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Fundamentals and applications of molecular photoelectron spectroscopy – Festschrift for Ivan Powis

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The year 2021 marks the 20th anniversary of the first experimental verification of a novel chiroptical phenomenon in the angular scattering of electrons upon photoionization of a chiral molecule by VUV circularly polarized synchrotron radiation.¹ This experimental proof appeared 25 years after the first phenomenological prediction by Ritchie² and Cherepkov³ but just one year after Ivan Powis^{4,5} published his first two seminal theoretical papers on this novel phenomenon. This experiment confirmed the predictions of detailed scattering calculations that the electron asymmetry, later called PhotoElectron Circular Dichroism

(PECD), was large and, as shown in subsequent experiments, could reach up to several tens of percent of the total cross section, indicating that it is exquisitely suited to the study of dilute chiral matter.

PECD belongs to a family of sensitive methods of chiral discrimination, those which do not depend on interactions with the weak magnetic field component of light. It is well known that a chiral probe is needed to recognize a chiral molecule. Helical light has been used for this purpose since the 19th century. However, the typical pitch of helical light is much larger than the size of a molecule, making standard chiroptical methods such as circular dichroism absorption spectroscopy highly inefficient.

The search for new approaches comprised several research fields, including

angle-resolved photoelectron spectroscopy (ARPES⁶), and yielded the concept of “chiral observer” – a combination of achiral electric fields or detectors which jointly form a chiral reference frame.⁷ This reference frame allows one to detect vectorial enantio-sensitive observables, which flip their direction for opposite enantiomers. For example, in PECD, the chiral reference frame is defined by the two orthogonal components of the circularly polarized electric field and positions of photoelectron (imaging) detectors placed along (imaging plane parallel to) the axis orthogonal to the polarization plane. Resolving the direction of the net photoelectron current orthogonal to the polarization plane yields enantiomer-specific information: the photoelectron current direction reverses upon switching enantiomers.

Enantio-sensitive PECD signals can reach several tens of percent of the total, reflecting the fact that PECD is a purely electric dipole effect. PECD is sensitive to both the initial electronic state and the photoelectron continuum. Besides, it appears to be very sensitive to the details of the molecular scattering potential experienced by the outgoing photoelectron. This sensitivity makes PECD a probe of both dynamic (vibrations) and static molecular structures (isomers, conformers, aggregates).⁸

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Following the early developments around 2000, the application of ARPES as a novel and ultra-sensitive spectroscopic technique for the detection of chirality in molecules has proliferated. Applications include a broad range of more complex chiral systems including chiral nanoparticles⁹ and chiral liquid jets,¹⁰ and the introduction of laser-based multi-photon ionization of chiral molecules^{11,12} allowed the development of table-top probes of chiral systems.¹³ Its extremely high enantio-sensitivity makes PECD a method of choice for dilute samples and, as such, it is currently being commercialized for direct mass spectrometric applications in the analytical laboratory instrumentation market.¹⁴

The extension of PECD from one-photon to the few-photon and strong-field ionization regimes demonstrated the universality of the effect. It also brought the ultrafast dynamics of the chiral electronic response into focus, leading to the concepts of chiral electronic currents in photo-excitation circular dichroism¹⁵ and even to the measurement of chiral structure-induced attosecond ionization delays in multi-photon ionization.¹⁶ The extension of photoelectron circular dichroism in angle-resolved photoionization spectra to the strong field regime opens new avenues for ultrafast imaging of chiral electron dynamics and chiral structures, for instance *via* sub-fs laser-induced electron diffraction.

The development of multi-photon PES opened the door to two-colour pump-probe schemes in both frequency (REMPI-PES) and time domains (time-resolved photoelectron spectroscopy, TRPES). The intermediate resonance gives access to the spectroscopy and ultrafast dynamics of electronically excited states in polyatomic molecules.¹⁷ These photoelectron concepts apply equally well to negative ions and, recently, PECD asymmetry in photodetachment from a negatively charged chiral ion was shown.¹⁸ Time-resolved ARPES in excited molecular electronic states and their non-adiabatic coupling to nuclear motions^{19,20} will lead to new discoveries at the interface of molecular chirality and electronic dynamics.

Beyond their application to chiral systems, ARPES techniques can be applied to gaseous isolated species, liquids, nanoparticles and adsorbates and offer unprecedented insights into many physical, chemical and biological phenomena. They additionally open new directions in materials diagnostics and analytical sciences. The advent of novel high-repetition rate solid state laser systems, next generation synchrotron facilities and novel free-electron-laser facilities, in combination with state-of-the-art single particle detection systems provided by new high-speed imaging detectors and advanced coincidence schemes, promises a new exciting decade of science on the fundamentals and applications of photoelectron spectroscopy.

The publication of this themed issue of *PCCP* coincides with the recent 69th birthday of Ivan Powis, who in 2019 became an emeritus professor at the University of Nottingham, UK. Ivan has been a key player in many of the above-mentioned developments of PES. He is particularly recognized as a pioneer of PECD, a field he launched *via* two seminal theoretical papers published in 2000.^{4,5} Impressively, Ivan has remained at the forefront of this growing field over the past two decades. More generally, Ivan has been and remains deeply involved in the broader field of valence- and core-shell photoionization dynamics of randomly-oriented and in some cases fixed-in-space molecular species, ranging from free small molecules, to larger floppy (bio-)molecules, clusters and liquid jets. From the early times Ivan applied methods of advanced PES that can be associated with electron-ion coincidence techniques.

In this Festschrift issue, we cover topics relating to and deriving from Ivan's work, including the modelling of photoionization dynamics from weak fields to strong and the inclusion of electron correlation and non-Franck-Condon effects. We also include here the use of PES (and time-resolved PES) as analytical tools sensitive to isomers and as a complement to mass spectrometry for the analysis of gas phase species in complex media, including chemical intermediates and final products in reactions and combustion processes.

In order to provide an overview of some of the most exiting avenues of modern molecular electron spectroscopy we invited key actors to write five perspective articles:

- “Quantum coherence in molecular photoionization” (M. Ruberti, S. Patchkovskii and V. Averbukh, <https://doi.org/10.1039/D2CP01562E>).
- “Trends in angle-resolved molecular photoelectron spectroscopy” (D. Dowek and P. Decleva, <https://doi.org/10.1039/D2CP02725A>).
- “Time-resolved photoelectron spectroscopy: the continuing evolution of a mature technique” (M. S. Schurman and V. Blanchet, <https://doi.org/10.1039/D1CP05885A>).
- “Photoionization of the aqueous phase: clusters, droplets and liquid jets” (R. Signorell and B. Winter, <https://doi.org/10.1039/D2CP00164K>).
- “Photoelectron spectroscopy in molecular physical chemistry” (I. Fischer and S. Pratt, <https://doi.org/10.1039/D1CP04984D>).

The collection of (currently) 45 papers gathered in this themed Festschrift issue is of course not exhaustive, but we believe that it provides a significant and comprehensive account of the current experimental and theoretical state-of-the-art of this vivid field and paves the way for exciting avenues of research for the next decade. We warmly congratulate Ivan and thank all the contributors!

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