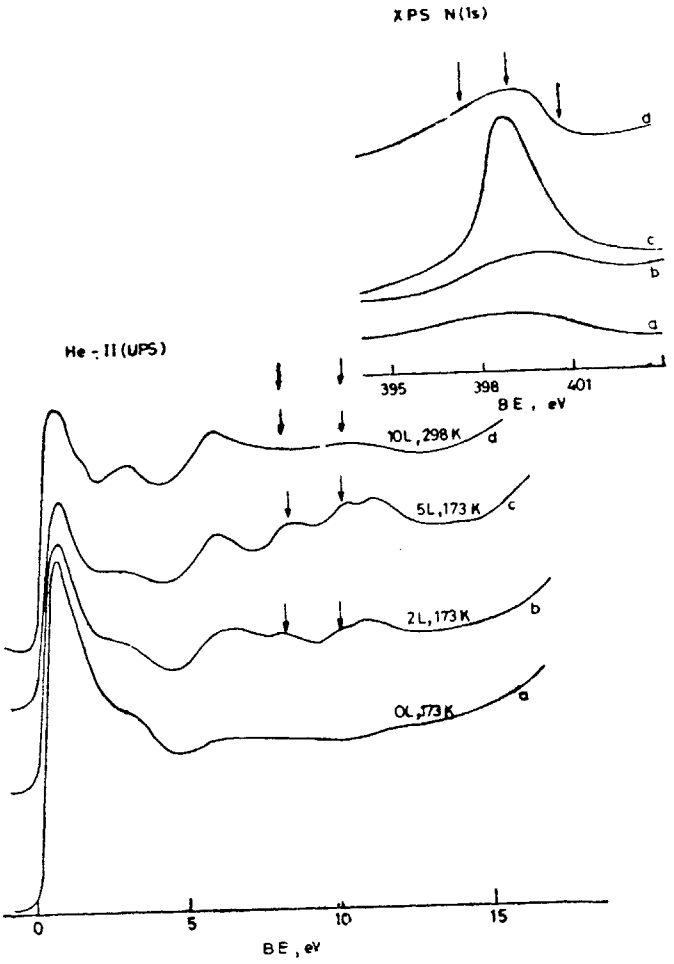


FIG. 33. He-II spectra of Fe-CH_3NH_2 system showing development of the valence bands. Inset shows XPS spectra of N(1*s*) levels under the same conditions of temperature and amine exposure.

ness during the experiment. The exciting molecules after scattering are detected in a mass spectrometer that is rotatable to detect the angular distribution by suitable chopping of the incident and the existing molecular beams (Fig. 38*a*). The reaction probability upon a single collision with the surface is readily determined from the experimental data. Using this technique, the exchange reaction

$$H_2 + D_2 \rightleftharpoons 2\,HD$$

was studied as a function of the angle of incidence of the beam of reactants on various stepped Pt surfaces. The reaction probability was found to depend markedly on the direction of approach of the reactants to the stepped surface structure (Fig. 38*b*) (Somorjai, 1979).

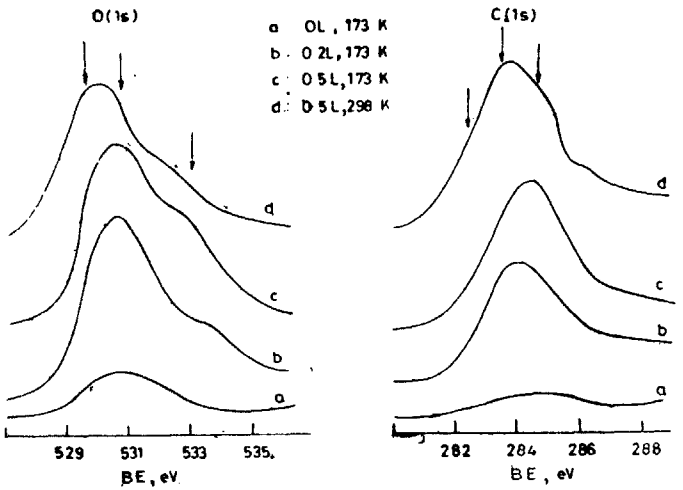
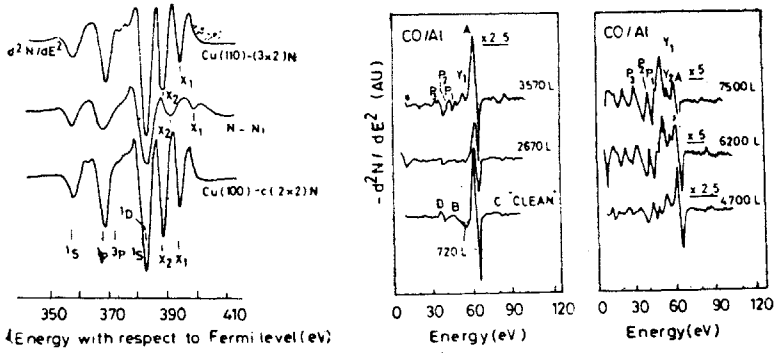


FIG. 34. XPS of Fe-CH_3-CHO system showing the development of O(1*s*) and C(1*s*) bands under different conditions of temperature and aldehyde exposure.

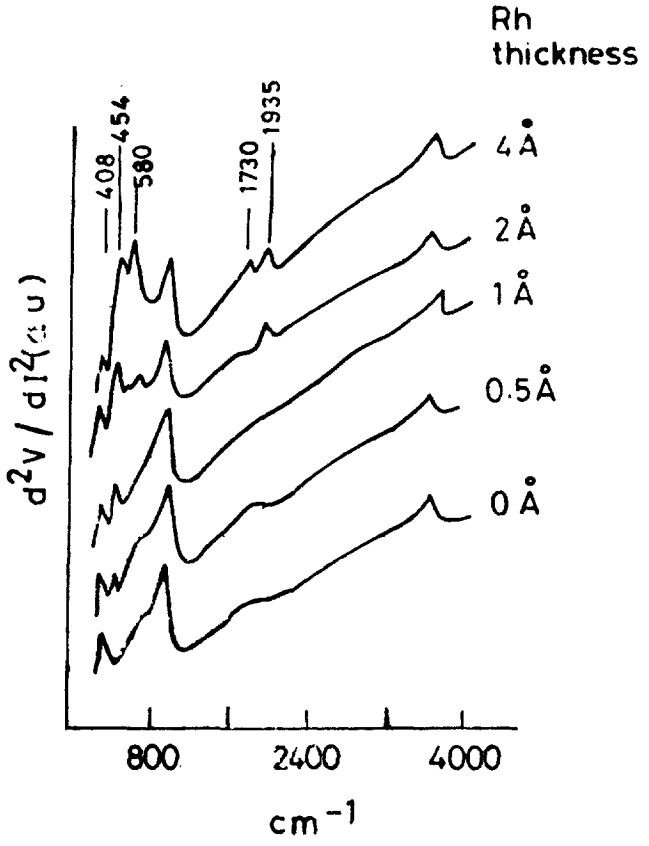


(35) (36)

FIG. 35. Auger spectra showing interatomic transitions of N_2 adsorbed on Cu and Ni surfaces (from Salmeron *et al.*, 1976).

FIG. 36. Auger spectra of CO adsorbed on Al showing interatomic transitions (from Katayama *et al.*, 1979).

The technique is also useful in obtaining structural information during adsorbate-substrate interaction. Adsorption of H_2 on Ni (110) surface at 100 K causes the formation of a (1×2) LEED pattern. With a Helium beam parallel to (001) azimuth angular distributions of the adsorbate-substrate system are as shown in Fig. 39. Based on the above experiments, a structural model with H-atoms located in two-fold bridge sites was proposed (Ertl, 1979).



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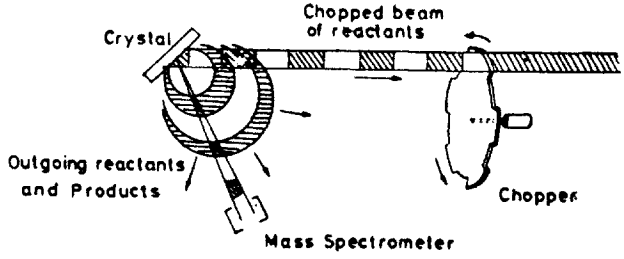

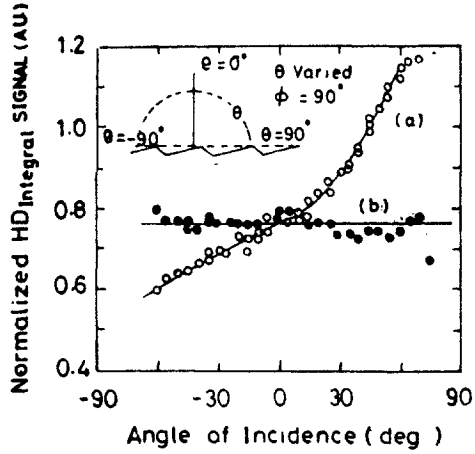

(38)

FIG. 37. Inelastic electron tunneling spectra of CO adsorbed on Rh/Al_2O_3 (from Hansma *et al.*, 1973).

FIG. 38(*a*). Schematic diagram of a molecular beam scattering experiment.

FIG. 38(*b*). Variation of reaction probability to produce H-D upon single scattering of a mixed H_2-D_2 molecular beam on a stepped Pt surface as a function of angle of incidence (1) step edge perpendicular to incident beam and (2) projection of beam on the surface is parallel to the step edges (from Somorjai, 1979).

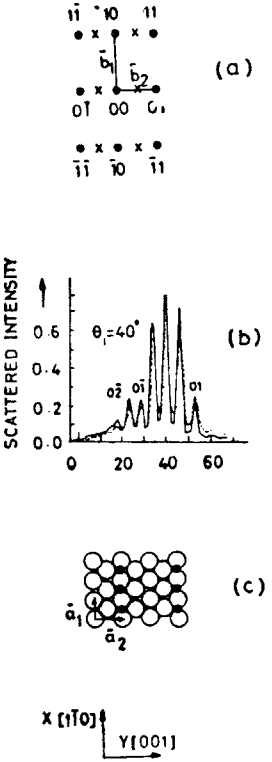

FIG. 39(*a*). Diffractive scattering of He (λ 0.57 Å) on a $p(1 \times 2)$-H overlayer on Ni(110) at 100 K. Sketch of LEED pattern.

FIG. 39(*b*). Intensity of scattered He as a function of scattering angle; the primary beam parallel to (001) azimuth at θ 40°

FIG. 39(*c*). Proposed structure model with H atoms in two fold bridge sites (from Ertl, 1979).

CONCLUDING REMARKS

Electron spectroscopy and cognate techniques have made a tremendous impact on the study of surfaces. It is always most beneficial if more than one techniqe is employed in an investigation. Spectroscopic methods in conjunction with LEED provide information which can be directly related to surface structure.

In the years to come, electron spectroscopic techniques will undoubtedly be employed to greater advantage. Synchrotron radiation has already made photoelectron spectroscopy a more powerful technique. In the last few years, ELS has been found to be immensely useful to study adsorbed molecules. I have no doubt ELS, UVPS, Auger and related studies will be used in the future more effectively to understand catalysis and such complex phenomena. Studies carried out on real systems (real surfaces of catalysts and so on under conditions close to real situations) will certainly be more useful, but there are some limiting problems like the vacuum employed in electron spectroscopy. Another aspect with some potential is the use of molecular beams to the study of surfaces.

ACKNOWLEDGEMENT

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REFERENCES

Andersson, S. (1977) Vibrational excitations and structure of CO adsorbed on Ni (100). *Solid State Commn.*, **21**, 75–81.

Campbell, C. T., Rogers Jr., J. W., Hance, R. L., and White, J. M. (1980) Auger spectra of ammonia on Al and oxidised Al. *Chem. Phys. Lett.*, **69**, 430–434.

Carlson, T. A. (1975) *Photoelectron and Auger Spectroscopy*. Plenum, London.

Demuth, J. E. (1980) On the nature of species formed from the reaction of ethylene on Pt (111) at room temperature. *Surf. Sci.*, **93**, L82–88.

Eastman, D. E., and Freeouf, J. L. (1974) Photoemission partial yield measurements of unoccupied intrinsic surface states of Ge (111) and Ga As (110). *Phys. Rev. Lett.*, **33**, 1601–1604.

Eastman, D. E., and Grobman, W. D. (1972) Photoemission densities of intrinsic surface states for Si, Ge and Ga As. *Phys. Rev. Lett.*, **28**, 1378–1381.

Ertl, G. (1979) Scattering of atomic and molecular beams at metal surfaces. *Surf. Sci.*, **89**, 525–539.

Ferrer, S., and Somorjai, G. A. (1980) UPS and XPS studies of the chemisorption of O_2, H_2 and H_2O on reduced and stoichiometric $SrTiO_3$ (111) surfaces: the effects of illumination. *Surf. Sci.*, **94**, 41–56.

Gartland, P. O., and Slagsvold, B. J. (1978) Angular resolved photoemission from intrinsic surface states on Al (100). *Solid State Commn.*, **25**, 489–492.

Green, J. C. (1977) Photoelectron spectroscopy : study of valence bands in solids. *Ann. Rev. Phys. Chem.*, **28**, 161–183.

Hansma, P. K., Kaska, W. C., and Laine, R. M. (1976) Inelastic electron tunneling spectra of CO chemisorbed on alumina supported transition metals. *J. Am. chem. Soc.*, **98**, 6064-6065.

Ibach, H. (1977) Comparison of cross sections in high resolution electron energy loss spectroscopy and infrared reflection spectroscopy. *Surf. Sci.*, **66**, 56-66.

Ibach, H., and Lehwald, S. (1979) Identification of surface radicals by vibration spectroscopy reactions of C_2H_2, C_2H_4 and H_2 on Pt (111). *J. Vac. Sci. and Tech.*, **15**, 407–415.

Ibach, H., and Rowe, J. E. (1974) Electron orbital energies of oxygen adsorbed on silicon surfaces and of silicon dioxide. *Phys. Rev.*, **B10**, 710–718.

Jagannathan, K., Srinivasan, A., Hegde, M. S., and Rao C. N. R. (1980) Interaction of CO with transition metal surfaces. *Surf. Sci.*, **97** (*in print*).

Jagannathan, K., Srinivasan, A., and Rao, C. N. R. (1981) An XPS study of the surface oxidation states of metals in some oxide catalysts. *J. Catal.* (*in print*).

Joyner, R. W., and Roberts, M. W. (1975) "Auger electron spectroscopy and its applications in surface chemistry" in: *Surface and Defect Properties of Solids*. Chemical Society, London, **4**, 68–102.

Katayama, Y., Kobayashi, K. L. I., and Shiraki, Y. (1979) Interatomic Auger transitions during the interaction of O_2 and CO with Al. *Surf. Sci.*, **86**, 549–554.

Lehwald, S., and Ibach, H. (1979) Decomposition of hydrocarbons on flat and stepped Ni (111) surfaces. *Surf. Sci.*, **89**, 425–445.

Lloyd, D. R., Quinn, C. M., and Richardson, N. V. (1977) Angle resolved UPS of clean surfaces and surfaces with adsorbed layers, in: *Surface and Defect Properties of Solids*. Chem. Soc., London, **6**, 179–217.

Madhusudan, W. H., Sheelavathi Kollali, Sarode P. R., Hegde, M. S., Ganguly, P., and Rao., C. N. R. (1979) Transition metal oxide perovskites by photoelectron and X-ray absorption spectroscopy. *Pramana*, **12**, 317–329.

Minachev, Kh. M., Antoshin, G. V., and Shpiro, E. S. (1978) Application of PES in the study of catalysis and adsorption. *Russian Chem. Rev.*, **47**, 1111–1132.

Netzer, F. P., Willie, R. A., and Matthew, J. A. D. (1977) Electron losses for adsorbed CO. *Solid State Commn.*, **21**, 97–100.

Page, P. J., Trimm, D. L., and Williams, P. M. (1974) Adsorption of gases on polycrystalline Ni films studied by X-ray and ultraviolet photoelectron spectroscopy. *J. chem. Soc. Farad. Trans., I*, **70**, 1769–1781.

Plummer, E. W., Waclawski, B. J., and Vorburger, T. V. (1974) Photoelectron spectra of the decomposition of ethylene on W (110). *Chem. Phys. Lett.*, **28**, 510–551.

Rao, C. N. R., Sarma, D. D., Vasudevan, S., and Hegde, M. S. (1979) Study of transition metal oxides by photoelectron spectroscopy. *Proc. R. Soc. London*, **A367**, 239–252.

Rao, C. N. R., Sarma, D. D., and Hegde, M. S. (1980) A novel approach to the study of surface oxidation states and oxidation of transition metals by Auger electron spectroscopy. *Proc. R. Soc. London*, **A370**, 269–282.

Rao, C. N. R., Srinivasan, A., and Jagannathan, K. (1981) Study of adsorbed molecules by electron energy loss spectroscopy. *Int. Rev. Phys. Chem. (to be published).*

Rao, C. N. R., and Sarma, D. D. (1980) in : *Science and Technology of Rare Earths Eds.*, Subbarao, E. C., & Wallace, W. E. Academic Press, New York.

Rao, C. N. R., and Hegde, M. S. (1981) in '*Spectroscopy of Solids*'. Pergamon Press, Oxford (*in press*).

Rye, R. R., Houston, J. E., Jennison, D. R., Madey, T. E., and Holloway, P. H. (1979) Chemical information in Auger spectroscopy. *Ind. Engng. Chem. Prod. Res. Develop.*, **18**, 2–7.

Salmeron, M., Baro, A. M., and Rojo, J. M. (1976) Interatomic transitions and relaxation effects in Auger spectra of several gas adsorbates on transition metals. *Phys. Rev.*, **B13**, 4348–4363.

Sarma, D. D., Hegde, M. S., and Rao, C. N. R. (1980) An Auger study of the surface oxidation of zinc. *Chem. Phys. Lett., (in print).*

Sarma, D. D., and Rao, C. N. R. (1980) XPES studies of oxides of second and third row transition metals including rare earths. *J. Electron Spectrosc. Rel. Phenom.*, **20**, 25–46.

Sheppard, N., and Nguyen, T. T. (1978) The vibrational spectra of CO chemisorbed on the surfaces of metal catalysts—a suggested scheme of interpretation in : *Adv. in Infrared and Raman Spec. Eds.* : Clark, R. J. H., and Hester, R. E. Z. Heyden, London, **5**, 67–148.

Somorjai, G. A. (1979) Catalysis and surface science. *Surf. Sci.*, **89**, 496–524.

Spicer, W. E., Yu, K. Y., Lindau, I., Pianetta, P., and Collins, D. M. (1975) UV photoemission spectroscopy of surfaces and surface sorption in : *Surface and Defect Properties of Solids.* Chem. Soc., London, **5**, 103–161.

Srinivasan, A., Jagannathan, K., Hegde, M. S., and Rao, C. N. R. (1979) Studies of surface oxidation of iron, nickel and copper by X-ray photoelectron spectroscopy. *Indian J. Chem.*, **18A**, 463–470.

Szalkowski, F. J., and Somorjai, G. A. (1974) Auger electron spectroscopic investigations of chemical shifts in some vanadium compounds. *J. chem. Phys.*, **41**, 2064–2070.

Vasudevan, S., Hegde, M. S., and Rao, C. N. R. (1979) XPES and UVPES studies of iron oxides. *J. Solid State Chem.*, **29**, 253–257.

Wagner, L. F., and Spicer, W. E. (1972) Observation of a band of Si surface states containing one electron per surface atom. *Phys. Rev. Lett.*, **28**, 1381–1384.

Watson, R. E., and Perlmann, M. L. (1975) XPS application to metals and alloys. *Structure and Bonding*, **24**, 83–132.

Weinberg, W. H. (1978) Inelastic electron tunneling spectroscopy: a probe of the vibrational structure of surface species. *Ann. Rev. phys. Chem.*, **29**, 115–139.

Wertheim, G. K. (1978) X-ray photoelectron spectroscopy of solids in : *Electron and Ion Spectroscopy of Solids.* (*Eds* : Fiermans, L., *et al.*). Plenum, New York.

Wertheim, G. K. (1979) The intermediate valence state in rare earth compounds, bulk and surface manifestations. *J. Electron Spectrosc. Rel. Phenom.*, **15**, 5–14.