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Spectroscopy in our age

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Abstract. The development of modern spectroscopy is summarized from Bunsen's detection of atoms as the beginning of spectral analysis to modern molecular spectroscopies including new high resolution techniques for molecular ions. Recent experiments involving long range charge migration in peptides and proteins are outlined.

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Historically, spectroscopy began with a word and concept as was defined by Isaac Newton in 1664. It progressed with the discoveries of Fraunhofer, who observed some 700 lines in the solar spectrum in 1814, to the epochal discovery by Bunsen and Kirchhoff in 1859 that these atomic lines could also be produced here on earth. This demonstrated for the first time that the same elements that exist in the sun also are present here on earth. Bunsen recognized the importance of this discovery and noted on the day before the experiment that this would be a major breakthrough, should the experiment be successful. Discussing this discovery with a banker, however, led him to agree with the banker that mining these raw materials on the sun was impractical. The experimental observation of these atomic lines was made possible by a fortuitous cooperation between the chemist Bunsen, who saw the colors in the flames, and the physicist Kirchhoff, who suggested resolving these lines spectrally for purposes of identification. This fortunate cooperation was the beginning of what is now known as spectral analysis. In fact, it led to the original incidental discovery of the elements rubidium and cesium by the analysis of sparkling water from the famous spa of Bad Dürkheim. Interestingly, the discovery was a case of serendipity, since the original task was to analyze for arsenic, which was contained in the spa's water of that day. This was only present in small quantities to be sure, but was used for purposes of improving facial complexion and beauty.
Some 140 years ago Bunsen recognized the need for chemists and physicists to work together and is quoted as saying "A chemist who is not also a physicist is nothing."

Over the years the subject of spectroscopy has matured and many new inventions and discoveries have taken place. This includes spectral analysis to the limits of resolution, down to tens of Hertz vibrations in the limit, but more routinely below the Doppler limit ($1\,\mathrm{GHz} = 0.03\,\mathrm{cm}^{-1}$), as an almost routine tool [1]. Similarly, the Fourier complement to frequency resolution is time resolution, where timing to 5 fs is now possible [2], but routine commercial instruments go to 200 fs, and even 25-fs instruments are now available. The energy uncertainty corresponding to 5 fs is so large that it encompasses all of chemistry, so that attoseconds, though now conceivable [3], are rarely observed directly, and in general will be of somewhat less interest considering the spread in energy and the much higher experimental effort required. Chemistry in the femtosecond realm, often termed femtochemistry, has now been recognized for its vast importance in molecular systems by the award of the last Nobel prize to Ahmed Zewail [4].

Not only have the extreme ranges of time and frequency been explored, but also many areas of interest have often required constructing tailor-made devices and had to await the discovery of new principles of spectroscopy. One such new field is the study of molecular ions, either positive or negative, which are fundamental methods of import in all of chemistry and physics. The study of ions goes back to early detection and analysis techniques, usually performed in mass spectrometers, in particular as seen in the first work of J.J. Thomson in 1907 [5], which marked the beginnings in that area. Although mass spectrometry measures ions and the fragments, it does not provide spectroscopic information about the molecular eigenstates of the ion. For this we had to await a technique that could couple ion detection with spectroscopy such as REMPI [6, 7]. This has become an important tool in most spectroscopy laboratories [8]. For molecular ions the first important results were obtained by molecular photoelectron spectroscopy, a technique invented by the group of Turner in England [9] and the group of Terenin in Russia [10]. Interestingly, this also provided the first information on deep lying eigenstates within the molecule characterized by the so-called molecular orbitals; a subject of profound influence on all of modern chemistry. The energy spectrum was obtained from the electrons emitted in the photoionization experiment and, considering the difficulties in measuring

precise electron energies, the energy bandwidth was of necessity always somewhat broad ($\sim 100\,\mathrm{cm}^{-1}$). Most recently, a new principle was put forth that now at last enables the determination of a true high resolution spectroscopy of molecular ions, ZEKE spectroscopy [11, 12]. This method involves looking at the zero kinetic energy electrons as a signature of an eigenstate of the ion as it is scanned by the light source. This new ion spectroscopy has the absolute accuracy of the light source an d bandwidth permitting measurements into the sub-Doppler region of some 100 MHz ($0.003\,\mathrm{cm}^{-1}$) – in fact now permitting resolution even into the microwave region [13]. Such resolution has been possible with the principle of ZEKE detection. Light sources are now available for ZEKE spectra at very high energies, e.g. synchrotron light sources. An example of this can be found in the work on high energy ZEKE pioneered by the ALS in Berkeley. Coincidence experiments have here led to well defined energetics such as are required for measuring the thermochemistry of chemical reactions [14].

Much as spectroscopy has recently shifted its attention to ions, the field has also shifted its attention to large systems, indeed even to biological systems. Here classic advances have provided major progress towards understanding the bioenergetics in two classic areas. The first is the reaction center as it is found in purple bacteria or in green plants. Here, spectroscopy has served to unravel many of the individual steps in the electron transport in the system from the antenna to the final ATP site [15]. Similarly, another area is that of the visual pigment of rhodopsin. Much work has been done in femtosecond spectroscopy to identify the original steps after the excitation of retinal by light, through its 13-cis isomerization, down to the proton shift into the proteins attached to the Schiff base [16]. The complexity of these issues has made for slow progress. The necessity of the 13-cis isomerization, as a precursor for the optical pump, is still an open question and a matter of contention. The quest for understanding some biological systems by spectroscopic techniques has thus been of great current interest. Lately there has also been some return to a reductionist principle in looking at small systems. Here, one tries to understand basic processes using appropriate model systems, which have the advantage of looking at only a few of the many possible processes. However, one needs to ascertain that these model systems are scalable to the real world and do not just solve some unrelated questions. This requires careful choices.

The study of DNA and of proteins have been the subject of many of these attempts to apply spectroscopy to model systems. Such studies are, of course, driven by the health and drug industry, but specifically by the international efforts to chart the human genome – a task whose completion is just now being touted by the press. We are, after solving most of the Drosophila genome, also now untangling the 100 000 genes of the human genome. Large as this effort is, and important as the results are, the genes are just the factories that produce the necessary proteins; hence, this is just the first step in our quest of total understanding. Now the problem of analyzing and evaluating the 1 million proteins that are produced by the genes begins. These proteins are the workhorses of the human cell. Genes are powerful, but in the end one needs to get at the proteins that carry out the bodily functions. Compared to proteins, DNA molecules are simple. Proteins contain some 20 amino acids and each is a chemical and electronic factory of its own – producing complicated and often unpredictable shapes that are constantly changing to accommodate the required bodily functions. They are involved in cellular processes, which we must master in our progress towards the control of disease. This is the subject of proteomics.

Charge transport and proton transport feed the engines inside the living cell membrane. Recently, model studies of small protein fragments, i.e. peptides, have been studied with spectroscopy, using UV excitation into the benzenoid moiety such as in tryptophan, and studying the extreme long range charge migration initiated by this highly local excitation [17]. Here we see a joint effect between the local electronic states of the amino acids cooperating with the internal torsional modes of the protein [18] (Fig. 1). In the more complex system of nerves we have a local charge impulse (action potential) originating in the brain and ending in the long range effect of the chemical reaction in the fingers by millisecond electrical impulses over long ranges.

Such a distal and extremely facile transport of charge and chemical information to the other end of a very large molecule constitutes one of the new frontiers in the spectroscopic approach to chemistry, both in spectroscopy and dynamics [19].

Hence, spectroscopy has now covered broad domains of time and frequency, it has been applied to small molecules and biological systems as well as to neutrals and to complex ions. In short, there is hardly a topic immune to its progress. Indeed one can say that any progress we make in the understanding of a process presupposes our understanding of structures. Present technological priorities unfortunately often forget that without structure – hence without spectroscopy – little progress is possible in any understanding of the chemistry

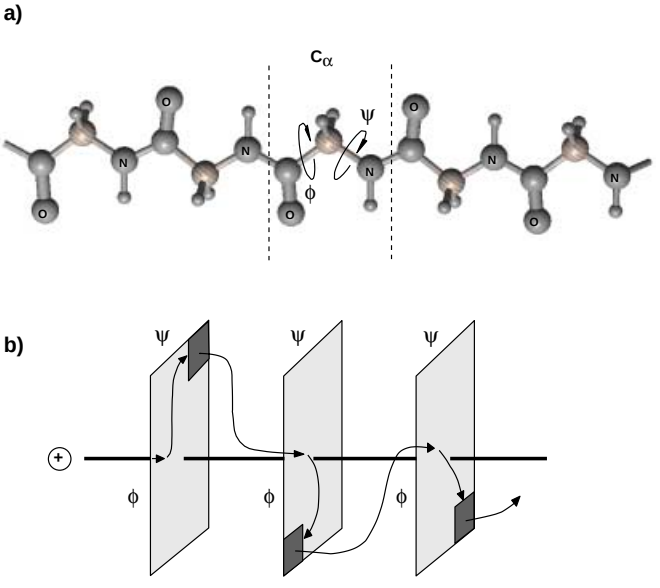

Fig. 1. a Charge transport in a polypeptide chain. Polypeptide chain with rotational motion around the bonds at the C_α-carbon of an amino acid subgroup with rotational angles Φ and Ψ. **b** The charge is excited in a donor and injected in the polypeptide chain. The charge will stay within the subgroup at the C_α-carbon, until the rotation of Φ and Ψ within the Ramachandran plot reaches a critical angle at which point the charge is transferred to the next subgroup providing the electronic energies match. The charge will stay there until next critical angle is reached and this will iterate until the final site is reached, where chemical reaction can occur. The final site need not be the end of the chain

and physics of molecules, large or small. The understanding of dynamics is then an important complementary field.

In our ever constant search for new bandwagons one should not forget that even the most sophisticated and most applied new technique requires first of all a deeper understanding of spectroscopy along with dynamics. In small systems this dialogue is realized – for biological systems it is yet to be discovered.

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