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Part I

Basics

1

Introduction

At the start it will be useful to cast ZEKE spectroscopy into a general context. The history of chemistry has been punctuated by major developments in spectroscopy. Spectroscopy has given us marvellous insights into molecular shape, structure and constitution. In short, it has taught us the nature of the building blocks of molecules and molecular systems. It has given us an idea of the architecture of chemistry – just as any road going around a city is made easier if one knows the size and shapes of its buildings. In my opinion, obtaining descriptions of such chemical buildings is the function of spectroscopy. Indeed, the structure of molecules serves as an architectural guide-post on our journey through chemistry. Our desire to seek new landmarks in chemistry sparks, of course, our interest in the realization of every new landmark as it comes into view. As chemistry evolves, and I think it is strongly and rapidly evolving, particularly now as one comes to the turn of the century, one is ever on the lookout for new ways of describing the architecture in order to guide us on to new roads for this great journey of chemical understanding. I think that this was once very aptly stated by Lord Todd at the 1985 IUPAC meeting in Manchester. He made the interesting remark that the last century was essentially the century of the chemistry of strong bonds, of tight linkages and the understanding thereof, and, of course, the associated spectroscopy. He felt very strongly at that time that the next century would see the importance of the weak bond, the fluctuating bond and rearrangements. One knows, of course, that this is certainly true, as has been demonstrated in our understanding of biochemical systems, which could not be thought of in terms of hard bonds, but rather in terms of very soft bonds often manifested in the subtle equilibria that make up biochemical transformations. So the subject of weak bonds has certainly emerged from what it was when I was a student of physical chemistry, namely a very small field in which one

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spoke parenthetically about weak bonded interactions such as van der Waals bonds as an inconsequential subject on the sidelines of physical chemistry. These weak bonds have since become increasingly a core subject of chemistry that is important for much of our new understanding. I think that Lord Todd's comment in 1985 will turn out to have been prescient and more true than most scientists thought at the time. Thus the problem of present day spectroscopy and the applications which are current today can be summarized as a question of the understanding of the architecture of this new chemistry that one is approaching. Here our new questions are not totally answered by our traditional methods, which are Raman spectroscopy, infrared spectroscopy and many other types of spectroscopy. One needs to learn about a series of new systems for architectural structures and landmarks in which these structures are quite different from those one had known hitherto. One example, already mentioned, is that of molecules bonded by van der Waals forces, which had been considered an esoteric area, but has become an emerging subject equal in importance to traditional strong bonding. As a consequence, the understanding of weakly bonded species, with its many consequences for large structures, will move increasingly into the core of our chemical thinking. In particular, one is now starting to understand how these 'soft' systems, which one began to understand in isolated systems, correlate with questions that had arisen in other areas such as in surface spectroscopies e.g. **H**igh-**R**esolution **E**lectron **E**nergy **L**oss **S**pectroscopy (HREELS), or **E**xtended **X**-Ray **A**bsorption **F**ine **S**tructure (EXAFS). The interlinking of different spectroscopies will perhaps become one of the very important areas one needs to address as one begins to understand the relationship between structures and soft intermediates.

To examine these unusual molecules with soft bonding, and even unconventional neutral molecules and clusters that can be produced only in mixtures, one must consider utilizing mass-selective experimental techniques. What methods are available for neutral molecule spectroscopy, particularly in a mixture, for which mass-selectivity is required? How should one investigate ions, positive or negative? How do charges interact with bonding? How do reactive intermediates appear spectroscopically? Consider for example H_3O^+, $NH_4{}^+$ or even more complicated species as typical cases. How can transition states or activated complexes be seen spectroscopically? Transition states in the Polanyi–Wigner–Eyring theory of chemical reactions are characteristically extremely short-lived, typical results suggesting life-times of half a picosecond. How are clusters formed? How do metal–metal and metal–non-metal transitions exist in clusters?

What do surface-bound molecules look like and how do they relate to clusters or to embedded reactions of the solid? How does the whole system interact when it reacts in the presence of the Fermi sea of electrons in the metal? It is in this vein that our initial journey through these new architectural landmarks in soft chemistry is to be launched.

2

Spectroscopy – a historical perspective

This chapter will provide an overview of the various spectroscopies which are of current and topical interest. In the next three chapters, I will naturally address in most detail those spectroscopic experiments that we have carried out in Munich and, in particular, focus on what we have come to call **Ze**ro **K**inetic **E**nergy (ZEKE) spectroscopy. The initial development in this direction was work done on the threshold spectroscopy of photoelectrons with W. Peatman at Northwestern University. In Munich, we started again with a variant of this technique. It was the work together with my first group in Munich, K. Müller-Dethlefs and initially, M. Sander, which started our work on the ZEKE variant of this **T**hreshold **P**hoto**e**lectron **S**pectroscopy (TPES).

In a short tour of spectroscopy (Table 2.1), I shall present my personal view of this development. Perhaps it is hard to define the origin of spectroscopy. Perhaps I should go back to Newton, who in 1666 dispersed white light into colours and first coined the word spectrum. Here I choose as a modern date to start with the year 1800, in which Herschel, a musician and astronomer, discerned that the spectrum of light when absorbed by a black body extended to the infrared, i.e. that the sun had a very strong spectrum in this invisible range. Stop number two on my journey is a contribution from Munich. Fraunhofer worked in a laboratory near Munich and was employed to make better optical quality glass. The problem one had in those days was to make glass without bubbles for lenses and for refractive optics. This was very difficult and a laboratory was set up by Utzschneider for this purpose in the Benediktbeuern monastery south of Munich. One can still see the original laboratory there today. Fraunhofer indexed 574 of the famous dark lines found in the sun's spectrum. More than 20 000 of these lines are known today. This pioneering work, published in 1817 in the annals of the Bayerische Akademie der Wissenschaften, was a milestone in spectroscopy.

Table 2.1. *The history of spectroscopy*

Newton 1666
Herschel: infrared 1800
Fraunhofer 1814
Bunsen and Kirchhoff 1859
Rayleigh 1871
Hallwachs 1887 and Einstein 1905
Rydberg 1890
Röntgen 1895
J. J. Thomson 1897
Aston 1912
J. Franck and G. Hertz 1914
Raman and Smekal 1928
Townes and Basov 1954
Maiman 1960
Turner, Terenin and Siegbahn 1962
Herzberg 1971
Bloembergen and Schawlow 1981

The next landmark I would choose is that associated with R. Bunsen and G. Kirchhoff (Fig. 2.1), who might well be referred to as the initiators of the field of chemical application of spectroscopy, i.e. spectral analysis, in which spectra are used for chemical analysis. The cooperation between these two men was very interesting. Although Bunsen was a chemist, he even then recognized the strong interaction between chemistry and physics. Bunsen said that 'a chemist who is not at the same time a physicist is nothing at all' (Ein Chemiker, der nicht gleichzeitig Physiker ist, ist garnichts). Kirchhoff was a physicist who originally worked in Breslau. Bunsen was performing his analysis of systems by looking through filters and observing the system by colour changes. Kirchhoff made the suggestion that, since spectrographs for the dispersion of light were then available, it would be useful to add such an instrument to improve the spectral analysis. So it was that, during a famous evening walk at sunset in Heidelberg on the Philosophenweg, Bunsen convinced Kirchhoff to join him in Heidelberg and abandon his position in Breslau in order to start work on this historic cooperation of physics and chemistry which led to what is now spectral analysis. Their initial application of this spectral method to the mineral springs in the Bad Dürkheimer Mineralbrunnen led to the discovery of the spectra of rubidium and caesium – although the real problem of the Maxquelle was arsenic.

Then, of course, came the early work of Hallwachs on the photoelectric effect, involving the observation of the charging of a metal plate when it is

Fig. 2.1 R. Bunsen and G. Kirchhoff on a walk (courtesy of Deutsches Museum München).

irradiated with UV light, and of Einstein, who interpreted it. At this point, I have to mention the great discovery of the electron by J. J. Thomson in Cambridge. In Cambridge there began the work which not only brought about our understanding of the electron, but also laid the foundation of early mass spectrometry. Spectroscopy continued in many centres, including the well-known work of Rydberg and his famous formula for cataloguing the hydrogen spectrum, Röntgen's original work with X-rays, first 100 years ago in Würzburg and later in Munich, the scattering experiments of Rayleigh utilizing the sun's rays, the determination of the energy levels in the mercury system in 1914 by the Franck–Hertz experiments, the first measurement by Raman employing what is now known as the Raman effect following an early suggestion by Smekal and the encyclopaedic work of G. Herzberg.

Photoelectron Spectroscopy (PES) has an equally rich history (Table 2.2). The three famous schools should be mentioned: those of David Turner in Oxford, Terenin, Kurbatov and Vilesov in Leningrad (now Sankt Petersburg) and Siegbahn in Uppsala. These three groups contributed enormously much to the pioneering work on which many people's understanding of photoelectron spectroscopy is based. Their work has been so important, indeed instrumental, to our understanding of molecular structure that I think much of what is known today about molecular structure is due to this beautiful work which encompassed the vacuum ultraviolet region of molecular orbitals as well as the atom-specific core excitations with X-rays.

The first demonstration of an optical laser, performed by Maiman, used the three-level ruby system. Recent work on lasers was carried out by Townes and Basov, on the basis of which Bloembergen, Schawlow and Hänsch developed atomic laser spectroscopy.

However, of course, spectroscopy provides understanding of systems and of their structures. Here an important individual was August Kekulé (Fig. 2.2), who was one of the early proposers of strange non-rigid structures in the benzene bonds and extended the discussion to the question of the alternating double and single bonds, which already was a departure from the idea of simple bonding. This is a story that continues today with the structure of benzene dimers and trimers.

It has been reported that much of what Kekulé did he invented on a tram in London. Some students decided during a bar-room celebration that what he was really talking about in benzene was that which is shown in Fig. 2.3. These well-known pictures were generated by them in a later spoof article.

To get into current practical examples in spectroscopy, let us consider whither the work of Kekulé leads us today. At the top of Fig. 2.4 one has an excitation spectrum of benzene at normal dye laser resolution. Now, at the resolution of one wavenumber (1 cm^{-1}), it shows the vibrational transitions which are involved in two-photon absorption, this being the absorp-

Table 2.2. *Spectroscopy with photons and electrons*

PIE		(1954)
Photo-ionization efficiency		
Watanabe	Cambridge, Massachusetts	
PES		(1961)
Photoelectron spectroscopy		
Siegbahn	Uppsala	
Turner	Oxford	
Terenin	Leningrad	
TPES		(1969)
Threshold photoelectron spectroscopy		
Peatman	Evanston	
REMPI–MS		(1978)
Resonance-enhanced multiphoton ionization-mass spectroscopy		
Boesl	Munich	
Bernstein	Columbia	
Letokhov	Moscow	
RETOF		(1973)
Reflectron time of flight		
Mamyrin	Leningrad	
Boesl	Munich	
ZEKE		(1984)
Zero electron kinetic energy		
Müller-Dethlefs	Munich	
Anion ZEKE		(1989)
Neumark	Berkeley, California	
Boesl	Munich	
European Science Conferences		
Kreuth		(1991)
Giens		(1993)
Lenggries		(1995)

tion of two photons at high laser intensity. In benzene, the electronic $S_1 \leftarrow S_0$ transition is forbidden both for one-photon and for two-photon absorption. The first band shown here is vibrationally allowed in the two-photon spectrum and is induced by the vibration called ν_{14}. This vibration has the same symmetry as the electronic S_1 state, namely b_{2u}; the transition is then allowed when the ν_{14} vibration is excited in S_1. Clearly, two-photon transitions have selection rules different from those for one-photon transitions, in the same way that a Raman transition has selection rules different from

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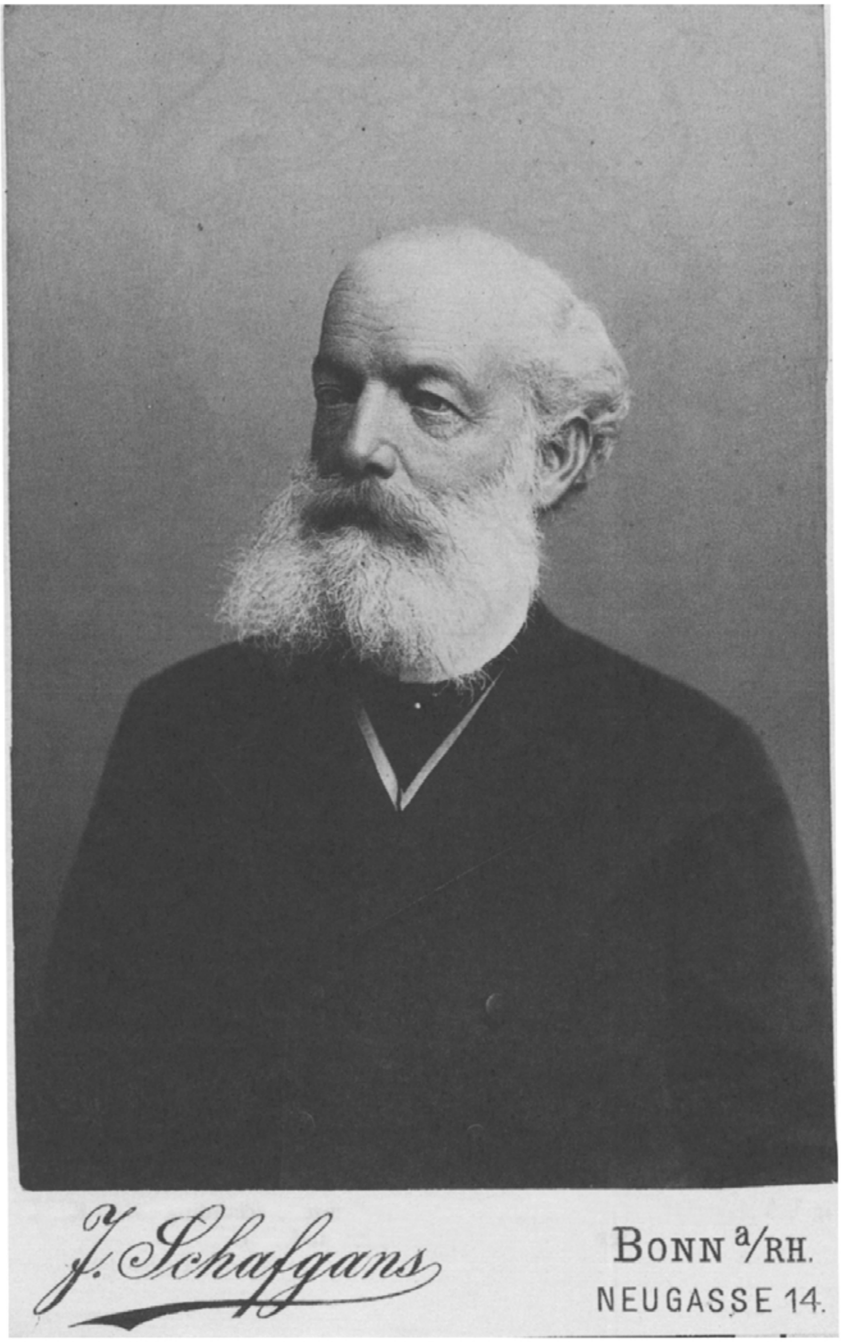

Fig. 2.2 August Kekulé (courtesy of Deutsches Museum, München).