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Photoelectron Spectroscopy

Chemical and Analytical Aspects

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PHOTOELECTRON SPECTROSCOPY

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PREFACE

PHOTOELECTRON spectroscopy has, within the past few years, become one of the most rapidly growing areas in chemistry. At the present time, more publications on the subject often appear within a couple of months than did over the whole of the period 1962–7. This has partly been due to the availability of commercial instruments since 1967, and to a growing recognition that electron spectroscopic techniques have widespread applications throughout chemistry and related sciences.

The authors of this book first worked together in 1968 when a grant from the Agricultural Research Council (U.K.) enabled one of the first batch of commercial photoelectron spectrometers to be set up at the University College of Swansea in order to study the applicability of photoelectron spectroscopy to the analysis of pesticides etc. One of the authors (D. B.) was at that time a lecturer in Analytical Chemistry at Swansea, and he was joined by the other author (A. D. B.) who came to Swansea as a Research Fellow from Oxford, where he had worked in the very early days of photoelectron spectroscopy as a student of Dr. D. W. Turner.

We hope that this book, which represents a balance of the interests of the two authors, provides a readable introduction to the principles of the technique, and its applications in structural and analytical chemistry. We are convinced that the method is of fundamental importance to chemists, and that many are at present put off the subject by the theoretical treatments which are a staple ingredient of most papers in the field. Our emphasis is on the business of obtaining spectra and on interpreting them without recourse to rigorous theoretical methods. We deal with both X-ray (ESCA) and UV-photoelectron spectroscopy (PES).

We are indebted to our colleagues in Swansea, and elsewhere, for their help and for making many valuable suggestions. In particular, we would like to thank Drs. M. Thompson, N. R. Kemp, R. E. Kirby and Mr. C. W. Haigh. We are also especially indebted to Mr. K. Francis, of the Graphic Arts Department, University College of Swansea, for helping to prepare many of the diagrams. Finally, we would like to thank the Agricultural Research Council (U.K.) for providing the funds to initiate a project in photoelectron spectroscopy.

Unless otherwise stated, the UVPE spectra have been drawn from our own work and the X-ray PE spectra from Siegbahn's.

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CHAPTER 1

BASIC PRINCIPLES

INTRODUCTION

One of the fundamental concepts of chemistry is that the extranuclear electrons of atoms and molecules exist in orbitals of well-defined energies. The technique of electron spectroscopy enables the different binding energies or ionization potentials (IPs) of electrons in different orbitals to be measured. We can refer to these values as the different "orbital ionization potentials".

Electron spectroscopy has proved to be the first experimental technique to provide, for a given atom or molecule, a complete set of orbital ionization potentials, from the valence electrons down to the *K*-shell electrons. Because these orbital IPs are characteristic features of the parent atom or molecule, electron spectroscopy affords a possible means of compound identification, as well as providing data which has had a profound affect on theoretical chemistry. It is a straightforward technique, which consists essentially of measuring the energy spectrum of the electrons ejected from a sample on bombardment with (usually) monoenergetic rays or particles. The energies of the ejected electrons differ according to their orbitals of origin, and may be related simply to the different orbital ionization potentials of the sample atom or molecule.

The recorded spectrum may thus serve to identify the elements present and/or provide information about the structure of the sample. For example, the *K*-shell ionization potentials for the first eighteen elements of the Periodic Table vary in a distinctive manner from

Table 1.1. Approximate Binding Energies (eV) for the Elements of the First and Second Rows of the Periodic Table*

H 14							He 25
Li 50	Be 110	B 190	C 280	N 400	O 530	F 690	Ne 867
Na 1070	Mg 1305	Al 1560	Si 1840	P 2150	S 2470	Cl 2823	Ar 3203

*More values are given in Appendix 1.

14 eV to 3203 eV (Table 1.1). An experimentally found ionization potential within a few volts of 400 would therefore indicate the presence of nitrogen in the sample, and the extent by which the IP differed from 400 eV, the "chemical shift", would give a clue to the molecular environment of the nitrogen atom, e.g. whether it were in a nitro-group or an amino-group. If there were two peaks of equal area close to 400 eV, it would indicate the presence of two nitrogen atoms in the molecule in non-equivalent positions. IPs in the range 5–30 eV relate to electrons in the valence shell, and the information obtained from this part of the spectrum is concerned with molecular bonding, with substituent effects, and with isomeric and steric changes.

The information to be obtained from electron spectroscopy is unique, although at this stage in its development, in which structural and electronic interpretations are inevitably compared with similar information given by established techniques, its uniqueness is not always emphasized. It is potentially a sensitive method, applicable to a wide range of compounds, and able to give information about all the atoms within a molecule. It is probable that it will become an important analytical method for qualitative, and possibly quantitative analysis.

This monograph aims to deal with the basic principles of instrumentation, and to show how the spectra may provide analytically valuable information.

GENERAL APPARATUS

The basic requirements of an electron spectrometer may be summarized as follows:

(a) Pumping equipment capable of evacuating the apparatus to about 1×10^{-6} mm mercury pressure.

(b) A source of ionizing rays or particles.

(c) A collision chamber into which the ionizing species and the material under investigation can be introduced, and from which electrons may pass into an electron energy analyser.

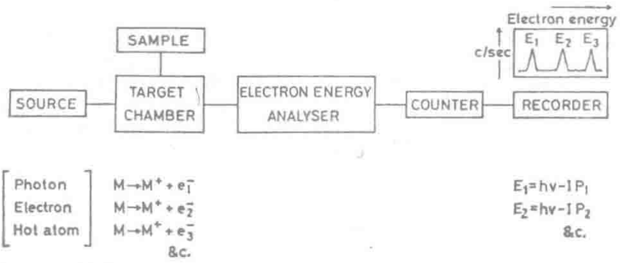

FIG. 1.1. Block diagram showing the arrangement of some of the principle parts of an electron spectrometer. Electrons e_1, e_2, e_3, etc., are ejected from various orbitals of M, with energies E_1, E_2, E_3, etc. The electron spectrum shows the relative numbers of electrons ejected over the possible energy range.

(d) A sampling system by which the appropriate amount of sample in the appropriate physical state can be introduced into the collision chamber.

(e) An electron energy analyser to monitor the electron flux emerging from the collision chamber.

(f) Counting and recording equipment to plot the spectrum.

A block diagram illustrating the arrangement of some of the principle parts is given in Fig. 1.1. In the usual type of investigation, monoenergetic ionizing rays or particles generated in the source are directed onto sample molecules in the target chamber. An electron can then be expelled from any orbital for which the associated ionization potential is less than the energy of the impacting species.

Every ejected electron will possess a quantity of kinetic energy, E, which will be approximately equal in magnitude to the difference between the energy, U, imparted by the impacting species, and the appropriate orbital ionization potential, I:

$$E = U - I. \tag{1.1}$$

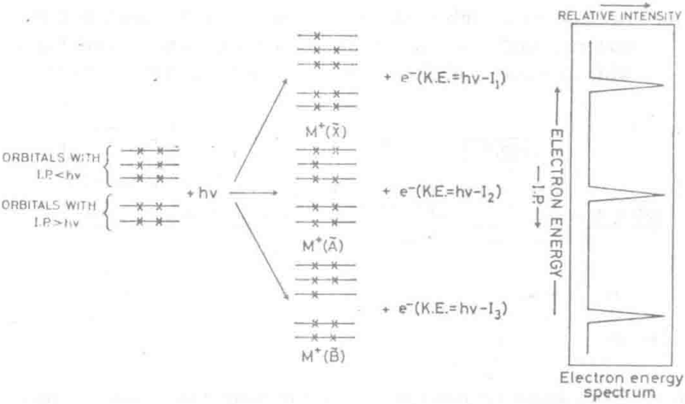

FIG. 1.2. Schematic representation of the processes represented by an electron spectrum. On left: molecule with 5 filled levels, 3 of which are acessible to the photons. In the middle: the molecular ions $M^+(\tilde{X})$, $M^+(\tilde{A})$ and $M^+(\tilde{B})$ resulting from ionization from 3 highest occupied orbitals. On right: PE spectrum reflecting MO levels.

In the case where the impacting species is a photon of frequency, ν, U is equal to $h\nu$ where h is Planck's constant, and

$$E = h\nu - I. \tag{1.2}$$

Since the impacting species are directed into an array of identical molecules in an electron spectrometer, electrons can be ejected from all the accessible orbitals (i.e. all those for which $U \geqslant I$). Groups of different energy electrons are thus emitted. All electrons ejected within the solid angle of acceptance of a slit within the target chamber then enter the focusing electron analyser through this slit.

Once inside the analyser, the electrons describe different paths depending upon their energies and the voltage applied to the analyser plates. For a given applied voltage, only electrons of one specific energy can be focused onto the exit slit of the analyser. To record a spectrum, the voltage on the analyser plates is swept so that progressively less energetic electrons come to a focus in turn on the exit slit, through which they can pass, be detected, and displayed as bands on chart paper. In this way, a "spectrum" of the kinetic energies of the ejected electrons is obtained. Every peak or band within the spectrum relates to one of the groups of ejected electrons, and therefore to one of the occupied orbitals of the parent substance. The processes which give rise to peaks in an electron spectrum are illustrated schematically in Figs. 1.1 and 1.2. A general view of one type of electron spectrometer is shown in Fig. 1.3, and the focusing electron energy analyser used in this spectrometer is illustrated schematically in Fig. 1.4.

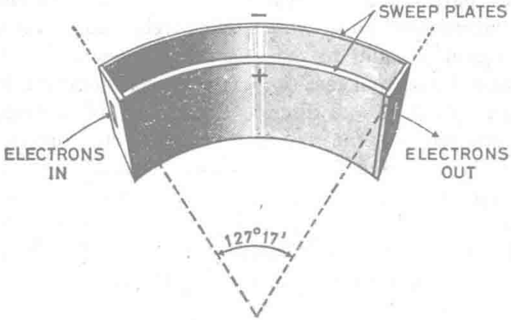

FIG. 1.4. A 127° electrostatic energy analyser. An energy spectrum is obtained by sweeping the voltage on the plates.

The spectrum as obtained on chart paper consists essentially of the count-rate registered by the focused electrons plotted against the voltage on the analyser electrodes. The voltage needed to focus an electron is clearly related to its kinetic energy, and thus to the parent ionization potential. For easy comparison of spectra obtained from different types of instruments, the x-axis of published spectra is normally calibrated in terms of "orbital ionization potential" expressed in electron volts (eV). One electron volt is numerically equal to 96·3 kJ mole^{-1}.

Multiple ionizations of the sort defined by equation (1.3) can occur

$$M + h\nu = M^{n+} + ne^{-} \tag{1.3}$$

but the ejected electrons do not give rise to discrete peaks in the spectrum. This is because the energy carried off by the n electrons is randomly partitioned amongst them so that overall there is a statistical "averaging" effect which effectively causes an increase in the background count to the spectrum of discrete peaks. This contrasts with the normal case ($n = 1$) when the single photoejected electron can only have one discrete energy. In this connection, it should be stressed that the second, third, nth, etc., orbital ionization potentials measured from the peaks in an electron spectrum are the energies needed to eject a single electron only from, respectively, the second highest, third highest, nth highest occupied orbitals of the substance being investigated, and not to the energies needed to expel respectively two, three, n, etc., electrons.

CHAPTER 2

FACTORS UNDERLYING INSTRUMENTATION AND THEIR BEARING ON THE INTERPRETATION OF RESULTS

SOURCES

(A) THE DIFFERENT TYPES OF SOURCES

The amount of energy needed to eject an electron from its parent orbital can vary from 5 to 30 eV, for valence-shell electrons, to several hundred or thousand eV for *K*-shell core electrons. Thus the prime requirement of the source is that it can provide monoenergetic energy within or in excess of this range. In principle a number of different sources, including electrons, photons, metastable atoms, etc., can be used. The manner by which the energy of the bombarding species is transferred to the target molecules varies with the type of source used, and this affects the instrumentation of the spectrometer and the interpretation of the results.

Spectra resulting from photon impact are the easiest to obtain and interpret and have accordingly found the widest application. Most of this book will in fact be concerned with photon-impact-induced spectra ("photoelectron spectra") but first, the other types of spectra, and their relation to each other and to photoelectron spectra, will be noted.

Electrons may be used as a source, but this gives rise to several problems. Firstly, there is the difficulty in generating a sufficiently intense monoenergetic supply.† Electrons emitted from a heated filament have a distribution of velocities and therefore of energies, and an electron lens has to be used to select only those electrons whose velocities lie within a chosen energy span.(1–3)‡ Secondly, more sophisticated ancillary counting equipment is required in order to differentiate primary bombarding electrons from those ejected from sample molecules, and thereby obtain a spectrum whose peaks can be simply related to orbital IPs. The main reason for this is that when one of the primary electrons scores a "hit" on a sample molecule, it does not give up all its energy, E_p, to the molecule (as a photon could), but is scattered with a lower energy, E_s. The difference between the primary and the scattered electron energies (E_p–E_s) is transferred to the molecule and can be used to expel an electron from one of the bound orbitals with a kinetic energy equal to ($E_p - E_s - I$) where I is the appropriate orbital ionization potential. Thus to examine the kinetic energy spectrum of only the ejected electrons would be of little use because ($E_p - E_s$) could assume any value, implying that electrons ejected from corresponding orbitals in different molecules of the same sample could have widely different kinetic energies. If the scattered primary electrons and the ejected electrons are examined together, meaningful results can be obtained.

The experimentation then requires coincidence counting techniques so that one examines only electrons ejected from sample molecules which have accepted a chosen specific amount of energy from the primary electrons. In practice, this requires the scattered and the ejected electrons to be sent into different energy analysers linked in a coincidence circuit. This type of approach was suggested independently by both atomic physicists and photoelectron spectroscopists,(4,5) but has only recently reached the experimental stage.(6) The practical problems are considerable, but if they can be overcome, this method of obtaining spectra could have a number of advantages since in principle the source can easily be varied in energy over a very wide range (impossible with photon sources).

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†Polyenergetic electron beams are suitable for exciting Auger electron spectra (Chapter 7), since Auger electron energies are independent of the incident ionizing energy.

‡References are given at the end of each chapter.

The use of metastable or "hot" atoms as the energizing source for electron spectroscopy has been more widespread than the use of electrons, but is of more interest to the student of collision phenomena than to the analyst. The overall equation for the ionization process brought about by a metastable (often known as "Penning ionization") is

$$A^* + B \rightarrow A + B^+ + e^-. \qquad (2.1)$$

The reaction does pass through a compound state (A^*B), however, and because of this Penning ionization spectroscopy can reveal information about processes not detected by photoelectron spectroscopy. Results from Penning ionization spectroscopy are described in a series of papers by Cermak and associates.(7–11)

Energies above the six or so electron volts needed to eject electrons from molecules correspond to photon wavelengths in the vacuum ultraviolet† (VUV) part of the electromagnetic spectrum. Siegbahn and his associates in Uppsala, Sweden were the first to investigate the use of K_α X-ray photon sources as sources for electron spectroscopy(12) whilst Turner and others in England(13) and Terenin and others in the Soviet Union(14) pioneered the use of VUV photons. The more energetic X-ray photons used by the Swedish workers enabled them to observe the results of electron emission from both the core and the valence shell orbitals of atoms and molecules, whilst the English group were limited by the VUV photon energies to just the valence shell. However, the diminished natural width of VUV photon band widths as compared with the X-ray photon band widths meant that spectra excited by using the former were much better defined, and allowed fine structure to be resolved.‡ The two approaches are thus complementary. The X-ray photoelectron work, also named "ESCA" (electron spectroscopy for chemical analysis) is usually useful only for the core electrons, whilst the VUV photon work ("PES"—photoelectron spectroscopy) is useful for only the valence-shell electrons. The broader-bands appearing

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†The vacuum ultraviolet encompasses the wavelength range from about 2A up to about 2000A. It is known as the "vacuum" ultraviolet because the atmospheric gases (and most other substances) have strong absorption bands in this region, and consequently have to be removed from instruments before measurements can be made.

‡The origin of this structure will be discussed in succeeding pages.