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Michael Allan − electron impact spectroscopy at its best[⋆]

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Early in 2016, Michael Allan, internationally well-known for his work on electron-impact spectroscopy involving gaseous atoms and molecules, retired from his professorship of physical chemistry at the University of Fribourg (Switzerland). It is fitting and a pleasure to recall on this occasion some of the lasting contributions which Michael provided to the field over more than 30 years.

Michael's roots lie in bohemia where he was born in 1949 in the town of Pardubice (about 100 km east of Prague) and received his school education. In 1968 his family emigrated to Switzerland, and Michael took up studies of chemistry at the University of Basel, graduating there in 1973. Under the guidance of John P. Maier, he stayed at Basel to work for a Ph.D. thesis involving photoelectron and optical emission spectroscopy of organic molecules and ions, respectively, and completed it in 1976. A postdoctoral fellowship brought him to Yale University (New Haven, USA) where he worked in the laboratory created by George Schulz (the discoverer of the prominent He$^-$ ($1s\,2s^2$) resonance) and led by Shek Fu Wong after Schulz's early death in 1975. Important results were obtained which elucidated the very strong dependence of dissociative electron attachment on rovibrational temperature for the molecules H$_2$, D$_2$, HF, and HCl. This period had a strong influence on Michael's future work.

In 1980 Michael accepted a position as Oberassistent in physical chemistry at Fribourg. Using an optimized home-built trochoidal electron monochromator (TEM) system including a double-pass trochoidal electron analyzer, Michael carried out an impressive series of inelastic electron scattering studies on gaseous targets which characterized in detail the properties of low-lying anion resonances in small molecules. This work, published as a review in the Journal of Electron Spectroscopy [1], was acknowledged by the habilitation and the Werner prize of the Swiss Chemical Society. To illustrate the quality
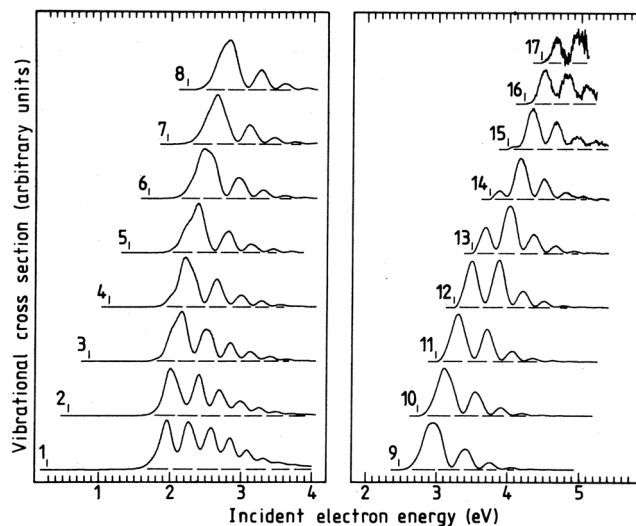
Fig. 1. Vibrational excitation functions for the $0 \rightarrow v$ transitions in e − N$_2$ scattering (Fig. 2 in Ref. [2]). The excitation thresholds are indicated by vertical lines.

of the experimental data, we show in Figure 1 relative cross sections for vibrational excitation (VE) of the nitrogen molecule (initially in the vibrational ground state) to final vibrational levels v up to $v = 17$ (!) through the prominent N$_2^-$ ($^2\Pi_g$) shape resonance at impact energies around 2.5 eV [2]. The excitation functions elucidate the nuclear dynamics (vibrational structure) in the anion resonance in fascinating detail. The peak cross sections for the final vibrational levels v vary over more than 6 orders of magnitude.

From 1988 on, Michael Allan served as a professor of physical chemistry at the University of Fribourg. Further work was carried out with the TEM machine which was used – with extensions – in different ways. Implementing time-of-flight analysis of the detected electrons, the experiment was able to separate the previously superimposed contributions due to scattering in the near-forward and − backward directions [3] and thus could produce measured data for backward-scattering in differential cross sections,

beyond the angular range accessible before the introduction of the magnetic-angle-changer (see below). Moreover, mass-spectrometric analysis of the anions allowed detailed studies of dissociative electron attachment (DEA) for a wide range of molecules. Absolute DEA cross sections, measured, e.g., for HCl, HBr, HCN, HCOOH and their deuterated analogues, provided decisive information on the quality of theoretical predictions and on the underlying reaction mechanism. On the other hand, implementation of a mass-analyzed source of slow atomic chlorine and bromine anions in combination with a thermal beam of hydrogen or deuterium atoms allowed high resolution studies of the energy spectrum of electrons resulting from associative electron detachment for the systems $Cl^-/Br^- + H/D$ (e.g. $Cl^- + H \rightarrow HCl(v) + e^-$) at collision energies below 1 eV; thus specific channel interactions could be elucidated, confirming the predictions of *non*local resonance theory.

With the aim to obtain angle-dependent cross sections for elastic and inelastic electron scattering from gaseous species down to very low impact and detection energies at narrow energy widths, Michael constructed and built a new apparatus involving double-pass electrostatic electron selectors [4,5]. This machine – when operated with Michael's skill and patience – produced low-energy electron scattering data for atoms and molecules in the gas phase at unprecedented quality with regard to resolution (energy width down to 6.6 meV), signal-to-noise ratio and reliability concerning the energy dependence and absolute size of the cross sections. This apparatus involved strong pumping on the effusive or supersonic target beam and differential pumping on both the double-hemispherical electron monochromator and the rotatable double-hemispherical analyzer (accessing scattering angles from 0° to 135°), thereby yielding excellent beam profiles with strongly reduced tails.

Following the introduction of the magnetic-angle-changer (MAC) by Read and Channing in 1996 [6], Michael constructed his own MAC and added it to the new machine [7]; this device is of amazing elegance (though not easy to build) and has the virtue of possessing a relatively open structure and thereby keeping an efficient pumping of the target beam (see Fig. 2b), a feature important for measurements of absolute cross sections and for the operation of a supersonic free jet. The MAC basically consists of two counterrunning magnetic coils with a common axis, designed such that the electron trajectories hit the scattering center and the scattered electrons emerge at angles different from those for field-free conditions (see Fig. 2a). It allows detection of scattering into angles θ (here $\theta > 135°$ up to 180°) which are not accessible mechanically, thus covering the full angular range and allowing the determination of angle-integrated cross sections. In Michael's special device (Fig. 2b) [7] both the inner and the outer solenoids consist of a *single* layer of self-supporting thin copper tubing, cooled by circulating water. The copper tubing is insulated by thin-walled shrinkable polytetrafluoroethylene tubing, painted with a thin layer of epoxy resin, and then with a layer of colloidal graphite to provide
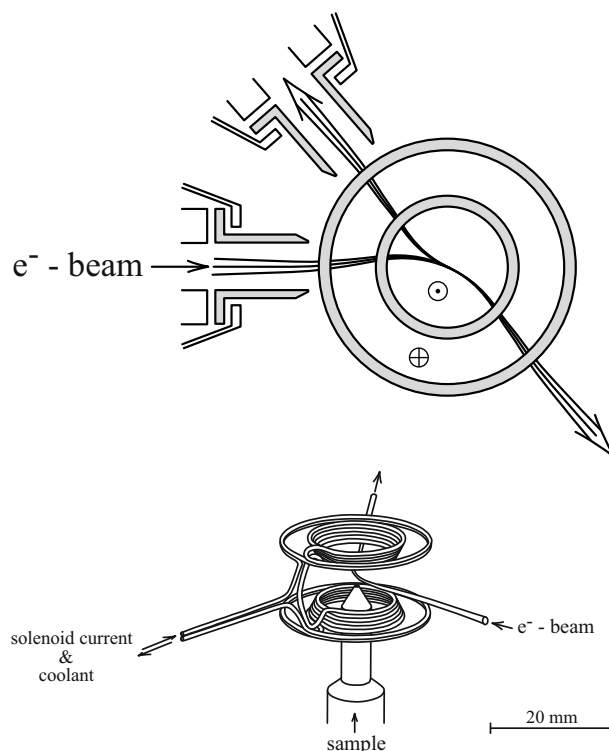

Fig. 2. (a: top) Schematic diagram of a Magnetic Angle Changer. The picture shows the electron analyzer placed at 135° and the magnetic deflection set to measure electrons elastically scattered into 180° (Fig. 2 in Ref. [8]). (b: bottom) Perspective drawing of the Magnetic Angle Changer used in Fribourg (Fig. 1 in Ref. [7]).

a conductive surface. The graphite coatings on the upper and lower parts of the structure are not electrically connected and their potentials are separately adjustable to provide a means of compensating stray electric fields in the collision region, thereby improving the effective energy resolution and the capability to detect scattered electrons with very low energy.

Using this optimized apparatus, many aspects in electron-molecule scattering could be elucidated; for illustration, we briefly present a few of the highlights. The Fermi dyad in CO_2, i.e. the Fermi-coupled superpositions FR_I and FR_{II} (energy separation 13 meV) of the normal vibrational modes (10^00) and (02^00), were fully resolved for the first time [9], thereby providing insight into the selective mechanisms for electron-induced excitation of FR_I and FR_{II} (see Fig. 3 for the respective cross sections). Only the vibration FR_{II}, representing the *in-phase* superposition of stretching and bending, is strongly excited near threshold through an *s*-wave type virtual anion scattering state. Both FR_{II} and FR_I (for the latter, stretching and bending occurs *out-of-phase*) are coupled to the $^2\Pi_u$ shape resonance, FR_{II} through its lower-lying bent $^2A_1$, and FR_I through the higher lying $^2B_2$ branch.

In the molecule $NO(X\,^2\Pi_\Omega)$ fine-structure changing ($\Delta\Omega = \pm 1$) collisions were measured from both the ground level ($\Omega = 1/2$) and the excited level ($\Omega = 3/2$) [10], located only 15 meV above the ground state
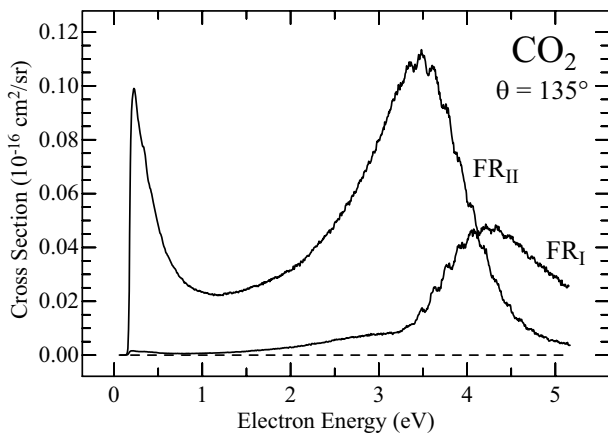
Fig. 3. Differential cross sections for vibrational excitation of the two members of the Fermi dyad (FR$_I$ and FR$_{II}$) of CO_2, recorded at the energy losses of 0.159 and 0.172 eV, respectively (Fig. 2 in Ref. [9]).
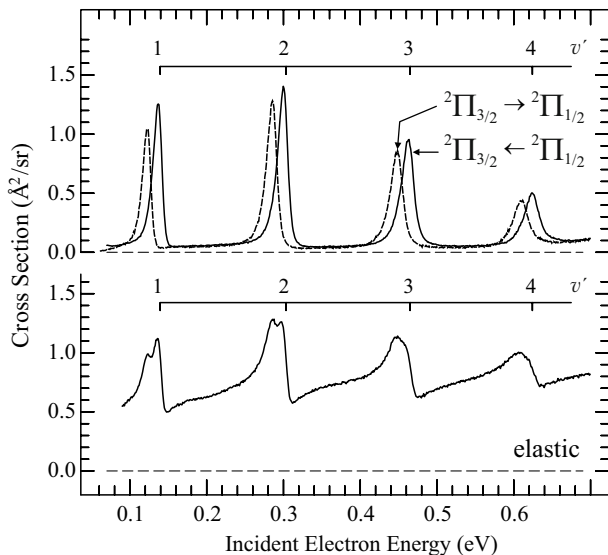

Fig. 4. Differential cross sections for elastic scattering ($\Delta\Omega = 0$) (bottom) and for inelastic ($\Delta\Omega = +1/2$) and superelastic scattering ($\Delta\Omega = -1/2$) with respect to the electronic fine structure transition in $NO(^2\Pi_\Omega)$ (Fig. 3 in Ref. [10]), measured at the scattering angle $135°$.

(thermally-excited fraction 36%). Figure 4 shows the respective $\Delta\Omega = \pm1$ cross sections and the elastic cross section ($\Delta\Omega = 0$) over the incident energy range $0.08-0.7$ eV. Similar to the findings for vibrational excitation, the $\Delta\Omega = \pm1$ cross sections are strongly enhanced in the region of the narrow $NO^-(^3\Sigma^-, v')$ resonances (deduced intrinsic width 7 meV for $v' = 2$) and have – compatible with the principle of detailed balance – nearly the same peak cross sections for the $\Delta\Omega = +1$ and $\Delta\Omega = -1$ processes with a particular v'.

In order to pinpoint the role of permanent electric dipole moments μ on the cross sections, molecules of the same atomic composition, but different symmetry were studied such as the cis- and trans-form of 1,2-difluoroethene. Whereas the elastic and VE cross sections
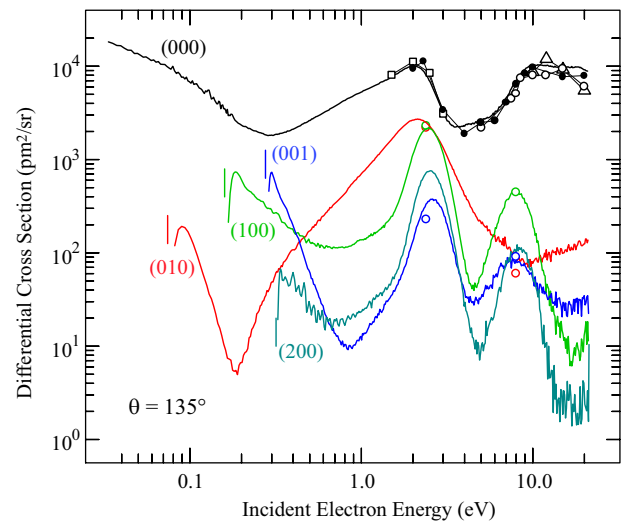

Fig. 5. Differential elastic and selected vibrational cross sections in e + N_2O scattering, measured at the scattering angle $135°$ and shown on a log–log scale (Fig. 9 in Ref. [12]; references to earlier results, shown by symbols, are given in Ref. [12]).

for the cis-form ($\mu = 2.42$ Debye) and trans-form ($\mu = 0$) are of similar magnitude in the energy range of the π^* shape resonance around 2.3 eV, the elastic cross section is strongly enhanced for the cis-form at energies below about 0.3 eV through the long-range electron-dipole interaction, and the VE cross section – e.g. for the C=C stretch mode – exhibits a strong dipole-mediated threshold peak only for the cis-form [11].

One of the strengths of the Fribourg spectrometer is the low-energy capacity which allows the measurement of elastic cross sections down to about 30 meV and of mode-resolved VE cross sections down to threshold. At the same time continuous coverage up to about 20 eV is achieved, i.e. the range of shape and core-excited Feshbach resonances which had been studied before by other groups. As an example we present in Figure 5 absolute differential cross sections, measured at $135°$ for vibrationally elastic scattering and for VE of one quantum of the three fundamental modes as well as of the (200) overtone in N_2O [12]. This figure nicely illustrates the gain in knowledge at energies below about 1 eV and the consistency with earlier work at higher energies.

To reveal the complex autodetachment dynamics of the temporary anions (resonances), formed in electron collisions with molecules, two-dimensional (2D) electron impact spectroscopy [13] is particularly suited. In this method, the cross sections are plotted as a function of both the incident electron energy E_i (ordinate) and the energy loss ΔE (abscissa). These diagrams are constructed from many energy loss spectra measured over the desired range of incident energies with a sufficiently dense grid, the cross sections being displayed in a colour-coded way. Along horizontal lines (E_i constant) energy loss spectra are observed, whereas excitation functions for processes with fixed energy loss are seen along vertical lines; the diagonal with $E_i = \Delta E$ depicts the "threshold line". Over the last
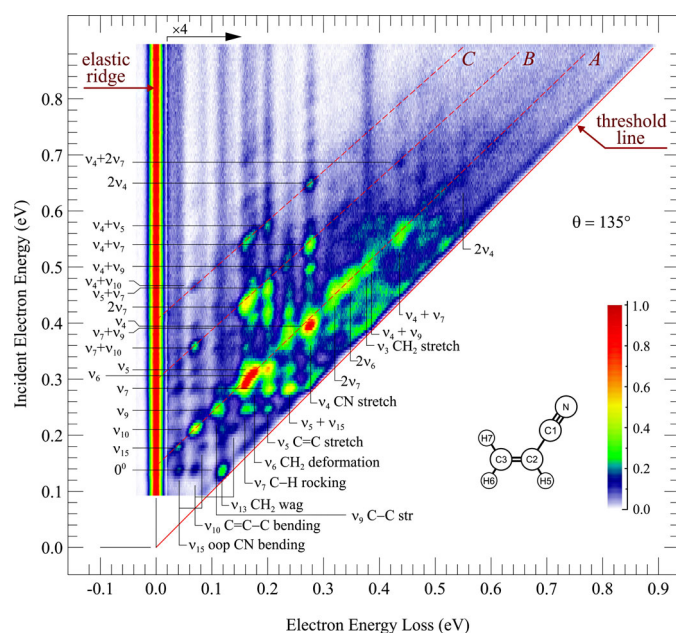
Fig. 6. Two-dimensional electron energy-loss spectrum of acrylonitrile, measured at the scattering angle 135° (Fig. 1 in Ref. [14]).

In about 160 publications on electron impact spectroscopy, Michael studied a broad range of molecules from H_2 to polyatomic species such as furan, phenyl azide, propellane, cyclooctene, and $Pt(PF_3)_4$; he also provided, in part motivated by atomic physicists, benchmark cross sections for elastic and inelastic scattering from the rare gas atoms. Michael's work was highly independent: on 46 papers, he took responsibility as sole author. At the same time he strongly supported his students and was open to cooperations with other experimental and theoretical groups in cases where he could provide essential data to make progress in the understanding of a topic. The quality of his experiments and his insightful contributions to the discussion of the results always enriched the combined efforts. Michael's scientific curiosity and excellence go along with modesty and integrity. His farewell lecture in Fribourg on 28 January 2016 was entitled: *free electrons and molecules – a lifelong passion.*

four years, Michael and his student Regeta applied this method to several polyatomic molecules at high energy resolution with emphasis on VE at low energies. So far, only few of the results have been published. As an example, we briefly discuss the 2D electron impact spectrum of the dipolar molecule acrylonitrile (CH_2CHCN) ($\mu = 3.86$ D), obtained for the range $E_i = 0.095-0.9$ eV at $\theta = 135°$ (see Fig. 6) [14]. Many of the 15 normal vibrational modes as well as overtones and combination modes are excited. Besides the expected horizontal (for given resonances) and the vertical (for given final states) patterns of peaks, striking diagonal arrangements of sharp peaks at given residual energies $E_r = E_i - \Delta E$ are observed; they reveal restrictive selectivity in the vibrational autodetachment process from the *valence* temporary anion $A^-(\nu_A)$ to the neutral molecule $M(\nu_m)$.

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