Angular studies of photoelectrons in innovative research environments

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Improving our understanding of chemical structure, particularly bonding character and reactivity, is vital if we are to improve the efficacy and performance of materials and medicines. Although current technology, such as X-ray diffraction, allows us to determine the positions of atomic nuclei in a material, this provides only part of the information required to understand its function.

Because bonding and reactivity depend on the electronic structure of a material, its function relies on the energies and spatial distributions of its electrons, and on the changes that they undergo. Photoelectron spectroscopy (the emission of electrons caused by the interaction of molecules with UV light) has long been known to be sensitive to electronic structure. However, more intimate details can be obtained by the measurement and analysis of the angles through which the photoelectrons are emitted; this measurement is known as the photoelectron angular distribution (PAD). If measurements can be made relative to bonds in individual molecules, we access the 'molecular frame' (MF), and the PADs provide more information. Measurements of this sort are challenging because free molecules rotate and therefore a series of measurements are averaged over all the possible molecular orientations. Furthermore, a full characterisation requires measurements taken over a wide energy range. Although the combination of these requirements has severely limited the scope of experiments to date, the recent parallel developments of techniques to align molecules in space, and new light sources have brought new prospects to this exciting area.

The ASPIRE ITN project was established to capitalise on these recent technological breakthroughs and brought together a unique team of internationally leading scientists to develop methods that enable the measurement of the PADs, referenced to the orientation of the MF of complex molecules.

Project structure

ASPIRE, led by Professor Katharine Reid at the University of Nottingham, is a collaboration between seven universities/national facilities and two small and medium enterprises (SMEs). This professional network, encompassing partners from academia and industry, has been devoted to advancing state-of-the-art research in molecular structure determination through the development of new techniques to enable the measurement of molecular frame photoelectron angular distributions (MFPADs) (Reid, 2012).

The project was organised into three scientific work packages (WP) with the recruited early career researchers (ESRs) being assigned individual research projects that required collaboration with others in the network. The project has resulted in the publication of 17 papers in leading scientific journals, with more in preparation. The ESRs also completed an extensive training programme, which included research secondments to both academic and industrial organisations that not only developed their scientific skills, but also developed their broader skill set and future career ambitions.

The first work package (WP1) explicitly focused on the main project goal of measuring MFPADs from complex molecules, and 11 ESRs worked on accomplishing these goals. Progress in this WP was contingent on technological developments made in

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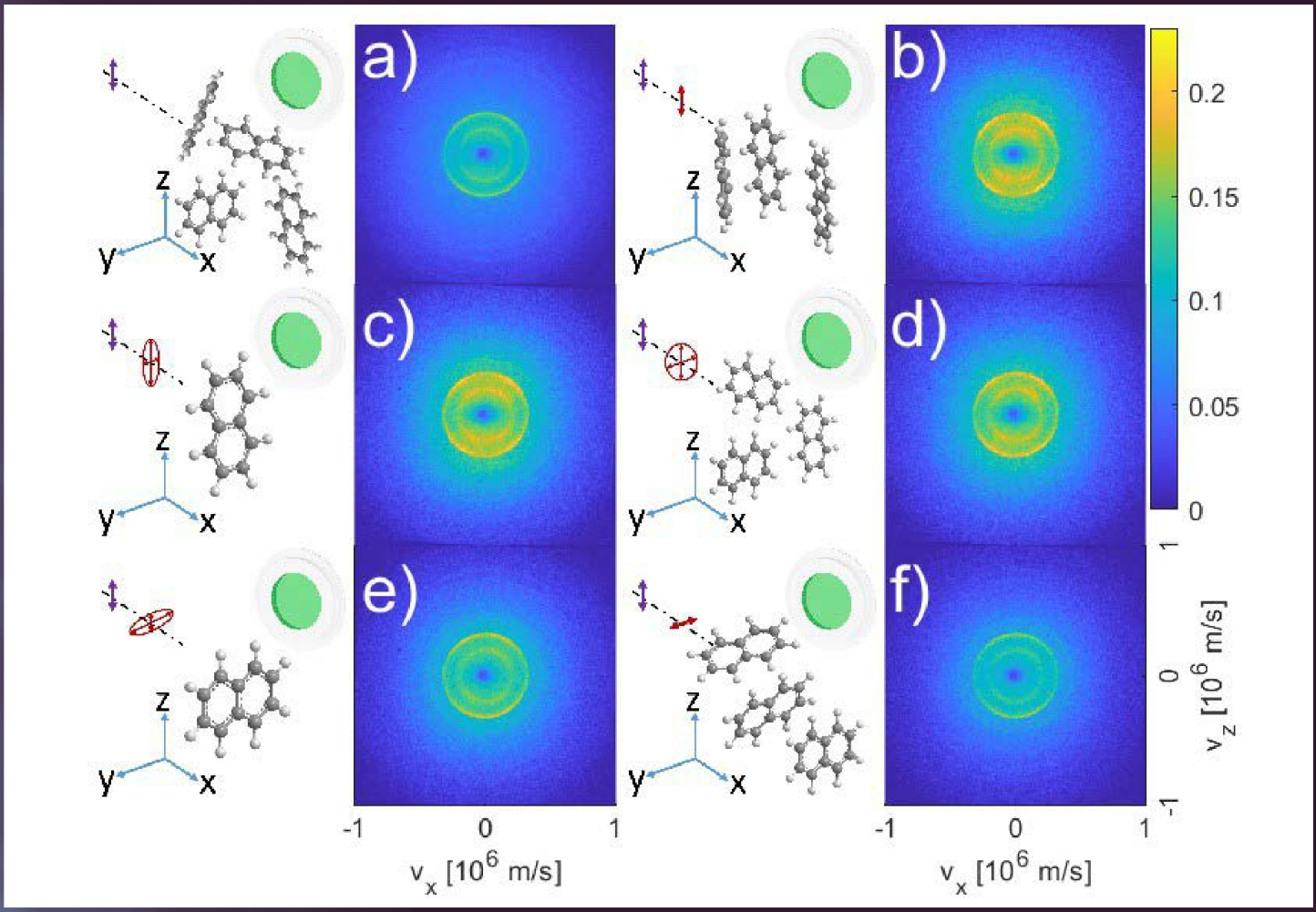

Figure 1: Two-dimensional velocity images of electrons produced when naphthalene molecules are ionised by an ultraviolet probe pulse (marked by the double-headed purple arrow). The different panels are correspond to different alignment geometries of the molecules obtained by an alignment pulse with different polarisation states (marked by the double-headed red arrows).

WP2 and WP3. Individual projects in WP1 included synchrotron-based experiments on chiral molecules including amino acids, measurements of PADs following the dissociative ionisation of small aromatic molecules, the development of a new apparatus capable of performing experiments on molecules embedded in helium droplets, and the characterisation of a new molecular beam required for low-temperature experiments.

WP2 concerned the development and integration of laser and advanced light source techniques. Two ESRs were primarily assigned to the delivery of this WP, but two additional ESRs contributed through secondments between partner organisations. The individual projects in this WP included the development of a novel laser system, the design of a new beamline, the development of a new technique to create strongly aligned molecules in the field-free environment of helium nanodroplets (Chatterley et al., 2019), and the development of a new optical configuration for impulsive alignment and orientation of molecular samples.

WP3 concerned the development and integration of detection technologies. Work in this WP was led by private sector laboratories at Roentdek and Photek, each of whom recruited one ESR. Individual projects included the successful development of new detection software and the evaluation of a new three-dimensional detection system, which supported experiments in WP1 and WP2. Industrial based ESRs benefitted from academic secondments throughout their research. Similarly, academically based ESRs had the opportunity to explore industry through secondments to Roentdek and Photek.

Project results overview

MFPAD measurements can provide enhanced descriptions of the fundamental quantum-mechanical processes in molecular photoionisation (Reid, 2012). Researchers in ASPIRE have used several techniques to measure MFPADs, and these techniques implicitly or explicitly determine the spatial orientation of the molecules being ionised. The two main approaches involved either the use of dissociative ionisation or the use of the electric field of intense infrared laser pulses to align molecules (Chatterley et al., 2020; Chatterley et al., 2019; Schouder et al., 2019; Kircher et al., 2019). Using these two approaches, ASPIRE researchers have studied the photoionisation dynamics of polyatomic molecules such as aniline, naphthalene (Figure 1), and methyl iodide. Further studies into molecular photoionisation in

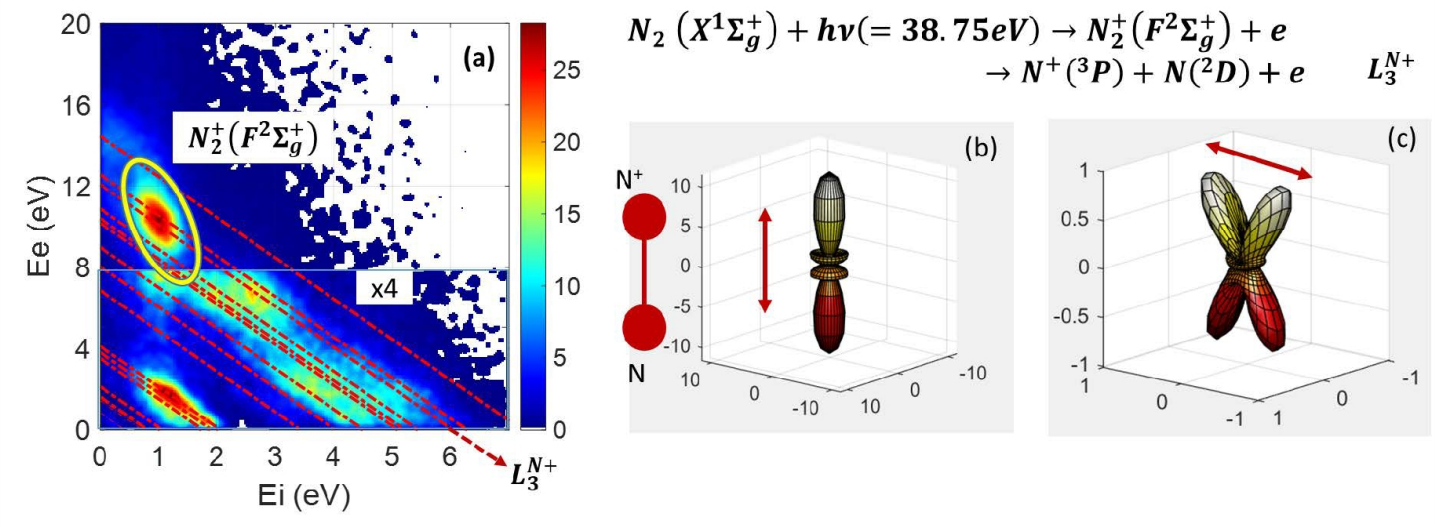

Figure 2: Molecular frame photoemission across shape resonances in XUV inner-valence ionisation of N_2 studied by electron-ion 3D momentum coincidence spectroscopy.
(a) Kinetic energy correlation diagram for dissociative photoionisation (DPI) of N_2 at a given photon energy (hv=38.75eV), which enables the resolution of all the DPI processes. (b) Under the axial recoil approximation, the (Ve, VN+) correlation provides the MFPADs, for each specific ionic state.

diatomic and small polyatomic molecules have measured MFPADs using electron-ion coincidence 3D momentum spectroscopy. Studies on dissociative photoionisation of small gas-phase molecules using well-characterised radiation sources (synchrotron radiation and attosecond laser sources) have been performed to help increase the understanding of the inner-valence photoionisation dynamics of small molecules (O_2, NO, CO, NO_2) (Figure 2). In a pioneering study, MFPADs have been measured from the chiral molecule methyloxirane.

A variant of angle-resolved photoelectron spectroscopy is photoelectron circular dichroism (PECD), a technique that provides a valuable probe of chiral molecules. In this project, PECD has been used as a simultaneous probe of enantiomer ratios of all the main compounds contained in several essential oils which include a mixture of terpenes such as alpha-pinene (pine scent) and limonene (lemon scent) (Rafiee Fanood et al., 2018). Circularly polarised light (CPL) generated by the third generation synchrotron facility (SOLEIL) was used for this work. PECD has also been used in ASPIRE to study molecular structures of several amino acids (alanine, proline, tryptophan and tyrosine), dipeptides and homochiral nanoparticles. Studying these systems is challenging because amino acids and peptides do not vapourise easily and can be thermally unstable. Vapourisation is essential in order to generate isolated species that can be interrogated in conditions that are free of intermolecular interactions with other species, including solvents. To overcome these difficulties, the research team used two complementary vapourisation methods: resistive heating and aerosol thermodesorption. Both were used to study PECD over a large vacuum ultraviolet (VUV) range using the DELICIOUS 3 double imaging electron/ion coincidence (i2PEPICO) spectrometer in the SAPHIRS chamber, linked to the DESIRS beamline at synchrotron SOLEIL (Hadidi et al., 2018). These studies have resulted in new insights into the origins of homochirality in amino acids or the reason why amino acids are composed of one enantiomer in all life forms (Figure 3).

Further studies of chiral molecules were conducted using resonantly enhanced multiphoton ionisation (REMPI)-PECD, which shows enhanced sensitivity and provides additional information relating to the electronic and vibrational dependence of the effect. This technique has the capability of providing a molecular 'fingerprint'. Using ultrafast pulsed lasers from the Artemis beamline of the UK Central Laser Facility, the research team measured the PECD of alpha-pinene using REMPI at multiple wavelengths. Alpha-pinene was chosen as it is one of the most frequently encountered terpenes in essential oil extracts. Tuning the wavelength in the REMPI-PECD experiments allows the researchers to examine vibrational state-to-state changes in the photoionisation selectively and to obtain insights concerning vibronic interactions in the molecules.

In recent years, the development and improvement of new laser sources, such as free-electron lasers and synchrotrons, has allowed scientists significant control over both the accessible wavelengths and pulse durations of the laser. The ability to control these two parameters enabled the study of 'ultrafast' dynamical processes in molecules; these include changes in electron density and nuclear dynamics on the attosecond (10^{-18} s) and femtosecond (10^{-15} s) scale. ASPIRE researchers have harnessed these latest techniques to measure MFPADS. For example, we have used laser pulses with a duration of 30 femtoseconds and a central wavelength of 1850 nm to study three polyaromatic systems (anthracene, naphthalene and biphenyl) and have been able to construct 3D-photoelectron momentum distributions for all test species.

In order to study ultrafast molecular dynamics, which naturally occur on the attosecond (10^{-18} s) timescale, a probe of comparable duration is needed, like extreme ultraviolet (XUV) laser pulses, which can be generated using table top laser systems through high-order harmonic generation (HHG) processes (Figure 5)

in different targets such as atomic and molecular gases, liquids and solids. HHG in noble gases (argon, krypton, neon, etc.) is the most investigated and well-understood method, and can be used for a wide range of experiments in the field of ultrafast spectroscopy. ASPIRE researchers have measured ultrafast electron dynamics that follow the photoionisation in diatomic molecules such as hydrogen, nitrogen and carbon monoxide.

Researchers based in two SMEs, Roentdek and Photek, have been working to address the increasing demands from the scientific community for 3D imaging detectors capable of registering fast arrival times and positions of multiple charged particles (electrons or ions) impinging on a detector surface. A big challenge for imaging detectors that aim to provide sub-nanosecond resolution timing data is that there is a greater dead-time imposed by the method of encoding, then transferring, the position data; worse, two or more nearly simultaneous particles arriving within this dead-time interval can cause the information to become corrupted. Consequently, count rates must be restricted. In short-pulse laser experiments—where the duty cycle is already low and the ionising pulse duration is comparable to a detector's encoding time—this requires restricting conditions to ensure less than one ionisation event per laser pulse which is highly inefficient and severely limiting for data statistics.

Researchers at Photek have been designing and developing alternative new registration and encoding technology to offer a genuine multi-hit capability (Figure 4a). The detector consists of microchannel plates (MCPs) together with an anode and an electronic read-out arrangement. The MCPs amplify the incident charge by a gain factor of at least 10^6, and the charge cloud is then delivered to a segmented anode with a novel structure. Each impact is fed into a parallel array of processing electronics, which digitises and buffers the arrival times and charge in each segment. Subsequently, the on-chip data registers are rapidly transferred to a processing computer where the position information can be improved by a centroiding interpolation. The detector is currently undergoing testing with a view to launching it as a new commercial product in the future.

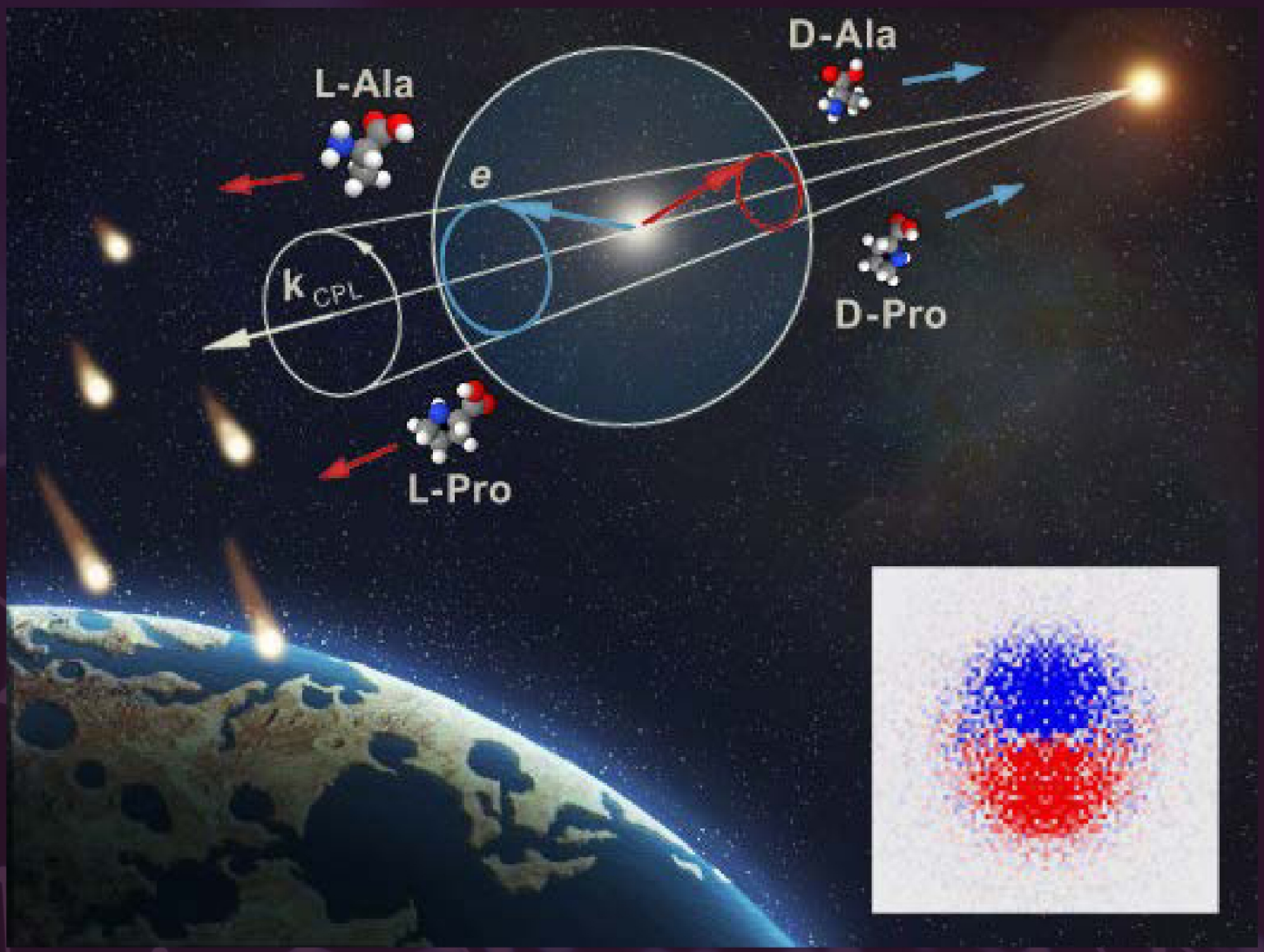

Figure 3: Artistic rendering of how parent amino acids ions, alanine and proline, could be created with an enantiomeric excess of the same sign when they interact with CPL. The inset shows measured ion recoil asymmetry associated with the PECD in alanine. This work supports a possible link between PECD and the origin of life's homochirality (Hadidi et al., 2018).

Work at Roentdek focused on developing software for the read-out and data treatment need for MCP detectors (Figure 4b), with special emphasis on multi-hit reconstruction from the best current-generation detectors. It also focused on comparing different multi-hit read-out concepts on fast digitising platforms. The resulting improved data acquisition software package allows researchers to process their data more quickly and easily through a new user interface. The detectors can be remotely controlled through Labview, and measurements simulated to allow the optimisation of experimental parameters ahead of performing experiments. The software also contains features for detector diagnosis and functions to improve the linearity of the detector image response. The ASPIRE project has worked with experimentalists at various synchrotron facilities (DESY, BESSY and SOLEIL) to use and optimise the new software.

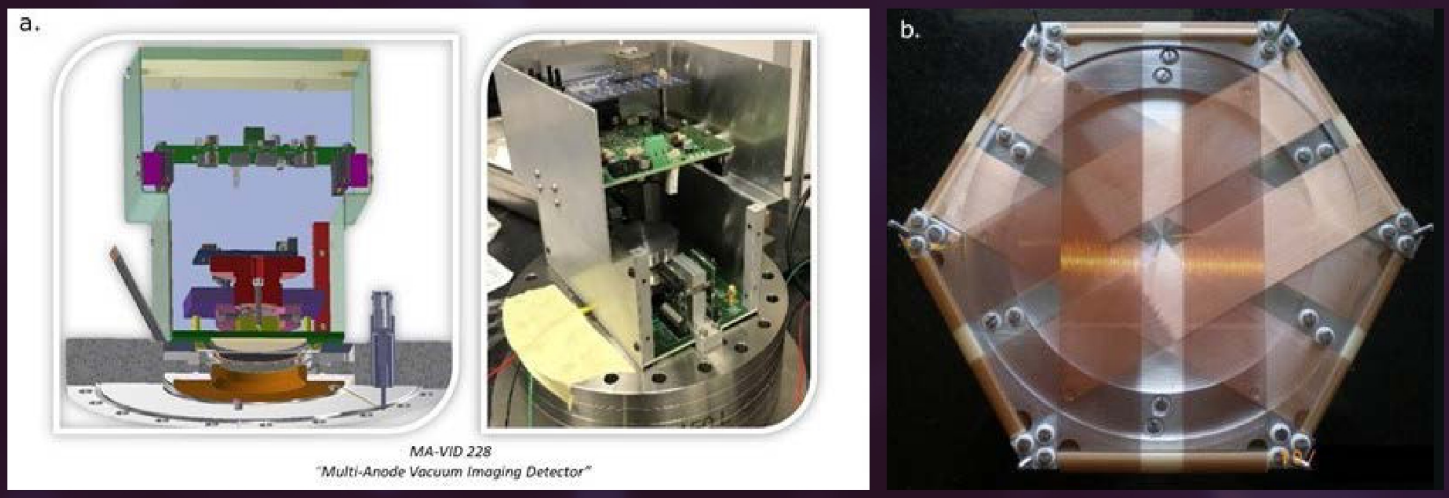

Figure 4: (a) Multi-Anode Vacuum Imaging Detector used at Photek. Image courtesy of Photek. (b) The novel Dual-Hexanode delay-line geometry comprises a multitude of independently addressed segments to improve the many-particle detection efficiency after fragmentation of a complex molecule. Image courtesy of RoentDek.

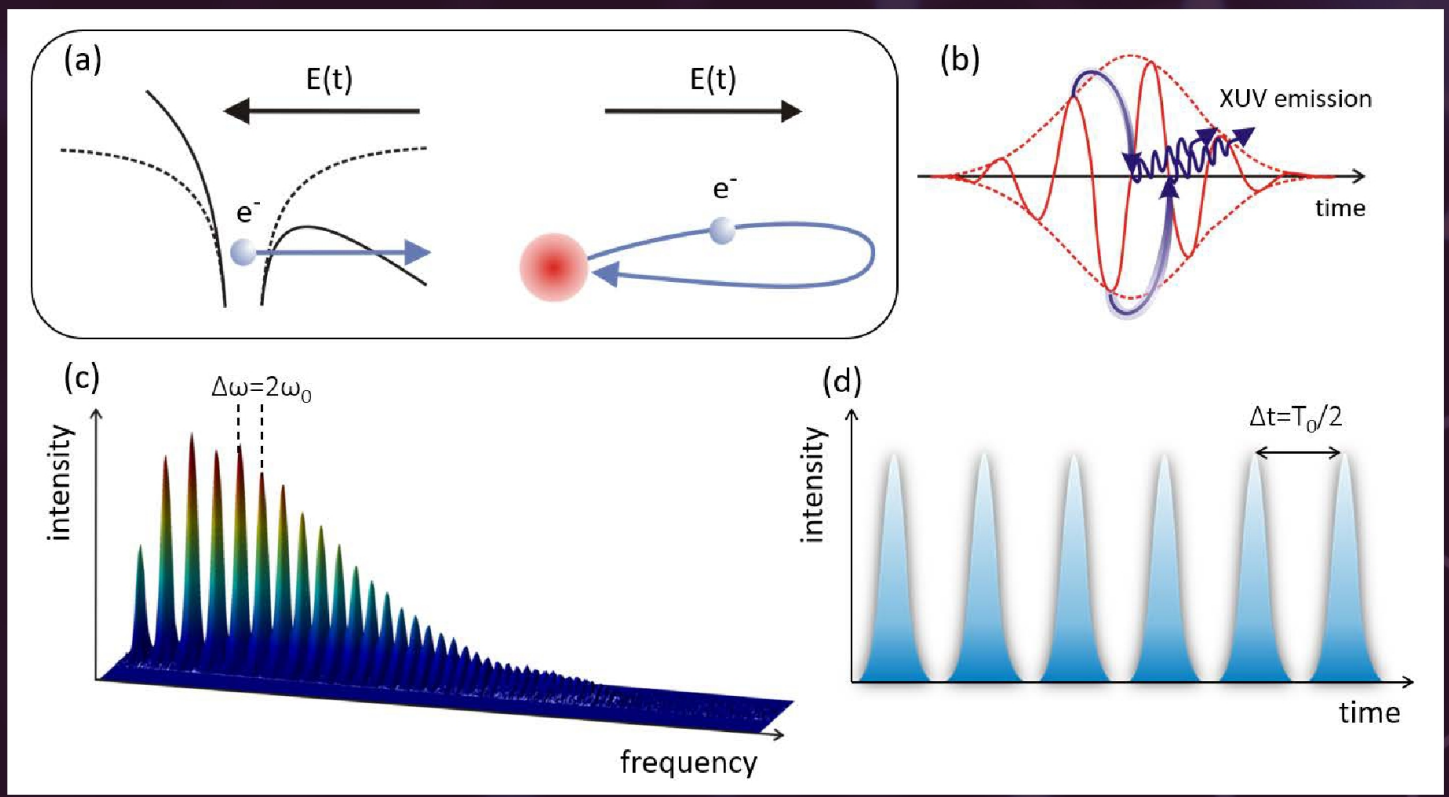

Figure 5: (a) Model of the high-order harmonic generation (HHG) process. An electron in the atom is ejected by the external laser field (right). Then an electron is accelerated in the external field and can eventually recombine with the parent ion emitting an HHG photon (left).
(b) The HHG process is repeated periodically every half cycle of the fundamental driving field.
(c) In the spectral domain, the harmonic emission appears as a sequence of peaks corresponding to the odd harmonic of the fundamental laser frequency \omega_0.
(d) In the temporal domain, harmonics are emitted as a sequence of attosecond bursts separated by half the driving laser period T0.

Summary

The ASPIRE project has designed and undertaken a range of state-of-the-art experiments and methods of data analysis that will enable improved understanding of the electronic structure and dynamics in a range of molecular systems. As well as experimental techniques and methods of data analysis, new technologies have been developed, requiring a partnership between industry and academia. Twelve ESRs have completed a comprehensive training programme that included inter-disciplinary research, as well as developing their communication and business awareness skills through secondments and other opportunities.

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ASPIRE

PROJECT SUMMARY

The Innovative Training Network "Angular Studies of Photoelectron in Innovative Research Environments (ASPIRE)" brings together a unique team of internationally leading scientists to develop methods suitable for determining Molecular Frame Photoelectron Angular Distributions (MFPADs), which are used to probe the electronic structure and nuclear dynamics of individual molecules. This information is important in understanding the function of medicines and materials.

PROJECT LEAD PROFILE

As well as original research papers, **Katharine Reid** has published highly cited reviews of the applications of photoelectron angular distributions and has organised international conferences in photoionisation and in the use of advanced light sources. Katharine is a Professor of Chemical Physics at the University of Nottingham in the UK.

PROJECT PARTNERS

ASPIRE is based at the University of Nottingham. Collaborating partners include: RoentDek, Frankfurt University, Photek Ltd, Central National de la Recherche Scientifique, Synchrotron SOLEIL, Aarhus Universitet, Consiglio Nazionale Delle Ricerche and Max-Born-Institut. CFEL, DESY, Kassel University, University of Oxford, Amplitude, Cronologic, Kore Technology, MassSpecpecD and Ottawa University are ASPIRE partners providing training and instrumentation access to the researchers.

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