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Determination of Organic Structures by Physical Methods

VOLUME 3

Edited by

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Preface

In the previous two volumes of this treatise the use of established physicochemical methods of organic structure elucidation was stressed. In the intervening years these older methods have found widespread use and are now considered classic. With increasing sophistication, both in design of apparatus and in interpretative skills, the development of new approaches has been so rapid as to necessitate three additional volumes to cover the progress made. The contributors to this volume not only discuss the refinements of some of the older methods, but also present certain techniques which have not yet found much application to structure research. It may well be that these new methods will be considered classic ten years hence.

Credit for the surveys of the status of these arts must go to the individual authors; for errors of omission or commission none but the editors are to blame.

> F. C. Nachod J. J. Zuckerman

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C. R. BRUNDLE* AND M. B. ROBIN†

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I. INTRODUCTION

When monochromatic radiation of sufficient energy, $h\nu$, strikes a free atom or molecule, electrons will be ejected from that atom or molecule with energies E_n given by the equation

$$E_n = h\nu - I_n \tag{1}$$

where I_n is the ionization potential to the *n*th ionized state of the atom or molecule. The measurement of E_n and hence I_n has come to be known over the past few years as "photoelectron spectroscopy." In the case of an atom, I_n consists of a single term representing the purely electronic transition, but for a molecule, vibrational and rotational excitations may also accompany the electronic process, so that I_n actually consists of three separate terms.

$$I_n = I_E + \Delta I_{\rm vib} + \Delta I_{\rm rot} \tag{2}$$

The ionization process is illustrated schematically for a diatomic molecule in Fig. 1.

Photoelectron spectroscopy can be divided into two classes, the distinction being in the type of radiation that is used to produce ionization. The first class involves the use of vacuum ultraviolet radiation (<60 eV energy). Since first ionization potentials are rarely below 5 eV and more generally start between 9 and 13 eV, vacuum ultraviolet is the lowest energy radiation that can be used to produce ionization. This class is sometimes termed "molecular photoelectron spectroscopy" because it is applicable only to the ionization of valence shell electrons, not having sufficient energy to eject inner core electrons.

The second class involves the use of X rays (>1000 eV energy) as an ionizing source and has generally become known as the ESCA (electron spectroscopy for chemical analysis) technique, a phrase coined by Siegbahn and co-workers,^{1,2} major contributors in this field. ESCA has its greatest importance in providing the inner core ionization potentials of atoms and molecules. Photoelectron studies using radiation energies in the range between the two classes have not been made primarily because of the lack of any suitable light source operating in this range. However, synchrotron radiation, when used with a monochromator, may become of great use in the intermediate range.

This article deals in detail with molecular photoelectron spectroscopy and also covers ESCA work where it is necessary to illustrate the comparative strengths and weaknesses of the two techniques and the types of chemical information each provides. Although photoelectron spectroscopy is to date the most developed and most useful technique to the chemist, it is only one