

Electron Spectroscopy

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1 Introduction

Electron spectroscopy (e.s.) may be defined as the study of electrons emitted when matter is irradiated with photons or particles. Figure 1 shows the funda-

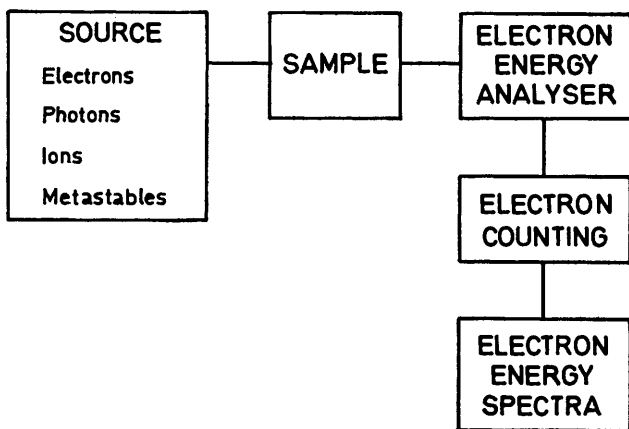


Figure 1 *The fundamental e.s. experiment*

mental e.s. experiment in which these electrons are both analysed according to their kinetic energies and counted. The resulting plot of count-rate *vs* energy is known as the 'electron energy spectrum'. The technique encompasses several closely related but distinct branches; these are ultraviolet photoelectron spectroscopy (p.e.s.),¹ X-ray photoelectron spectroscopy, more commonly known as

¹ D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy', Wiley, London, 1970.

electron spectroscopy for chemical analysis (ESCA),² Penning ionization spectroscopy (p.i.s.),³ Auger spectroscopy (a.s.),⁴ ion neutralization spectroscopy (i.n.s.),⁵ and electron impact energy loss spectroscopy (e.i.s.).⁶ After an introduction to their relevance in chemistry, the principles of the techniques and the information that can be derived from them will be discussed in more detail.

The bombarding radiations in ESCA and p.e.s. are X-rays and monochromatic photons in the vacuum-u.v., respectively. The kinetic energies of the ejected electrons differ according to their orbitals of origin, and these energies may be related to the different orbital ionization potentials of the sample atom or molecule. Clearly, measurements such as these are of great importance in the study of electronic configurations of molecules, and for establishing experimental data which can be compared with molecular parameters calculated by quantum mechanical methods. X-Rays can eject electrons from both inner-shell and valence-shell orbitals, whereas vacuum-u.v. photons can only eject those in valence-shell orbitals. The experimental result of this is that X-ray work is more useful for the core electrons, while vacuum-u.v. work is useful only for the valence shell. (In general, valence-shell orbitals within a narrow energy range are unresolved in an X-ray excited spectrum.) Therefore, ESCA and p.e.s. are complementary in that the X-ray spectrum can reveal the atomic make-up of the sample (different atoms have distinctive core-electron binding energies), whereas the vacuum-u.v. spectrum can give information about the valence shell, and in particular about molecular bonding and substituent, isomeric, and steric effects. Furthermore, both techniques appear to have considerable potential as tools for the analytical chemist.

The use of metastable atoms (*e.g.* He 2^1S and 2^3S) as ionizing particles for electron spectroscopy (p.i.s.) gives results similar to those obtained with vacuum-u.v. photon sources. In addition, p.i.s. yields information on short-lived complexes formed between the bombarding metastable and the target molecule.

In the Auger process, electrons are detached from atoms or molecules in a secondary step occurring after initial electron or X-ray bombardment. Such electrons are therefore observed in a standard ESCA spectrometer. The peaks present in an a.s. spectrum can imply, in a similar manner to those in an ESCA spectrum, that certain atoms are present in the emitting material. At present, the principal application of a.s. is as a sensitive technique for surface analysis. I.n.s. is a branch of a.s. in which rare-gas ions are used in place of electrons or photons.

In e.i.s. monochromatic electrons are allowed to pass through a sample, and the energy spectrum of the emergent electrons is measured. The spectrum reveals

² (a) K. Siegbahn *et al.*, 'ESCA-Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy', Almqvist and Wiksells, Uppsala, 1967; (b) K. Siegbahn *et al.*, 'ESCA Applied to Free Molecules', North-Holland, Amsterdam, 1969.

³ V. Čermák, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2739.

⁴ (a) L. A. Harris, *Analyt. Chem.*, 1968, **40**, 24A; (b) C. C. Chang, *Surface Science*, 1971, **25**, 53.

⁵ H. D. Hagstrum, *Phys. Rev.*, 1966, **150**, 495.

⁶ R. S. Berry, *Ann. Rev. Phys. Chem.*, 1969, **20**, 357.

discrete peaks where the difference in energy between the incident and emergent beam is equal to an excitation energy of the molecule being studied. The information obtained is similar to that given by conventional optical absorption spectroscopy. Additionally, e.i.s. spectra are useful for complementing and interpreting p.e.s. spectra.

2 Electron Energy Analysers

In most of the commercially available electron spectrometers, the electron beam enters the analyser through a narrow slit in the target or ionization chamber. Focusing lenses are sometimes also used. Once inside the analyser, the electrons come under the influence of a deflecting magnetic or electrostatic field, whereupon they describe different paths depending on their energies. For a particular value of the deflecting field, only electrons within a small energy range describe appropriate paths to pass through the exit slit of the analyser. To obtain an electron energy spectrum, the electron flux emerging from this slit is continuously recorded as the deflecting field is changed, thereby bringing electrons of appropriate energy to a focus in turn. Analysers of this and other types have been reviewed recently.^{1,7}

3 Ultraviolet Photoelectron Spectroscopy

In a p.e.s. instrument, a sample, normally in the vapour phase, is irradiated with monoenergetic vacuum-u.v. photons ($\lambda < 2000 \text{ \AA}$). These photons are usually generated in a microwave or d.c. discharge lamp; the helium lamp, which produces a copious flux of 584 \AA photons ($h\nu = 21.22 \text{ eV}$), is most common.⁸ The ionization chamber has two ports, one to admit photons from the lamp, the other to admit sample. A slit a few millimetres wide also permits electrons ejected from the sample molecules to enter the energy analyser (see above). Sample vapour can likewise escape from the ionization chamber through this slit into the chamber housing the analyser, from which it is pumped away. However, a sample flow system, controlled by a needle valve, can be used to maintain a constant pressure in the ionization chamber. The chamber containing the electron energy analysis and detection system is maintained below a pressure of *ca.* 1×10^{-4} Torr by a diffusion pump. A p.e.s. spectrometer is illustrated schematically in Figure 2.

Any photoelectron ejected from a sample has kinetic energy, E , which obeys the Einstein equation

$$E = h\nu - I_1 - \Delta E_{vib} - \Delta E_{rot} \quad (1)$$

where $h\nu$ is the energy of the bombarding photon, I_1 is one of the ionization

¹ (a) D. W. Turner, *Adv. in Mass Spectrometry*, 1968, **4**, 755; (b) H. Hafner, J. A. Simpson, and C. E. Kuyatt, *Rev. Sci. Instr.*, 1968, **39**, 33; (c) H. Z. Sar-El, *ibid.*, 1970, **41**, 561.

⁸ (a) D. C. Frost, C. A. McDowell, and D. A. Vroom, *Phys. Rev. Letters*, 1965, **15**, 612; (b) J. A. R. Sampson, 'Techniques of Vacuum Ultraviolet Spectroscopy', Wiley, New York, 1967; (c) D. W. Turner, *Proc. Roy. Soc.*, 1968, **A307**, 15; (d) C. R. Brundle and M. B. Robin in 'Determination of Organic Structures by Physical Methods', ed. F. Nachod and G. Zuckerman, Academic Press, New York, 1971, Vol. 3, p. 1.

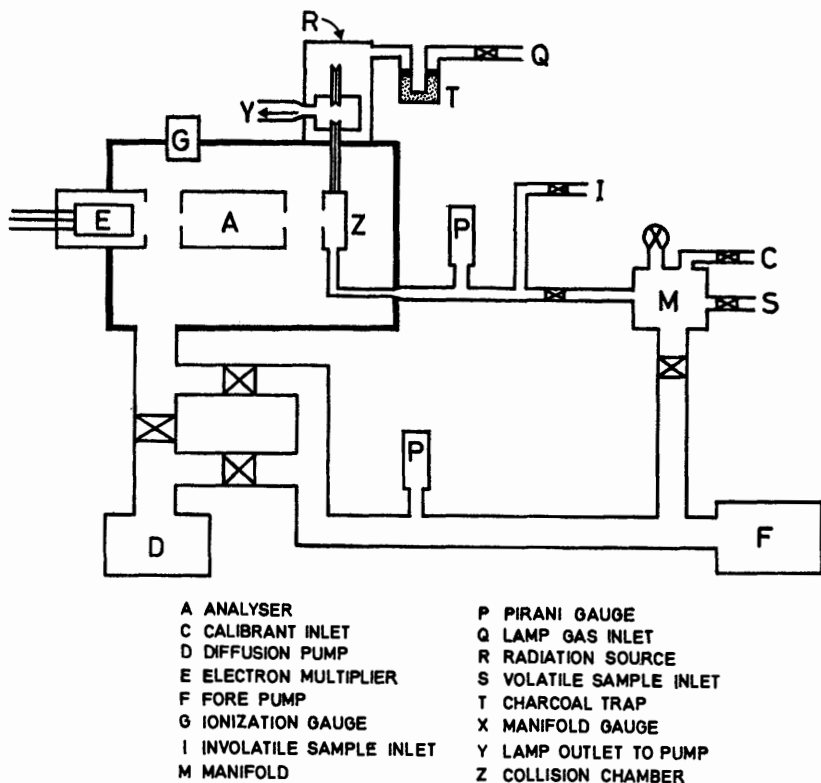


Figure 2 Schematic view of a typical p.e.s. spectrometer

potentials of the molecule, and ΔE_{vib} and ΔE_{rot} represent the amount of vibrational and rotational excitation energy imparted to the molecular ion formed in the ionizing act. Energy analysis of the electrons leads to a photoelectron spectrum. Different bands in the spectrum relate essentially to the ejection of electrons from the different valence-shell orbitals. Fine structure may be present and is due to the excitation of vibrational and rotational motion in the molecular ions.^{1,8d,9}

The energy scale in published spectra is generally calibrated in terms of ionization potential given in electron volts (eV). This IP scale is more correctly an $(h\nu - E)$ scale, and is thus a measure of the total energy needed to bring about an ionization process, *i.e.* the sum of the energy required to overcome an orbital binding energy, plus any vibrational or rotational energy imparted to the ion produced ($I_1 + \Delta E_{vib} + \Delta E_{rot}$). The low IP onset of any band corresponds to a molecular ion being formed in its vibrational and rotational ground states

⁹ A. D. Baker, *Accounts Chem. Res.*, 1970, 3, 17.

($\Delta E_{vib} + \Delta E_{rot} = 0$), and gives the minimum energy needed to eject a particular electron from its parent orbital (the adiabatic IP*). Thus, the most straightforward application of p.e.s. is the measurement of IP's, or binding energies, characterizing electrons in different orbitals. All the IP's of an atom or molecule which are less than $h\nu$ can be measured from the different bands in a p.e. spectrum. Since IP's are the physical realities of orbital eigenvalues, considerable importance is attached to their values by those working in theoretical chemistry and on chemical bonding phenomena. Mulliken,¹⁰ addressing the Royal Society in 1969, summarized the impact made by p.e.s. in this area by these words: 'Photoelectron spectroscopy has already shown, and will continue to show, unique ability to see down into the depths of molecules. It has given a new reality to the idea of molecular orbitals, by determining quantitative values for their binding energies, and also by giving information about their bonding characteristics.'

It is the shapes of bands within p.e.s. spectra that provide information about the bonding characteristics of the orbitals to which they relate. This is discussed in greater detail elsewhere^{1,8d,9} and some examples will be given below, but briefly, broad bands indicate strongly bonding or antibonding character whereas narrow bands imply non-bonding or weakly bonding or antibonding character. Where fine structure is resolved, the spacings of the peaks give the frequencies of vibrational modes in the molecular ion (a spacing of 0.1 eV is equivalent to 806.57 cm⁻¹). Comparison of these frequencies with the corresponding molecular frequencies (measured by Raman or i.r. techniques) affords an additional indication of the bonding character of the electron removed. A lower frequency in an ionic state shows that a reduction in bond force-constant has taken place on ionization, implying that the ejected electron was bonding. Conversely, an increase in frequency suggests that the ejected electron was antibonding. Spectra of complex molecules provide hitherto unobtainable information on electronic effects, *e.g.* substituent effects, and provide a qualitative method of analysis.

Studies of atoms and simple diatomic and triatomic molecules featured prominently in the early years of the development of p.e.s. High-resolution spectrometers frequently enabled vibrational structure to be detected in bands. The bandshapes, ionic vibrational frequencies, and orbital IP's measured from the spectra allowed the electronic configurations of these molecules to be unambiguously assigned, and comparisons to be made with calculated orbital eigenvalues.¹ Two spectra of simple molecules illustrating different bandshapes are those of H₂ and N₂ (Figure 3). Both these spectra were obtained using 584 Å photons. The H₂ spectrum shows one band corresponding to the only occupied orbital (1sσ_g) of the hydrogen molecule. A long series of converging peaks stretches across the entire band. The IP value (15.45 eV) of the first peak gives the energy needed to eject an electron from H₂ and simultaneously form an

* In a few cases it may not be possible for a significant number of ions to be formed in the ground vibrational and rotational states (Franck-Condon principle, see ref. 1) in which case the lowest IP, as given by p.e.s., may be higher than the true adiabatic IP.

¹⁰ R. S. Mulliken, *Phil. Trans. Roy. Soc.*, 1970, **A268**, 3.

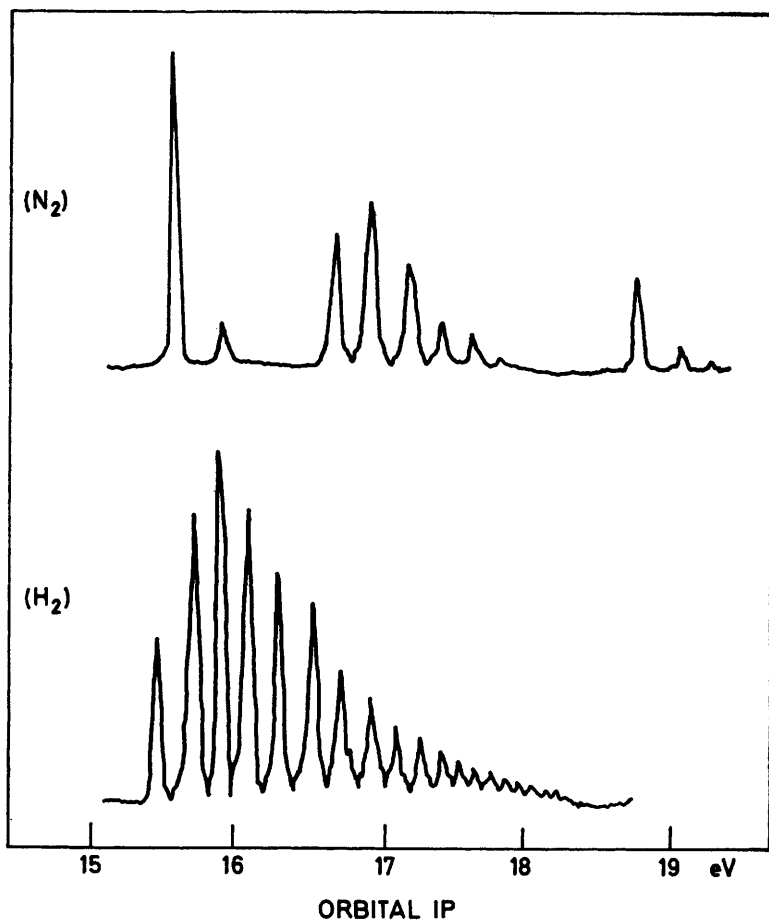


Figure 3 He 584 Å spectra of N_2 and H_2

H_2^+ ion in its ground vibrational state ($v' = 0$). The other peaks correspond to the production of H_2^+ ions in higher vibrational states. The fifteenth peak is only about 0.2 eV away from the energy needed to dissociate H_2^+ (18.2 eV). The vibrational frequency of the ionic state is 2240 cm^{-1} , compared to 4280 cm^{-1} of the H_2 molecule. This large reduction in frequency reflects the much diminished bond strength of the ion, indicating that a strongly bonding electron has been removed.

The N_2 spectrum shows three distinct bands. There are actually four orbitals in N_2 with IP's less than 21.22 eV*, but two of these (the two π -orbitals) are degenerate, and are represented by just one band in the spectrum. The first and

The electronic configuration of N_2 is $KK(2s\sigma_g)^2(2s\sigma_u)^(2p\pi_u)^4(2p\sigma_g)^2$.

third bands are similar, in that they both show a strong $v' = 0$ peak, and minimal associated structure. This implies that the equilibrium bond lengths in the N_2^+ ions formed by electron ejections from the first and third orbital levels of N_2 are both nearly equal to that in the molecule. These results suggest that the orbitals are almost non-bonding, and this is confirmed by the vibrational frequencies of the two ionic states being similar to that of the molecular state (Table 1). The second band in the spectrum corresponds to the two degenerate π -orbitals, The most intense peak in this band is associated with the formation of an N_2^+ ion in its $v' = 1$ level. (The energy required to produce the N_2^+ ion in this vibrational level is known as the vertical IP.) There are other peaks of moderate to low intensity for the formation of N_2^+ ions in much higher vibrational levels. This implies that the removal of a π -electron produces an ion with an equilibrium bond length appreciably different from that of the molecule. The considerable decrease in the N—N vibrational stretching frequency on removal of a π -electron (Table 1) confirms the bonding nature of the original orbital.

Table 1 Ionization potentials, electronic states, and observed vibrational frequencies of N_2 and N_2^+

Molecule or ion	State	Band in spectrum	Adiabatic IP/eV	Vibrational frequency/cm ⁻¹
N_2^+	$\tilde{X}^2\Sigma_g^+$	first	15.58	2150
N_2^+	$\tilde{A}^2\Pi_u$	second	16.69	1810
N_2^+	$\tilde{B}^2\Sigma_u$	third	18.76	2390
N_2	$X^1\Sigma_g^+$	—	—	2345

The conclusions above are in good accord with deductions based on MO theory, and provide the principles upon which the technique can be applied confidently to molecules that are too complex for a rigorous MO treatment. In this regard, it is instructive to compare the measured orbital IP's for N_2 with calculations of the orbital eigenvalues (Table 2). According to Koopmans'

Table 2 Calculated and experimental ionization potentials of N_2

Orbital	Observed vertical IP/eV	Koopmans' theorem IP/eV
$2p\pi_u$	16.98	17.10 ^a
$2p\sigma_g$	15.58	17.36 ^a
$2s\sigma_u$	18.76	20.92 ^a

^aP. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.*, 1966, **44**, 1973.

theorem,¹¹ an orbital IP is equal to the negative of the orbital eigenvalue. However, the calculation ignores the influence of other electrons in the molecule which cause an orbital IP to be less than the corresponding orbital eigenvalue. Nevertheless, as IP's relate to a real situation they are the more relevant to

¹¹ T. Koopmans, *Physica*, 1934, **1**, 104.

studies of bonding and substituent effects. Results for several diatomic and triatomic molecules have been discussed in detail elsewhere.¹²

Processes observed by p.e.s. are often represented as transitions between molecular and ionic states on a potential energy diagram. For example, Figure 4

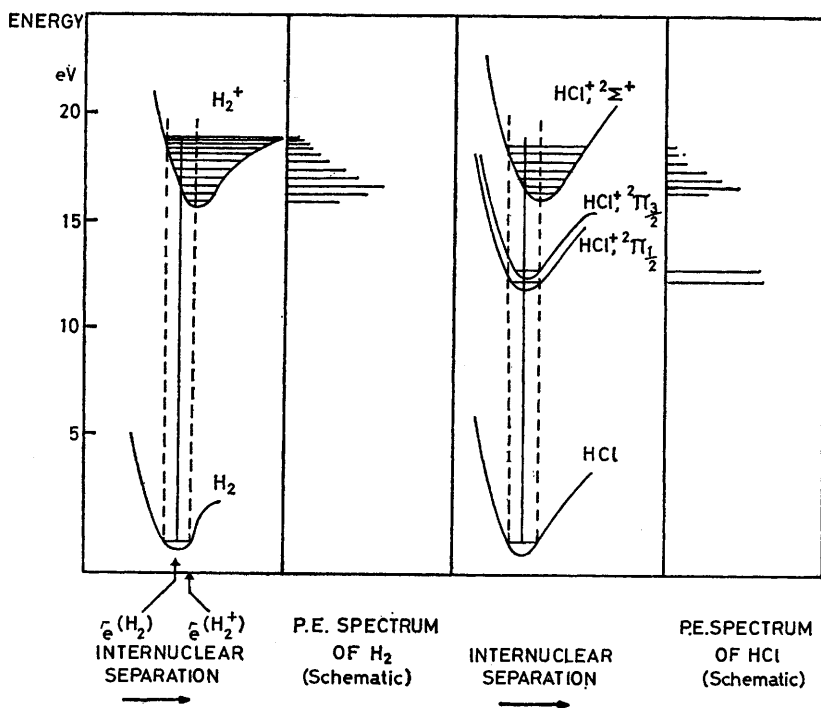


Figure 4 Production of ions (H_2^+ and HCl^+) in excited vibrational levels causing the presence of fine structure in spectral bands. The first band of the HCl spectrum is a doublet due to spin-orbit coupling

shows the 584 Å spectra of H_2 and HCl schematically together with potential energy curves depicting the transitions that occur. An interesting feature of the HCl spectrum is the doublet character of the first band, corresponding to the ejection of a chlorine 3p lone-pair electron. This doublet arises because spin-orbit coupling can result in HCl^+ ions being formed in distinct $^2\Pi_{3/2}$ or $^2\Pi_{1/2}$ states. The energy differential between the two possible ionic states resulting from chlorine 3p lone-pair ionization decreases with increasing molecular size, e.g. there is no evidence of coupling in the first bands of the spectra of $MeCl$, SiH_3Cl , and GeH_3Cl (Figure 5).¹³ Furthermore, the three spectra exhibit marked differ-

¹² C. R. Brundle and D. W. Turner, *Internat. J. Mass Spectrometry and Ion Phys.*, 1969, **2**, 195.

¹³ S. Cradock and E. A. V. Ebsworth, *Chem. Comm.*, 1971, 57.

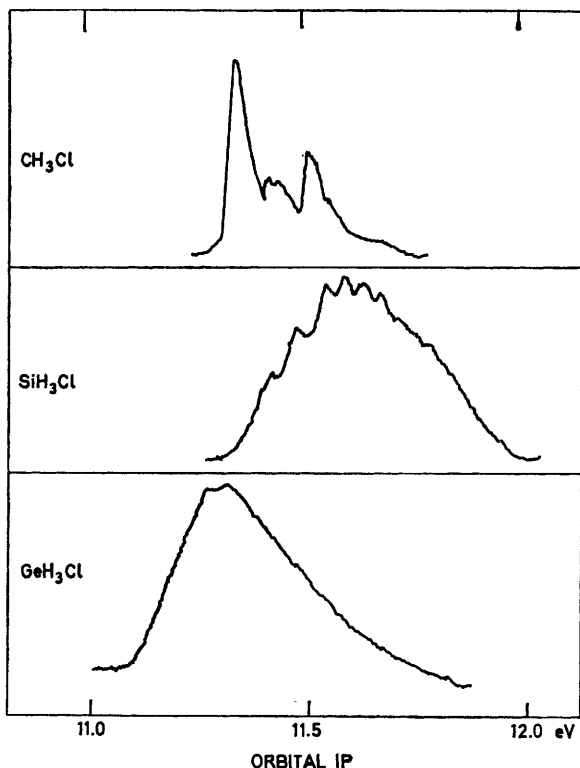


Figure 5 He 584 Å spectra of methyl, silyl, and germyl chlorides

ences in the shapes of the chlorine $3p$ bands. Although the chlorine band of MeCl shows more extensive fine structure than that of HCl, the $v' = 0$ peak is still the most intense, implying only a very small amount of C—Cl character in this highest occupied orbital. In marked contrast, the most intense peak in the chlorine band of the SiH₃Cl spectrum indicates an SiH₃Cl⁺ ion in a state of considerable vibrational excitation. No fine structure is resolved in the GeH₃Cl spectrum, but the profile of the first IP band again suggests a vibrationally excited ion. These results imply that there is appreciable bonding character associated with the highest occupied orbitals of SiH₃Cl and GeH₃Cl, consistent with there being ($p \rightarrow d$) π -bonding through donation of the Cl $3p$ lone-pair into the empty low-lying d -orbitals of the metal atoms. Thus, p.e.s. provides evidence for the significant double-bond character of the metal-to-chlorine linkages in these compounds.

Photoelectron spectroscopy has been used extensively to study electronic substituent effects, since the spectra of a series of compounds, AY (Y = substituent), give a direct representation of the manner in which the orbitals of A are modified by different substituents. Both inductive and mesomeric effects

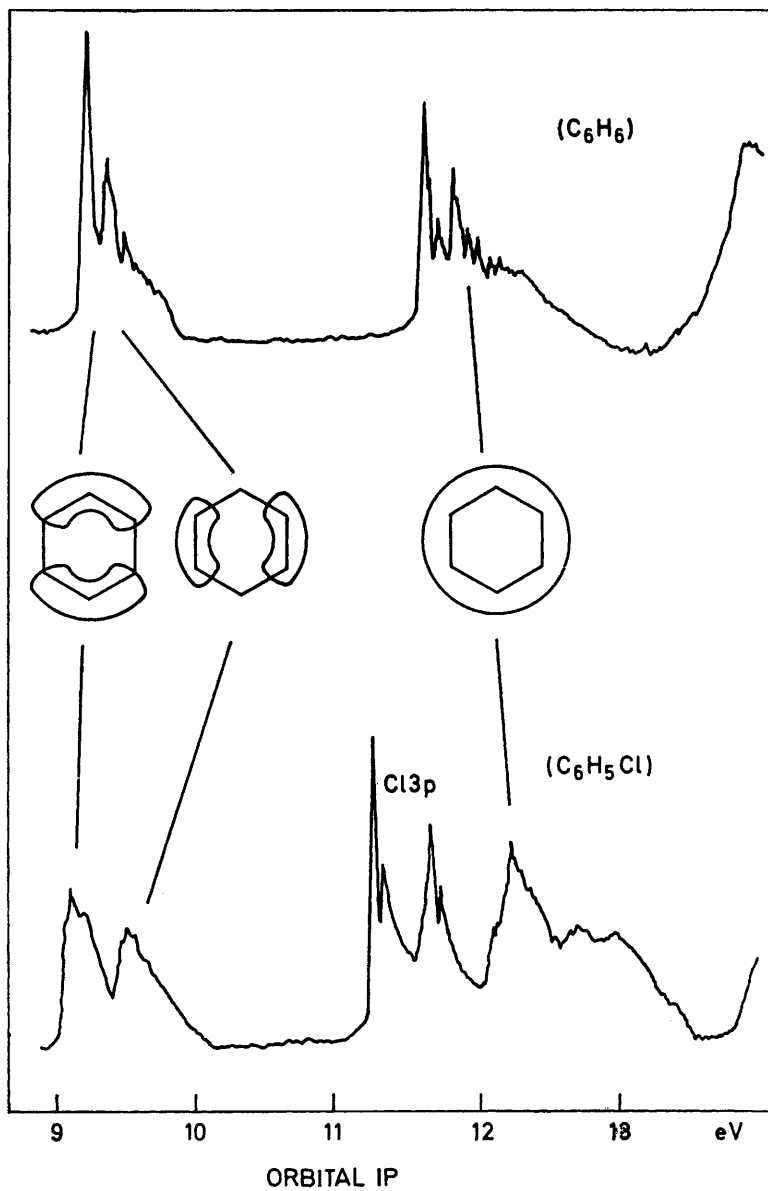


Figure 6 He 584 Å spectra of benzene and chlorobenzene. The latter shows the lifting of π -orbital degeneracy

can be measured. Thus, the spectra of a series of aliphatic alcohols, ROH, provide a measure of the electron-releasing abilities of different R groups (alkyl) by showing the variations in the IP's of the oxygen $2p$ lone-pair electrons.¹⁴ The greater the $+I$ effect associated with an alkyl group, the lower is the oxygen lone-pair IP. Similar effects are found for the iodine $5p$ lone-pair IP's in alkyl halides. Furthermore, a plot of the oxygen lone-pair IP's of alcohols against iodine lone-pair IP's in alkyl iodides is linear,¹⁴ demonstrating a consistency of substituent effects from one series of compounds to another.

Photoelectron spectroscopy is superior to many other techniques for investigating substituent effects since it shows the changes which occur in the binding energies and bonding characteristics of all valence-shell electrons. This is particularly useful in the study of substituent effects in organic molecules containing π -bonds, since here both mesomeric and inductive effects can take place. The spectra of benzene and a series of benzene derivatives have, for example, been reported by Turner *et al.*¹⁵ The 584 Å spectrum of benzene itself contains several bands corresponding to the valence shell π - and σ -orbitals. The lowest IP band relates to two degenerate π -orbitals distinguished by their different nodal characteristics (Figure 6). The introduction of a substituent atom will lift the degeneracy since only one of the orbitals has a node at the point of substitution. Thus, a clear splitting of the band near 9 eV can be seen in the spectra of many benzene derivatives (*e.g.* C₆H₅Cl, Figure 6). The magnitude of the splitting and the shift of the band (from that in benzene) reflects the nature of the substituent. Similar results have been reported for halogenoacetylenes.¹⁶

The spectra of isomers and other structurally similar compounds often show important differences. For example, Betteridge *et al.*^{17,18} have demonstrated this effect in the spectra of *cis*- and *trans*-1,3-dichloropropene and of 2- and 3-bromothiophen.

Sometimes, differences in the spectra of similar molecules may be related to steric effects. For example, Brundle and Robin¹⁹ found that the p.e.s. spectra of butadiene and hexafluorobutadiene indicated that the interaction of the two ethylenic groups was three times as great in the former as in the latter. They concluded on the basis of this that the carbon skeleton of hexafluorobutadiene is non-planar. In a similar manner, Baker *et al.*¹⁵ showed that steric effects have an effect on the p.e. spectrum of *t*-butyl phenyl ether.

It has occasionally been observed that corresponding bands in spectra obtained by using different energy vacuum-u.v. sources are not the same.^{1,20,21} The reason for this is that if the incident quantum, $h\nu$, is equal to the energy needed to

¹⁴ A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1971, **43**, 375.

¹⁵ A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc. (B)*, 1968, 22.

¹⁶ H. J. Haink, E. Heilbronner, V. Hornung, and Else Kloster-Jensen, *Helv. Chim. Acta*, 1970, **53**, 1073.

¹⁷ A. D. Baker and D. Betteridge, *Analyt. Chem.*, 1970, **42**, 43A.

¹⁸ A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1970, **42**, 1064.

¹⁹ C. R. Brundle and M. B. Robin, *J. Amer. Chem. Soc.*, 1970, **92**, 5550.

²⁰ J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, 1969, **51**, 2341.

²¹ W. C. Price, Proc. 4th Conf. Molecular Spectroscopy, ed. P. Hepple, Inst. Petroleum, 1968, p. 221.

promote an inner electron into an unoccupied orbital, autoionization (spontaneous ejection of an electron to give an ion) can then occur as a secondary step if $h\nu$ exceeds one of the orbital IP's of the molecule. The ionized state thereby produced may differ from the corresponding ionic state resulting from a direct electron ejection in that there may be greater probabilities of forming it in higher vibrational states. This will result in the fine structure being modified.²⁰

Photoelectron spectra of solids have been reported.²² Such studies, usually on metals, are often referred to as 'photoemission studies'. Whereas gaseous studies give spectra showing discrete bands attributable to the discrete molecular orbitals of free atoms or molecules, solid-state studies are used to give information about the band structures of the materials concerned.^{22,23} Most studies of this type have been carried out using an LiF window to separate the solid from the photon source (usually a continuum or many-lined source in conjunction with a monochromator), but this limits studies to $h\nu < 11.6$ eV.

4 X-Ray Photoelectron Spectroscopy

The experimental conditions and fundamental principles of ESCA are identical with those of p.e.s. (Section 3), except that the excitation energy consists of soft X-rays rather than vacuum-u.v. photons. Therefore, many of the previous comments concerning p.e.s. are also applicable to ESCA. The use of soft X-rays allows study of core- as well as valence-shell electrons, although for the latter ESCA is inferior to p.e.s. because of the greater linewidths of the X-rays (~ 1 eV) as opposed to vacuum-u.v. photons (a few meV). This causes correspondingly broader bands in ESCA spectra, resulting in loss of fine structure and a merging of the closely situated levels in the valence-shell region. Bands due to core electrons, however, are generally well separated so that solid-phase as well as gas-phase ESCA spectra frequently show completely resolved bands in the core electron region. Thus, solid samples examined by ESCA routinely yield meaningful results, making it a more versatile technique than p.e.s.² Vapour-phase ESCA studies do nevertheless provide sharper bands and are accordingly sometimes desirable, despite a loss in count-rate.² Small shifts in band maxima, or changes in bandshapes may occur on going from gas- to solid-phase spectra. This is because the former relate to free atoms and molecules, whereas the latter are influenced by factors such as hydrogen-bonding, crystal lattice effects, and by the Fermi level of the irradiated material.^{2b}

Unlike p.e.s., ESCA can often give the atomic composition of the substance being investigated. This is because the core electrons of different atoms have quite distinct binding energies.^{2,24} For example, the binding energies of the 1s electrons of the atoms of the first two rows of the Periodic Table are, in electron volts: H, 14; Li, 50; Be, 110; B, 190; C, 280; N, 400; O, 530; F, 690; Ne, 867;

²⁰ D. E. Eastman, 'Photoemission Spectroscopy of Metals', to appear in 'Techniques in Metals Research VI' ed. E. Passaglia, Interscience.

²² (a) C. N. Berglund and W. E. Spicer, *Phys. Rev. (A)*, 1964, **136**, 1030, 1044; (b) N. V. Smith and W. E. Spicer, *ibid.*, 1969, **188**, 593; (c) W. F. Krolkowski and W. E. Spicer, *ibid.*, 1969, **185**, 882; *Phys. Rev. (B)*, 1970, **1**, 478; (d) H. Kanter, *ibid.*, p. 2357.

²⁴ K. Siegbahn, *Phil. Trans. Roy. Soc.*, 1970, **A268**, 33.

Na, 1070; Mg, 1305; Al, 1560; Si, 1840; P, 2150; S, 2470; Cl, 2823; Ar, 3203. Of all the elements, only hydrogen uses its $1s$ orbital to form multicentred molecular orbitals in its compounds. The $1s$ electrons of the remaining elements retain their 'atomic' character in their compounds; therefore, the binding energies of these elements do not alter very much from one compound to another. Thus, a peak in the ESCA spectrum of an unknown compound near 280 eV would indicate the presence of a carbon atom in that compound. In many cases, other inner-shell orbitals, *e.g.* Cl $2p$, S $2p$, may be as useful as the $1s$ orbital for identification purposes.

Some small perturbations of the core electrons of an isolated atom do nevertheless occur when the atom becomes part of a molecular system, *e.g.* an alloy or a chemical compound. The origin of such a perturbation lies in the electrostatic interaction between the valence and core electrons and gives rise to 'chemical shifts' of core-electron binding energies. The magnitude of the chemical shift observed by ESCA provides evidence as to the way in which the atom concerned is bonded, *e.g.* whether a nitrogen atom is in an amino- or a nitro-group. An example of chemical shifts in an inorganic compound is seen in the ESCA spectrum of sodium azide.²⁴ The two terminal nitrogen atoms of the azide anion, N_3^- , are in a different chemical environment from the middle

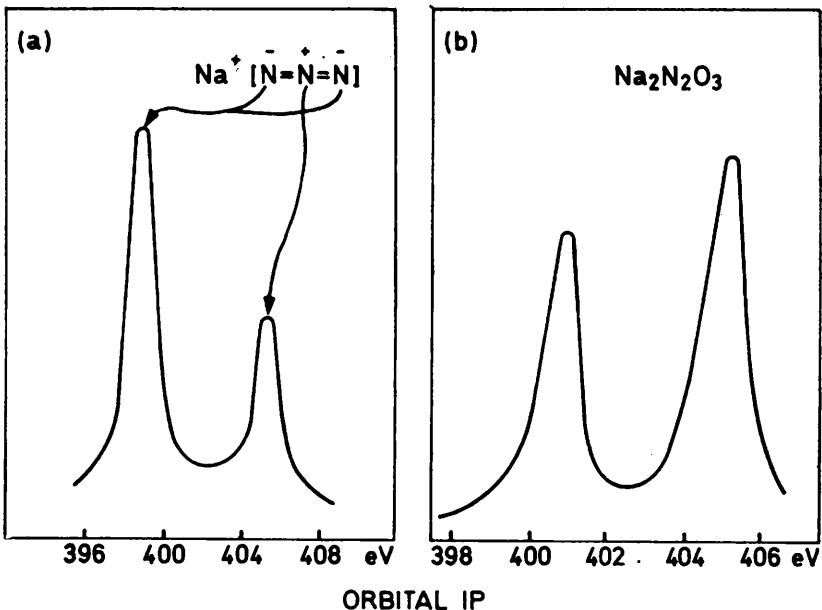
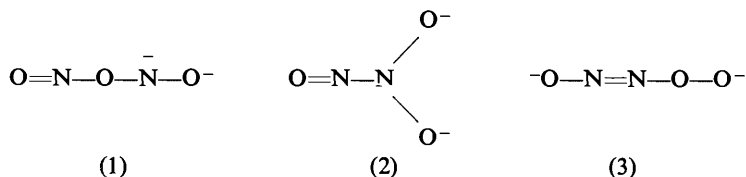


Figure 7 (a) N $1s$ ESCA spectrum of sodium azide. Peaks due to positively and negatively charged nitrogen are clearly distinguished; (b) N $1s$ ESCA spectrum of sodium oxyhyponitrite. The two peaks are due to non-equivalent nitrogen atoms

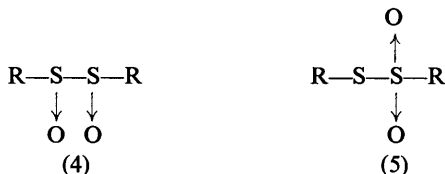
nitrogen atom, and this causes the binding energies of the 1s electrons to be different. The result is that in the part of its ESCA spectrum near 400 eV (*i.e.* the N 1s region, see above), two peaks in the intensity ratio equal 2 : 1 can be seen [Figure 7(a)].

ESCA studies have already solved many chemical structural problems. One example is the structure of the oxyhyponitrite anion, $N_2O_3^{2-}$.²⁵ Three possible structures (1)—(3) had been suggested before the ESCA studies;



the N 1s part of the ESCA spectrum [Figure 7(b)] clearly shows the presence of structurally non-equivalent nitrogen atoms, and this rules out the symmetrical structure (1). MO calculations and considerations of the actual binding energy values observed further showed that only structure (2) was compatible with all the observations.

A second example is the structure of cystine *S*-dioxide.^{2a} Of two possible structures (4) and (5), only (5) was compatible with the ESCA spectrum, which showed two distinct sulphur peaks.



More complex structural elucidations have been reported by Hedman *et al.*²⁶ These workers deduced the structures of the products resulting from the reactions between H_2S and pentane-2,4-dione, and between H_2S and α -angelica lactone.

Carbon ESCA chemical shifts are of obvious interest to organic chemists. However, the C 1s peak is only shifted 11 eV on passing between the extreme examples of CH_4 and CF_4 .²⁷ This shift range is sufficient to allow the observation of discrete peaks from carbon atoms in very different environments in fairly small molecules; *e.g.*, the four different carbon atoms of ethyl trifluoroacetate, $CF_3CO_2CH_2Me$, all show up as separate peaks in its ESCA spectrum.^{2a} However, for larger molecules, or even for small molecules containing a few carbon atoms in similar environments, separate peaks due to the different carbon atoms

²⁵ J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, 1970, 3, 193.

²⁶ J. Hedman, P. F. Hedén, R. Nordberg, C. Nordling, and B. J. Lindberg, *Spectrochim. Acta*, 1970, 26A, 761.

²⁷ D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, 1970, 52, 3295.

are not resolved. This is illustrated by the ESCA spectra of the sodium salts of some aliphatic carboxylic acids (Figure 8).^{2a} Although the carbon atom attached

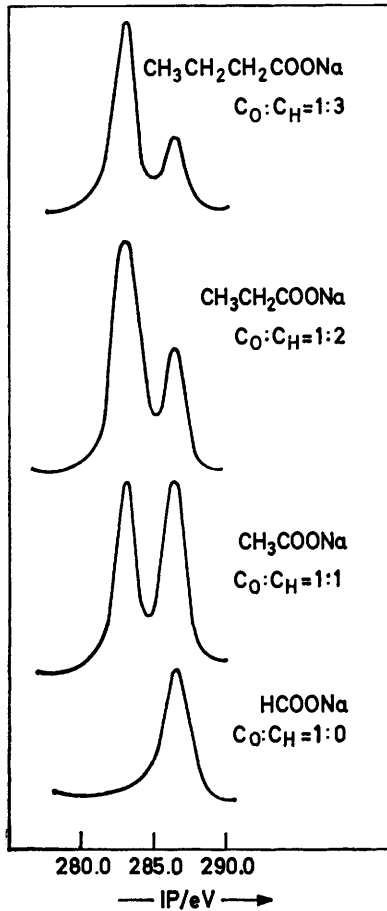


Figure 8 C 1s ESCA spectra of the sodium salts of some aliphatic carboxylic acids. Carbon peaks correspond to hydrocarbon and carboxyl carbon, respectively

to oxygen (C_O) stands out as distinct from the carbon atoms of the alkyl chain (C_H), the individual carbon atoms of the alkyl chain do not appear as separate peaks. However, peaks in complex spectra can be sometimes resolved. For example, Barber and Clark²⁸ have reported determining the N 1s and C 1s binding energies for all the different nitrogen and carbon atoms in compounds as

²⁸ M. Barber and D. T. Clark, *Chem. Comm.*, 1970, 22, 23, 24.

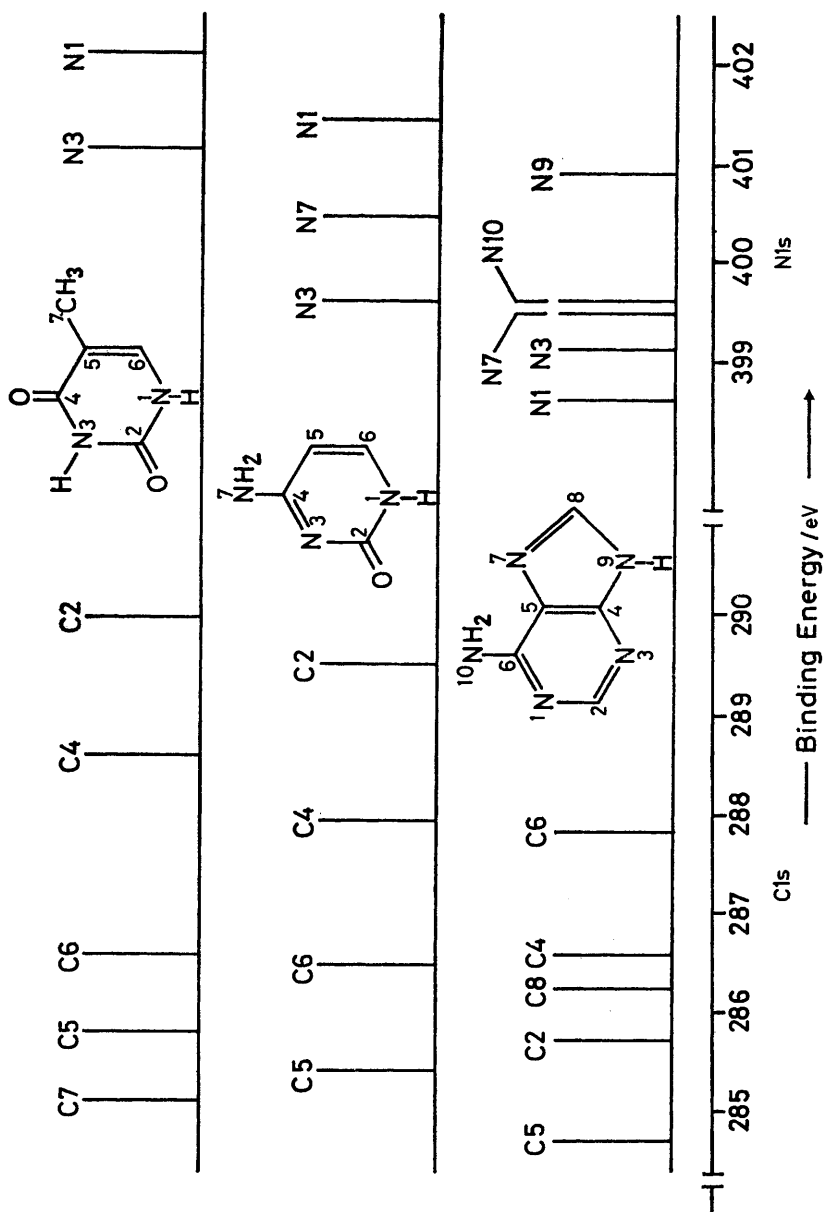
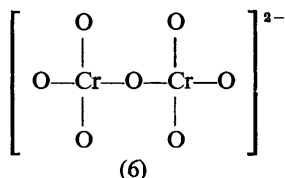


Figure 9 C 1s and N 1s binding energies of thymine (top), cytosine (centre), and adenine (bottom) as assigned by comparison with calculations of orbital energies

complex as the nucleic acid bases, adenine, thymine, and cytosine. Their results are shown in Figure 9. The assignments of different bands in the spectra to particular carbon or nitrogen atoms were accomplished by comparison with quantum mechanical calculations of orbital energies. Brundle²⁹ has questioned the validity of these results and, in general, curve-resolving procedures should be used with caution.

The identification of non-equivalent heavy-metal atoms may prove to be more difficult in many cases than might at first be expected. The study of heavy-metal compounds by ESCA is an important area because of the great variety of oxidation states involved. There are numerous cases where the technique has worked straightforwardly (*e.g.* the distinction between Eu^{2+} and Eu^{3+} in complexes³⁰), but there are cautionary examples also. For example, sodium dichromate has



the structure (6), and one might reasonably expect two distinct lines in the O region of the ESCA spectrum in a ratio 1 : 6 representing the two different types of oxygen present. Only one line is observed.^{8d} Prussian Blue, $\text{KFe}_2(\text{CN})_6$, contains iron in the Fe^{3+} and Fe^{2+} states in a 1 : 1 ratio. At first sight, the Fe 3*p* region of the ESCA spectrum^{8d,31} (two components, Fe 3*p*_{1/2} and Fe 3*p*_{3/2}, compare spin-orbit splitting in p.e.s. Section 3) indicates only one type of iron since there is no 1 : 1 doubling of the peaks. There has been much speculation^{8d,29} on the reasons for this, but it now seems likely²⁹ that the observed Fe 3*p*_{1/2} and Fe 3*p*_{3/2} peaks represent only the Fe^{2+} state, the Fe^{3+} being represented by a collection of small peaks almost merging into the background and each other. This 'multiplet' splitting of what naïvely should be a single peak has been discussed by Fadley *et al.*³² in relation to other cases.

Considerable attention has been directed toward the development of methods suitable for predicting the binding energies of core electrons in any given molecular structure. The success of such a method would clearly have far-reaching implications on the future of ESCA as a tool for structural elucidations. A match between the predicted ESCA spectrum for a structure proposed for an unknown material, and the experimental spectrum for that material, would confirm the structure. So far, correlations between ESCA chemical shifts and parameters derived from Pauling electronegativities, and from semi-empirical MO calcula-

²⁹ C. R. Brundle, *Appl. Spectroscopy*, 1971, **25**, 8.

³⁰ C. S. Fadley, S. B. M. Hagstrom, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.*, 1968, **48**, 3779.

³¹ G. Wertheim and A. Rosencwaig, personal communication.

³² C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Letters*, 1969, **23**, 1397.

tions have been reported. Jolly *et al.*³³ have also used thermochemical parameters to calculate ESCA chemical shifts. In addition, a scheme for calculating the actual count-rate for a given peak in an ESCA spectrum has been proposed.³⁴

5 Penning Ionization Spectroscopy

The ionization of gaseous atoms or molecules by electronically excited neutral species is known as the Penning effect.³⁵ Such processes occur if the IP of the target atom or molecule is lower than the excitation energy of the neutral particle. Unlike the ionization caused by electron or photon impact, collisions occur between uncharged particles; therefore, the force field is small and the collision time increased with the consequence that collision complexes between the particles are favoured in certain cases.

Much of the work in this area has been concerned with the mass spectrometric investigations of positive ions produced by Penning ionization.³⁶ However, Čermák and Herman^{36b} suggested the measurement of the kinetic energies of released electrons, and later investigated the use of He 2^1S and 2^3S metastable atoms as ionizing particles for e.s.^{3,37} Experimentally, the He metastables were produced by bombardment of He with an electron beam.³⁸ The information obtained from p.i.s. in these experiments can be illustrated by the examples of N_2 and NO .³⁷ The p.i.s. spectrum of N_2 exhibits six peaks, three due to ionization by 2^1S atoms (20.61 eV) and three by 2^3S atoms (19.81 eV). As in Section 3, the basic pattern of three peaks corresponds to the ionic states of N_2^+ , $\tilde{X}^2\Sigma_g^+$, $A^2\Pi_u$, and $\tilde{B}^2\Sigma_u$. Although no fine structure is seen, the narrowness of the peaks of the $\tilde{X}^2\Sigma_g^+$ and $\tilde{B}^2\Sigma_u$ states (relative to those of the $A^2\Pi_u$ state) is indicative of the excitation of vibrational levels in the $A^2\Pi_u$ state. These results are identical with those obtained by p.e.s. With NO , the absence of peaks due to the states $^1\Sigma^+$ and $A^3\Sigma^+$ has been taken as evidence that a collision complex $HeNO$ is formed, and that autoionization of the complex determines the populations of the various states of NO^+ ions. Additionally, there is a suggestion that transformation of the internal energy of the $HeNO$ complex into kinetic energy of He and NO^+ takes place.

Clearly, p.i.s. gives information similar to that derived from p.e.s.; however, it is also apparent that the technique is important for studying unusual short-lived collision complexes.

6 Auger Spectroscopy

In an Auger spectrometer a beam of electrons strikes the sample and electrons

³³ (a) W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, 1970, **92**, 1863; (b) W. L. Jolly, *ibid.*, p. 3260.

³⁴ G. F. Crable and H. D. Seaman, unpublished work. See also U. Gelius, Uppsala University, Institute of Physics, 1971, UUIP 753; A. D. Baker and D. Betteridge, 'Photoelectron Spectroscopy—Chemical and Analytical Aspects', Pergamon, Oxford, 1972.

³⁵ F. M. Penning, *Z. Physik*, 1928, **46**, 335; 1929, **57**, 723; 1931, **72**, 338.

³⁶ (a) W. P. Scholette and E. E. Muschlitz, *J. Chem. Phys.*, 1962, **36**, 3368; (b) V. Čermák and Z. Herman, *Nature*, 1963, **199**, 588; (c) *Coll. Czech. Chem. Comm.*, 1965, **30**, 169.

³⁷ V. Čermák, *J. Chem. Phys.*, 1966, **44**, 3781.

³⁸ V. Čermák, *J. Chem. Phys.*, 1966, **44**, 3774.

leaving are energy-analysed in an analyser of the type described in Section 2 or, more usually for solid samples, by using a retarding potential grid analyser.^{4b,39} The Auger process follows the ejection of an inner-core electron. The resultant hole is filled by an electron from a less tightly-bound level, releasing sufficient energy for another electron (the Auger electron⁴⁰) to be ejected (processes 1,1' and 2,2' in Figure 10). The energy of the Auger electron 1,1' is given by $E_{\text{Auger}} \simeq E_W - 2E_X$ where W and X are inner-core levels; therefore E_{Auger} is charac-

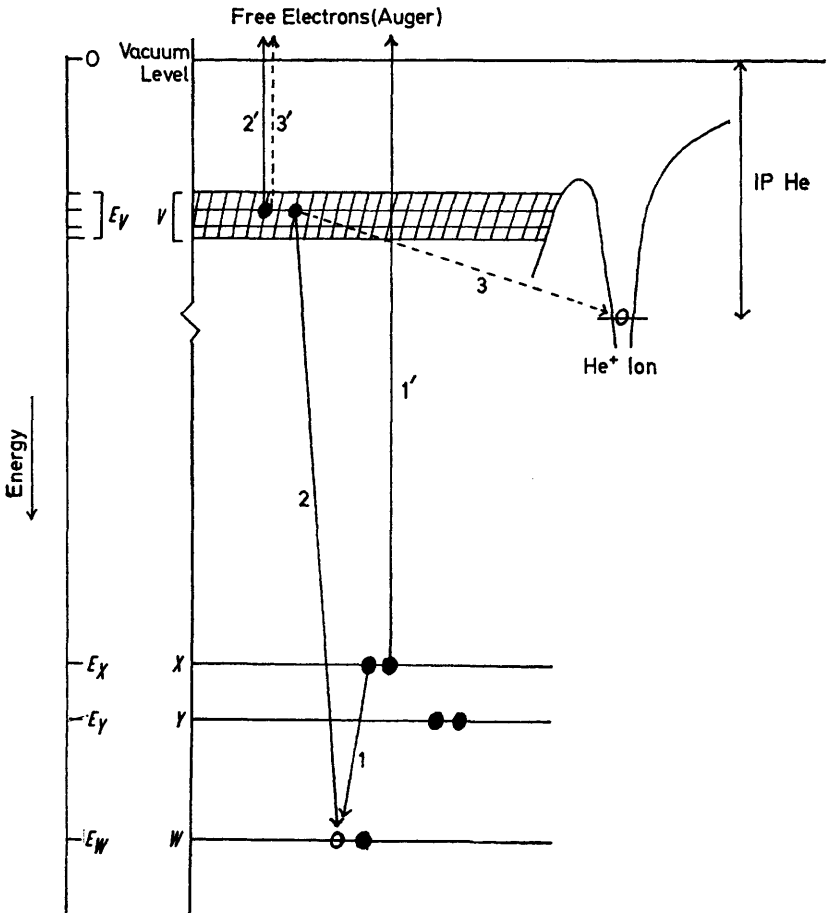


Figure 10 Energy level diagram showing three types of Auger process; these are the 1,1' and 2,2' processes, and the i.n.s. process induced by He^+ bombardment, 3,3'. X, Y, and W levels are inner-core levels. V is the valence region and consists of discrete levels only for gases. (See also D. S. Urch, *Quart. Rev.*, 1971, 25, 343)

³⁹ N. J. Taylor, *Vacuum*, 1969, 19, 575.

⁴⁰ P. Auger, *J. Phys. Radium*, 1925, 6, 205.

teristic of a particular atom, as in ESCA *e.g.* an Auger peak near 164 eV is characteristic of tantalum. Chemical shifts can be used for bonding studies, but are more complex than for ESCA because shifts in both W and X are involved. E_{Auger} is independent of the energy of the incident electron beam, meaning that the beam need not be monoenergetic. The only requirement is that the incident energy, E_0 , is greater than E_W . In practice it is found that maximum intensity is achieved when E_0 is about three times E_W .⁴¹

The Auger peaks in the spectrum of electrons leaving a sample represent only a fraction of the total number of electrons being analysed, particularly when solid samples are involved (solid studies are of a surface nature—see Section 9). A hypothetical solid spectrum is given in Figure 11(a). Small Auger peaks are superimposed on a high background. The major contributor is the incident beam elastically scattered from the surface. There are also numerous energy-loss peaks (see Sections 7 and 8), Auger peaks being distinguished from these because they fall in a different energy region and also, since their energy is independent of E_0 , the Auger peaks will appear at the same kinetic energy if E_0 is changed. The high background represents incident beam electrons multiply-scattered in their progress through the solid sample. The small Auger peaks are made more conspicuous by differentiating the spectrum. An example is given in Figure 11(b) (titanium). Peaks not corresponding to titanium Auger lines allow the identification of impurity elements present.³⁹

The majority of Auger transitions are 2,2' rather than the 1,1' type, *i.e.* a valence-shell region (V) is involved. E_{Auger} is then given by $E_W - 2E_V$. For 2,2' Auger electrons there will be no real chemical shift behaviour because valence region changes cannot be related to individual atoms.^{4b} Since E_W is so much larger than E_V the energy region of the transition will still be characteristic of an atom; *e.g.* an Auger peak at approximately 250 eV is characteristic of a carbon 2,2' transition.

For solids, 2,2' peaks can be quite broad because of the broad valence-band structure. Though no true chemical shift behaviour occurs, changes in the valence-band structure will result in changes in the shape of the Auger peak which may be used to identify chemical changes in a sample. In this fashion, Chang has been able to demonstrate the presence of SiO_2 on the surface of a silicon sample.^{4b,41} With gases many discrete peaks are obtained, covering approximately the same energy spread as a broad solid 2,2' peak, representing transitions involving all the discrete valence region MO's instead of the band structure of a solid. Vibrational structure may be present (compare p.e.s. spectra). CO and CO_2 have many 2,2' peaks stretching from 220 to 270 eV⁴² that are characteristic of carbon, but the detailed structures are characteristic of the individual molecules. Similarly there are 2,2' transitions in the characteristic oxygen region (460—510 eV) but the detailed structures are again charac-

⁴¹ C. C. Chang, *Surface Science*, 1970, **23**, 283.

⁴² W. E. Moddeman, T. A. Carlson, M. O. Krause, and B. P. Pullen, *J. Chem. Phys.*, 1971, **55**, 2317.

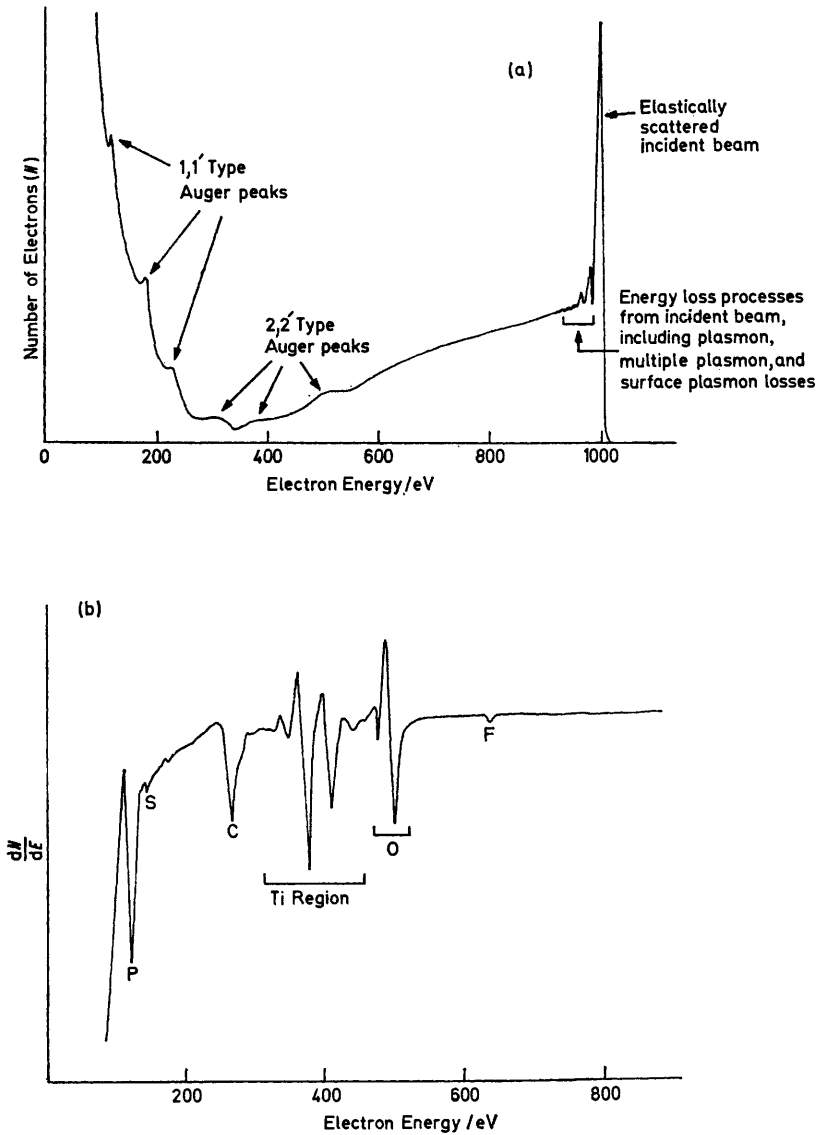


Figure 11 (a) Hypothetical Auger spectrum from a solid. Also shown are energy loss features. (b) Differential spectrum of a titanium sample

teristic of CO and CO₂.⁴² Thus we have both an elemental and a molecular analysis.

Much of the work on gaseous molecules has been performed using X-rays

rather than an electron beam to form the inner-core hole. A disadvantage with X-rays is that they are less intense than electron beams and cannot be focused to small spots. An advantage, particularly for solids, is that without an incident electron beam one has a much lower background of multiply-scattered electrons.⁴³ 1,1' transitions and chemical shifts have been studied using X-rays, e.g. the Auger peaks from the two different sulphur atoms in solid sodium thio-sulphate are separated by a shift of 4.7 eV.^{2a} When using X-rays to study Auger spectra one of course also obtains a normal ESCA spectrum (Section 4) and so both studies can be carried out simultaneously.^{2a}

7 Electron Impact Energy Loss Spectroscopy

Electrons, like photons, when traversing an array of atoms or molecules may induce excitation phenomena. Photons, however, usually transfer all their energy and are therefore annihilated, whereas electrons continue with a fraction of their initial energy. Conservation of energy requires that the energy loss suffered by an impacting electron (*i.e.* the energy of the incident electron less that of the continuing or scattered electron) is exactly equal to an excitation potential of the bombarded species.

In e.i.s., a monochromatic beam of electrons is passed through a gaseous sample (or directed on to a solid surface) and the energy spectrum of the inelastically scattered electrons recorded. The spectrum reveals peaks attributable to the different excitation energies of the target atoms or molecules. The same information is also obtained from optical absorption spectroscopy, but in e.i.s. the entire excitation spectrum from the i.r. to the far u.v. is covered in one instrument, admittedly with worse resolution than optical instruments in the visible and i.r. regions.

A further distinction between e.i.s. and optical spectroscopy is that excitations forbidden by the selection rules of the latter may be observed in the former under certain conditions; for example, under optimized conditions of impacting electron energy and scattering angle. In particular, electrons are effective in causing transitions between states of different spin-multiplicity through electron-exchange mechanisms if their energies are within approximately 25 eV above the threshold for such an excitation. For example, Trajmar *et al.*⁴⁴ have compared the gas-phase e.i.s. spectra of ethylene and acetylene with the corresponding optical spectra and discussed the importance of singlet-triplet transitions in the former.

Spectra of other gaseous atoms and molecules, mostly simple ones, have also been reported and discussed in terms of the electronic or vibrational transitions that occur.^{6,44} Recent work describing results for formaldehyde is of interest because it reveals structured bands indicative of autoionizing Rydberg states 2–3 eV above the ionization threshold.⁴⁵ There is undoubtedly considerable scope for further studies on chemically more interesting molecules, and the

⁴³ C. R. Brundle, *Surface Science*, 1971, **27**, 681.

⁴⁴ S. Trajmar, J. K. Rice, and A. Kupperman, *Adv. in Chem. Phys.*, 1970, **18**, 15.

⁴⁵ M. J. Weiss, C. E. Kuyatt, and S. Mielczarek, *J. Chem. Phys.*, 1971, **54**, 4147.

possibility of developing e.i.s. as a complementary tool for structural and analytical work. In this regard, it is interesting to note that Lindholm *et al.*⁴⁶ have made use of e.i.s. results to substantiate orbital sequences suggested by p.e.s. E.i.s. has been used extensively to study solids.⁴⁷ Promotion of electrons from filled to empty energy levels (bands) are termed band-to-band transitions. Of perhaps more interest are plasmon excitations, which may be thought of as the collective oscillations of the Fermi gas, induced by interaction of the electron beam with the solid. Plasmon and multiple plasmon losses can be seen in Figure 11(a). Since their energies are dependent on solid structure, plasmon losses may be used for chemical studies, *e.g.* alloy properties.⁴⁸ In practice, the virtual surface nature of the technique (Section 8) has caused much experimental disagreement, because contaminated surface layers were involved.⁴⁷

Ionization brought about by electron bombardment of energy, E , results in two electrons leaving the collision site, the scattered, E_1 , and the ejected electron, E_2 . The excess energy of the process, $E - IP$, is shared between the two electrons, unlike photon impact (Section 3) where it is completely transferred to the ejected electron. Therefore, in e.i.s. a weak continuum rather than a peak starts at the energy loss equal to the IP since the two resultant electrons may take any values provided $E - IP = E_1 + E_2$. (Compare vacuum-u.v. absorption spectroscopy where band-to-band transitions give discrete peaks but ionizations produce continua.) By using co-incidence techniques to record the spectrum for only a fixed value of E_1 , a discrete peak spectrum giving IP values from measured E_2 values becomes possible.⁴⁹

8 Electron Spectroscopy and Surface Studies

Electrons travelling out from deep within a sample lose energy through collisions and so do not appear at their expected energies in the electron spectrum, which is therefore characteristic of only a surface slice. Factors controlling electron 'escape depths', d , have been discussed elsewhere;⁵⁰ d is dependent on the kinetic energy, E , of the escaping electron and the nature of the solid. For low E (< 10 eV) $d \propto 1/E^2$ for high E (< 200 eV) $d \propto E$; in between d is fairly constant, and can be as little as 5–50 Å. Materials of high atomic number have low d values.

In ion neutralization spectroscopy (i.n.s.),⁵ He⁺ ions strike a solid sample, an electron is transferred to the ion, neutralizing it, and an Auger electron is ejected by the energy released (process 3,3', Figure 10). The important difference from a 2,2' Auger process is that since the He⁺ ions cannot penetrate the sample the phenomenon is entirely a surface one. I.n.s. has been used to study the surface state band structure of metals,⁵ and to study the electronic structures of adsorbed

⁴⁶ E. Lindholm, O. Edqvist, L. E. Selin, D. L. Åsbrink, C. E. Kuyatt, S. Mielczarek, J. A. Simpson, and I. Fisher-Hjalimars, *Physica Scripta*, 1970, 1, 172.

⁴⁷ O. Klemperer and J. P. G. Shepherd, *Adv. Phys.*, 1963, 12, 355.

⁴⁸ B. M. Hartley and J. B. Swan, *Austral. J. Phys.*, 1970, 34, 655.

⁴⁹ (a) U. Amaldi, A. Egidi, R. Marcomero, and G. Pizzetta, *Rev. Sci. Instr.*, 1969, 40, 1001; (b) E. Ehrhardt, M. Schulz, T. Tekaas, and K. Willman, *Phys. Rev. Letters*, 1962, 22, 89.

⁵⁰ C. R. Brundle, 'The Application of Electron Spectroscopy to Surface Studies', in 'Surface and Defect Properties of Solids', ed. M. W. Roberts and J. M. Thomas (Specialist Periodical Reports), The Chemical Society, London, 1972, Vol. 1, p. 171.

gases on metals.⁵¹ In some cases narrow peaks superimposed on the metal band structure seem to indicate the discrete MO's of 'surface molecules' *e.g.* H₂Se on Ni(100) may form an Ni₂Se array in C_{2v} symmetry with the Se atoms above the Ni plane.⁵¹

For Auger transitions in the intermediate energy range, escape depths of < 50 Å can be obtained. A.S. is therefore used routinely to detect elements present at a surface;^{4b,39,50} *e.g.* the titanium Auger spectrum of Figure 11(b) shows surface contamination. The phosphorus comes from 'cleaning' by etching with acid. There are many applications in the area of thin film technology where < 1% monolayer is detectable.⁵² Cleaning procedures can be evaluated, surface and grain boundary segregation studied, doping followed, *etc.* Hass and Grant⁵³ demonstrated the applicability of Auger chemical shifts to surface work by showing that different monolayer oxide phases on Ta(100) had different shifts, which were also different from the bulk oxide shift. Detection of surface SiO₂ by shape changes in the 2,2' Si peak was also mentioned in Section 5. Surface carbide can be similarly distinguished from adsorbed CO.⁵⁴ Shape changes in 2,2' Auger peaks are equivalent to changes in i.n.s. spectra.

In *e.i.s.* plasmon losses and the 0—2 eV loss region which relates to molecular vibrational excitations (compare *i.r.*) are of surface importance. Electrons with low *d* values should be studied (easily arranged by varying incident beam energy). 'Surface' plasmon losses may be distinguished from bulk losses and used to follow surface conditions. The intensity of surface plasmons can be sensitive (reduced) to as little as 0.04 monolayers of an impurity.⁵⁵ Propst and Piper⁵⁶ studied the first 1 eV loss region under high resolution for the adsorption of gases on to tungsten and related the losses to the vibrational modes of the surface species formed. This would seem an area of potential which has not been further investigated.

P.e.s. studies on solids have conventionally used energies below 11.6 eV (Section 3), and it has been considered that the band structures obtained were bulk properties. Recent studies indicate that photoemission may be primarily a surface effect.⁵⁷ When using higher photon energies (*e.g.* HeI at 21.2 eV) the ejected electrons have lower *d* values and definitely come from the surface layers. Apart from variation in escape depth the results are similar to *i.n.s.*, yielding information on the bonding of adsorbed layers to substrates. Bordass and Linnett⁵⁸ attempted to obtain the *p.e.* spectrum of methanol on tungsten, and Eastman has observed the superimposition of a broad band, attributable to surface nickel oxide, on the band structure of nickel.²² The chemisorption of CO on to nickel has also been studied.⁵⁹

⁵¹ H. D. Hagstrum and G. E. Becker, *J. Chem. Phys.*, 1971, **54**, 1015.

⁵² W. E. Weber, *Solid State Technol.*, 1970, Dec., 49.

⁵³ T. W. Hass and J. T. Grant, *Phys. Letters (A)*, 1969, **30**, 272.

⁵⁴ T. W. Hass and J. T. Grant, *Appl. Phys. Letters*, 1970, **16**, 172.

⁵⁵ G. W. Simmons, *J. Colloid and Interface Sci.*, 1970, **34**, 343.

⁵⁶ F. M. Propst and T. C. Piper, *J. Vac. Sci. Technol.*, 1966, **4**, 53.

⁵⁷ N. V. Smith and G. B. Fisher, *Phys. Rev. (B)*, 1971, **3**, 3662.

⁵⁸ W. T. Bordass and J. W. Linnett, *Nature*, 1969, **222**, 660.

⁵⁹ D. E. Eastman, private communication.

Siegbahn *et al.*^{2a} estimated the probing depth of ESCA by monitoring a marker peak (Br 3d) while covering a surface with dilayers of stearic acid. Their estimate of 80 Å is likely to be greater than for non-organic compounds, particularly metals, but again the values will depend on the energies of the electrons concerned. E.s.c.a. instruments in operation are not of ultra-high vacuum and so a full appraisal of surface applicability has not been possible. Delgass *et al.*⁶⁰ have made preliminary studies of chemical shifts for nitrogen compounds adsorbed on to zeolites; for the dispersion of active metals on a support (a common method of increasing catalytic activity); and from crystalline oxides before and after catalytic use. Fadley and Shirley⁶¹ demonstrated that the two Fe 3p peaks present for an iron sample were due to bulk iron and surface iron oxide.

9 Analytical Aspects

Auger spectroscopy will not be discussed here as its use as a powerful tool in surface analysis was described in Section 8. The potential of p.e.s. and ESCA in analytical chemistry has recently been cited.^{17,62} As the p.e.s. spectra of structurally similar compounds are often quite different,^{14,18} it is clear that the technique can be used with some success to give qualitative or 'fingerprint' information. For example, the spectra of phosphorus-containing pesticides have been investigated with a view to their identification, and with later developments quantitative estimation, in materials causing public concern.⁶³ In principle, quantitative measurements are distinctly possible as electron count-rates are functions of the numbers of molecules. Furthermore, the analysis of simple mixtures of compounds is a possibility, and perhaps with the aid of a g.l.c.-linked system more complex mixtures could be studied. The main problems of quantitative measurement are, in fact, those associated with any analytical instrument, *viz.* the problems of sample handling and introduction, memory effects, and output data treatment. These problems will undoubtedly be solved by future improvements in instrumental design. Many of the above comments also apply to other e.s. techniques.

At the present time, the main use of ESCA lies in the mapping of elements in solid surfaces, with the advantage that information can be obtained non-destructively on a small amount of sample (< 1 mg). In a qualitative sense, Jack and Hercules⁶⁴ recently studied the ESCA spectra of a number of quaternary nitrogen and phosphorus compounds in an attempt to test the feasibility of a one-atom correlation (quaternary nitrogen or phosphorus). The authors pointed out that once sufficient information is available to do multiple-atom correlations, ESCA will become a complementary tool to i.r., n.m.r., and mass spectroscopy. With regard to gas analysis, Siegbahn *et al.*^{2b} have shown that the 0.9% of argon in air is easily detectable by ESCA. In addition, the N 1s binding

⁶⁰ W. N. Delgass, T. R. Hughes, and C. S. Fadley, *Catalysis. Rev.*, 1971, 4, 179.

⁶¹ C. S. Fadley and D. A. Shirley, *Phys. Rev. Letters*, 1968, 21, 980.

⁶² D. M. Hercules, *Analyt. Chem.*, 1970, 42, 20A.

⁶³ D. Betteridge, M. Thompson, A. D. Baker, and N. R. Kemp, *Analyt. Chem.*, in the press.

⁶⁴ J. J. Jack and D. M. Hercules, *Analyt. Chem.*, 1971, 43, 729, 1066.

energies of N_2 and NH_3 were clearly distinguished, in a mixture of these gases. Similarly, a mixture of CO , CO_2 , and CH_4 could be analysed *via* the appropriate $O\ 1s$ and $C\ 1s$ binding energies.

E.i.s. appears to have considerable potential as a technique for the analysis of gases and vapours, and in particular for the determination of trace contaminants in the atmosphere.⁶⁵ In this regard, Rendina and Grojean⁶⁶ were able to detect a 'trace' of CO introduced into a sample of air of pressure 0.1 Torr. The authors also suggested that argon peaks can be used as an internal standard for accurately measuring concentrations of trace gases in air.

⁶⁵ J. A. Simpson and C. E. Kuyatt, *Amer. Lab.*, 1968, Oct.

⁶⁶ J. F. Rendina and R. E. Grojean, *Appl. Spectroscopy*, 1971, **25**, 34.