

BOOK REVIEW

Spectroscopy in Catalysis : An Introduction

by J W Niemantsverdriet

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In modern day society, catalysis has got an important role in every sphere, be it in chemical industry or environmental pollution control and even more important will be in near future. Now, the catalyst characterization is a lively and highly relevant discipline in catalysis— it can lead to developing an active, selective and stable catalyst. In this regard, spectroscopic information provides an undoubtedly valuable insight. The book 'Spectroscopy in Catalysis, an introduction' by J W Niemantsverdriet is a very timely and welcome publication about the information that spectroscopic techniques provide concerning catalyst or catalytic phenomenon. The book comprises nine chapters and one appendix, of them Chapter 2 to Chapter 8 are devoted to different techniques and their applications are described in Chapter 9. In Chapter 1, the author gives a necessary introduction in heterogeneous catalysis, aim of catalyst characterization and research strategies with different techniques. Chapter 2 deals with different temperature programmed reaction methods applicable to real catalysts succinctly. A short treatment of transition state theory reaction rate included in this chapter will give a feeling about desorption mechanism. Photoemission spectroscopy *i.e.* X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and Auger electron spectroscopy are described briefly in Chapter 3. Actually, these techniques readily provide composition of surface of a catalyst and also a vertical distribution of elements as a function of depth. Other useful techniques based on the interaction of ions with solid *i.e.* ion spectroscopies and their underlying physical phenomena like sputtering, scattering, neutralization and ionization are described elegantly in Chapter 4. Mössbauer spectroscopy is a very important tool in giving useful information on a limited number of catalysts. In Chapter 5, the author in a lucid way has taken the reader from Mössbauer effect to the spectral information it yields about catalysts and the advantages it has specially under *in situ* conditions. X-ray

diffraction (XRD) happens to be one of the oldest and most frequently used techniques in characterization of catalyst. While XRD is only applicable to single crystal surfaces, its analogue, Low energy electron diffraction (LEED) reveals the structure of surfaces and ordered adsorbate layers. In Chapter 6, these techniques along with extended X-ray absorption fine structure (EXAFS) have brilliantly been discussed along with inherent merits and demerits. Rapid development over the years has made electron microscopy and the related techniques to yield remarkable image of the surface at atomic resolution. In Chapter 7, the author gives a nice overview of SEM, TEM, EDA, EDAX, AFM, STM, FEM and FIM and their respective applicabilities. Perhaps, infrared spectroscopy is the foremost of all modern spectroscopic techniques that are used widely in catalysis for the identification of adsorbed species. Chapter 8 discusses about all types of vibrational spectroscopic techniques, be it by absorption of photons (IR) or by scattering of photons (Raman) or electrons (EELS) and their relative advantages. Having discussed all necessary types of techniques used in catalysis, the author in Chapter 9 illustrates the catalyst characterization of down-to-earth problems of supported rhodium catalyst, cobalt-molybdenum sulphide and how the alkali promoters perturb the catalyst surface. The appendix gives a brief introduction of physics of metal surfaces, chemisorption on metals and a short treatment on magnetism, which not only helps the beginner to embark upon the subject but also refreshes the memory of an expert in this field.

Though this book is intended for students at the start of world of catalyst characterization, this reviewer is of the opinion that it is an excellent accompanying text for those plunging into a serious research in catalysis. The beautifully organized subject with illustrations, makes the reading very enjoyable. The reviewer congratulates the author for putting up this invaluable book.

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Femto-second Chemistry : (Vol. 1 – Pt I and II)

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The time-frame in which events happen in a system needs to be greatly expanded when its size/mass decreases. While macroscopic objects move rather sluggishly allowing us to observe the motion, the nuclei within a molecule move in a femto-second (10^{-15} s) time-

frame and the electrons within an atom move still faster. In the absence of an appropriate tool to follow superfast nuclear motions, and discouraged by the blurred picture provided by the energy-time uncertainty principle, scientists have given up the classical habit of picturing nuclear motion; instead, they most often prefer working with time-independent states. What changed the scenario is the generation of stable femto-second light pulses by Shank and Ippen in the middle eighties when the 'race against time'—started by George Porter in 1949 as he pressed the millisecond flash lamp into the service of chemical dynamicists—almost ended. This development of the photonic tool was matched by concurrent development of the molecular beam technique. A set of isolated, collision-free, ultra-cold molecules in a well-defined state provides an ideal system for the coherent laser pulse to interact with and for following in real time the movement of the nuclei. Briefly, the approach followed by these single-beam time-domain experiments is as follows. The ground-state stationary nuclear wavefunction is raised by a pump pulse to an upper potential energy surface (PES) where the localised wavepacket, being non-stationary with respect to the new PES, evolves with time. The motion of the wavepacket is then followed by a second delayed pulse, the wavelength or polarisation of which could be varied to probe different nuclear configurations. This allows one to almost 'see' a molecule rotating, vibrating, dissociating, pre-dissociating, transferring energy from one mode to another (or a collection of modes)—in-short, the dissolution and reformation of nuclear configurations. These fascinating experiments on tracking the nuclei over the entire PES, which covers the initial reactant state, the transition region and also the final product state, were pioneered by Zewail's group in 1987. These are discussed in Chapter 2. The core of the book lies in this beautiful summary of the works at CALTECH by Zewail, which includes discussions on rotational coherence spectroscopy, intra-molecular vibrational relaxation (IVR), non-statistical dynamics of small and large organic systems, transition-state probing, solvation dynamics and finally the control of chemical reaction by pulse manipulation. The rotational coherence spectroscopy (RCS) has further been elucidated and reviewed in a comprehensive manner in Chapter 5 (Pt. II) by Felker and Zewail where the authors demonstrate the advantages of the RCS for structure determination of large molecules and weak complexes. These demonstrations will possibly mellow down the skepticism often expressed by 'real-life' chemists who find no virtue in these esoteric experiments. Chapter 1 of the book contains an introduction by Sir George Porter who offers a chronological summary of the technological advances in trigger and detection techniques. Experimental and theoretical developments in small molecules have been discussed in Pt II. Sorokin and his co-workers at IBM have discussed real-time studies of photo-initiated, gas-phase, unimolecular reactions by transient absorption techniques. In Chapter 4, J L Knee has

discussed another time-resolved technique, namely pump-probe threshold photo-electron spectroscopy and its application to vibrational dynamics of large organic molecules including weak complexes. The rest of the Chapters (6–11) focus on theoretical developments. The wave-packet dynamics, first formulated by Heller in the late seventies, dominates the theoreticians' perceptions, and has been discussed by Schinke and Huber in Chapter 8 and S Y Lee in Chapter 7. Meier and Engel in Chapter 11 present detailed analysis of nuclear vibrational dynamics in diatomic molecules. Bandruk in Chapter 6 addresses the question of laser-dressing of molecules by an intense field, while Shapiro in Chapter 9 and Johnson and Kinsey in Chapter 10 have limited their discussion to the intricacies of the photodissociation process. Parts III, IV, V of the book are not included in Volume 1. These contain articles on more complex systems including clusters, surfaces, liquids, solids and photosynthetic centres, as well as on wave packet control and things yet to come.

The volume strikes a balance between theory and experiment, and within experiment, between techniques and results. Most of the chapters are easy to follow; however, in some sections more details of the experiments are needed. Because of the beauty of the experiments as much as their fundamental nature, I recommend this book not merely to specialists but everyone interested in chemical bond breaking and forming. The experiments are not above criticism; these are branded as one-time experiments with no 'surprise element' in it. I, for one, do not subscribe to this philosophy. S Y Lee in his article quotes the following line from H Weyl—"If I had to choose between truth and beauty, I would choose beauty anytime". It is perhaps too strong an avowal, but between utilitarian chemistry and aesthetic aspects of chemistry, the book has certainly made out a strong case in favour of the latter.

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