

Threshold Photoionisation of Atoms and Molecules

George King



School of Physics and Astronomy and Photon Science Institute

University of Manchester, UK.

Introduction

When you excite a reaction just above its threshold energy, something interesting usually happens and often something unexpected. In the present case the reaction is the photoionisation of an atom or molecule, with the removal of one or more of its electrons. For such *threshold* measurements, it follows that we must be able to vary the energy of the incident photon. This is where the use of tuneable synchrotron radiation becomes essential. Indeed this tunability opens up many new avenues of experimental investigation in atomic and molecular physics.

Our initial use of synchrotron radiation arose from an interest in the three-body Coulomb problem as described by the Wannier theory; in particular, the photo double ionisation of helium. In this reaction, two very low energy photoelectrons are emitted and the reaction is dominated by the correlations between these two outgoing electrons. The threshold for this reaction is 79 eV and indeed one of the gratings of the toroidal grating monochromator (TGM) on Beamline 3.3 at the Daresbury SRS was designed specifically to deliver maximum photon flux near to this energy. In fact, our experiments on the photo-double ionisation of helium were some of the first to be undertaken at the SRS and indeed the author was present at the opening of the facility by the Secretary of State for Science and Education, Mark Carlisle on the 7th November 1980.

Following our first experiments in helium, we exploited the techniques of threshold photoelectron spectroscopy to explore a wide range of atomic and molecular systems, as we will describe. For these studies, we exploited the high photon energy range provided by the TGM and the high photon energy resolution provided by the 5m McPherson monochromator. We benefited greatly from the SRS scientific staff at Daresbury including John West, Ian Munro, Michael McDonald and David Holland. We also benefited greatly from international and national collaborators including Mariusz Zubek (Gdansk), Richard Hall (Paris), Lorenzo Avaldi (Rome) and Andrew Yench (Albany, USA). On a personal note, the author met his future wife, Michele Siggel-King, at Daresbury! She was working on the TGM, while he was working on the adjacent beamline; the 5m McPherson monochromator.

Here we give illustrative examples of how we exploited the advantages of threshold photoelectron techniques together with the high performance of the TGM (Beamline 3.3) and the 5m McPherson monochromator (Beamline 3.2).

Experimental technique

The basis of our experimental technique is to collect and detect very low energy (\sim few meV) photoelectrons, i.e. *threshold photoelectrons*. This technique employs the penetrating field technique [1], which is illustrated schematically in Figure 1.

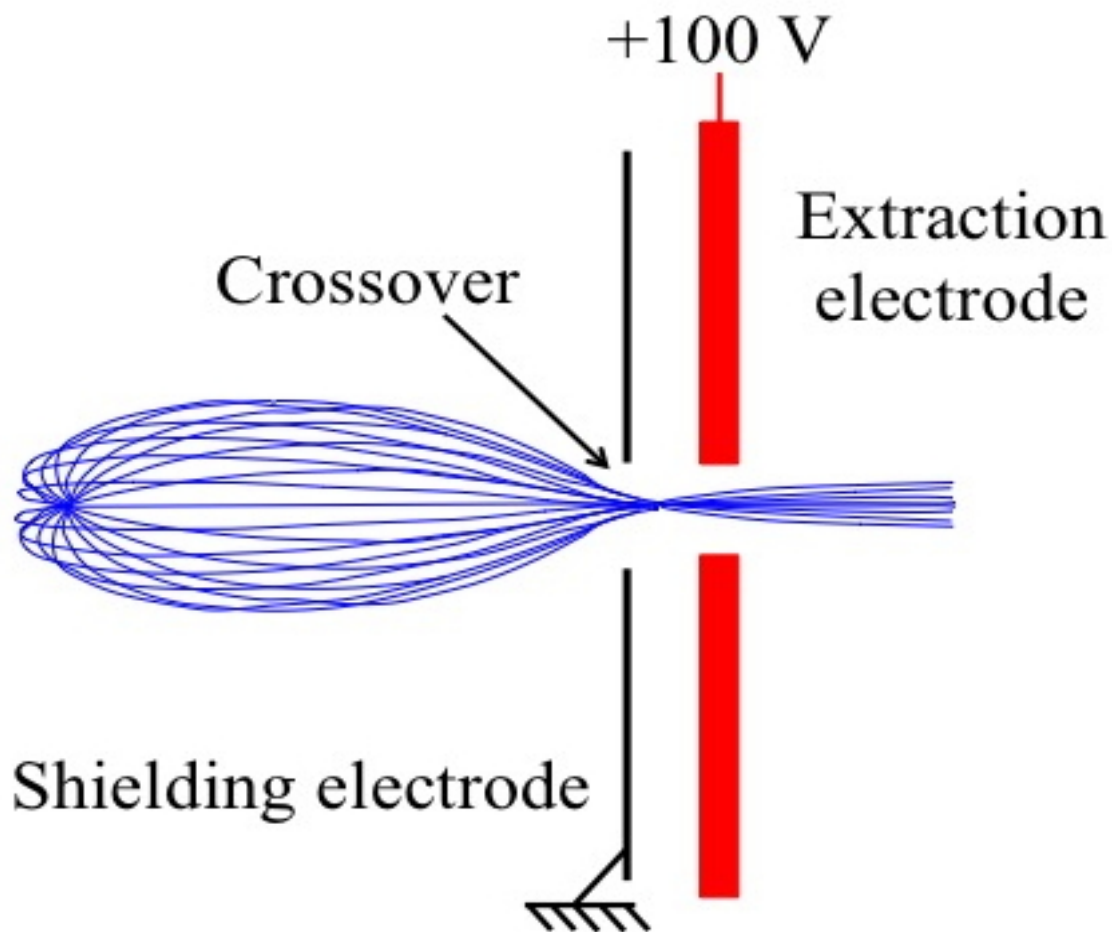


Figure 1. A computer simulation of the trajectories of 2 meV photoelectrons, illustrating the principle of the penetrating field technique.

An *extraction electrode* is positioned behind a grounded *shielding electrode* with respect to the photon-gas beam interaction region. Both electrodes have apertures of ~ 2 mm diameter and

the distance between the grounded electrode and the interaction region is ~ 10 mm. The extraction electrode is held at a voltage of typically 100V and its action is to draw out photoelectrons emitted from the interaction region and moreover to draw out preferentially those photoelectrons with very low energy \sim few meV. This is illustrated by Figure 1, which shows the computed trajectories of photoelectrons of 2 meV energy. These low energy photoelectrons are collected over a collection angle of almost 4π sr, i.e. with a collection efficiency close to 100%. This efficiency falls off dramatically with increasing photoelectron energy so that the *threshold resolution*

of the system is also a few meV. More energetic photoelectrons that are emitted within the solid angle subtended by the aperture in the grounded electrode are removed by a 127° electrostatic analyser that is positioned after the extraction stage. This is illustrated in the practical example of a threshold photoelectron spectrometer that is shown in Figure 2, and which is described in detail elsewhere [2].

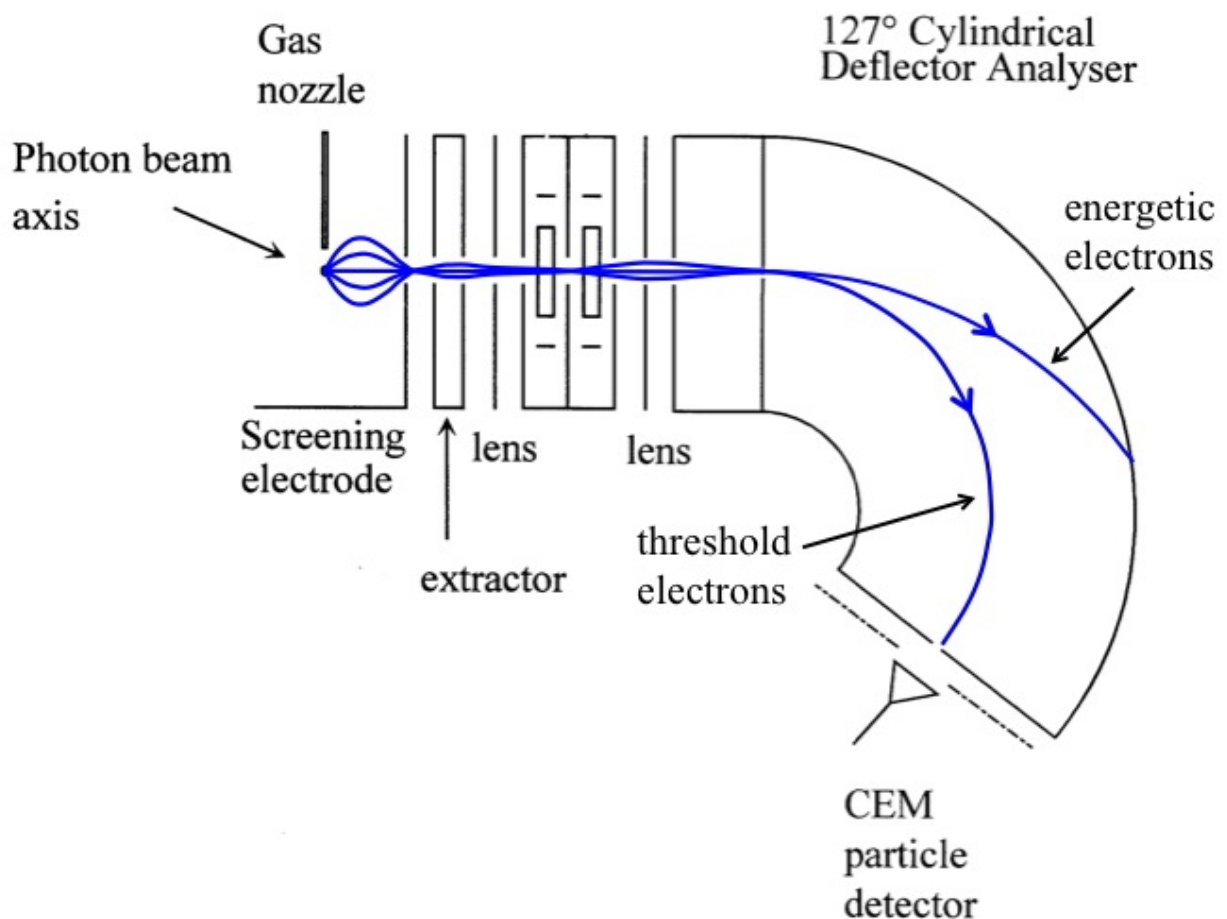


Figure 2. A threshold photoelectron spectrometer. The purpose of the 127° cylindrical deflector analyser is to filter out energetic photoelectrons that are emitted within the solid angle subtended by the aperture in the shielding electrode.

Note that the extraction field produces a crossover in the electron trajectories that is imaged by the electrostatic lens system onto the entrance slit of the analyser. The resultant transmission function of the threshold spectrometer is illustrated schematically in Figure 3. We see that the spectrometer delivers very high energy resolution and very high efficiency.

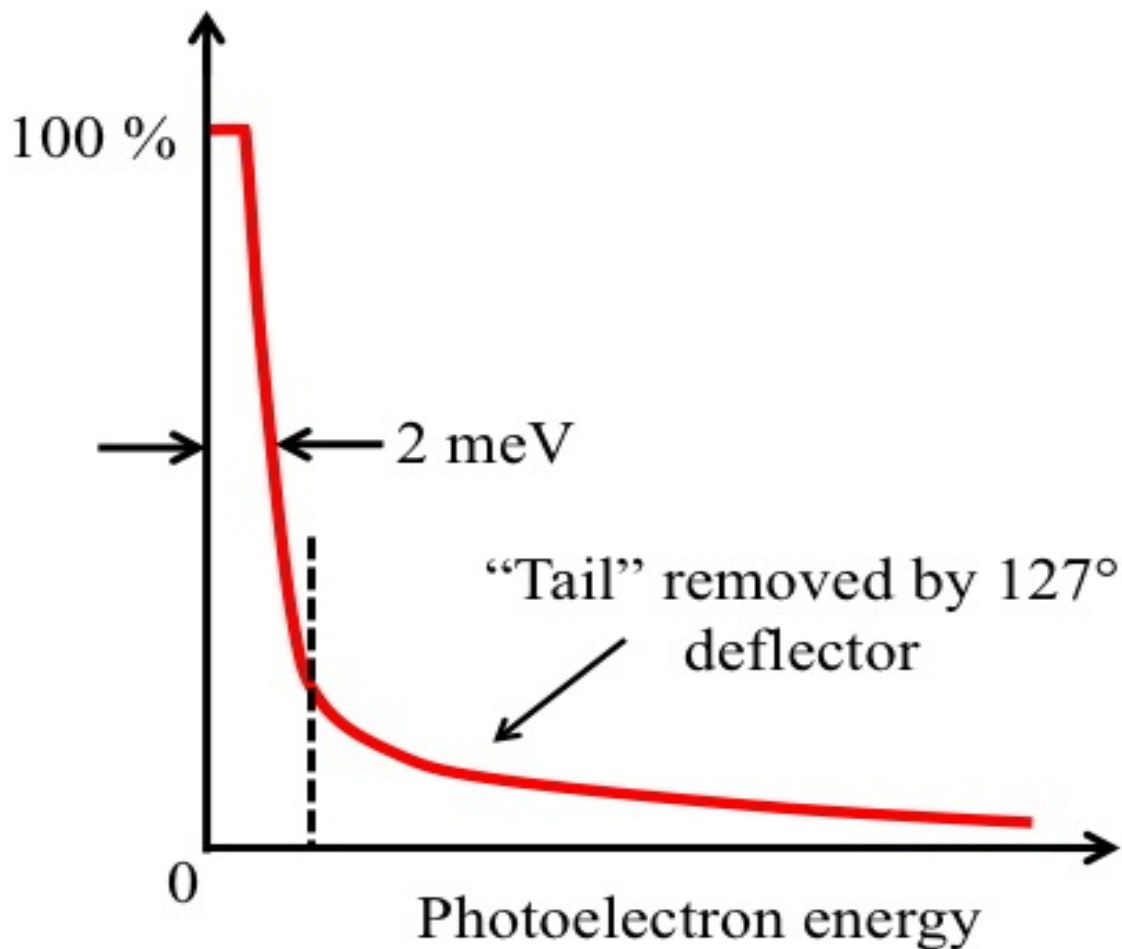


Figure 3. Transmission function of the threshold analyser. The width of the function is ~ 2 meV and photoelectrons of energy less than this value are collected with $\sim 100\%$ efficiency.

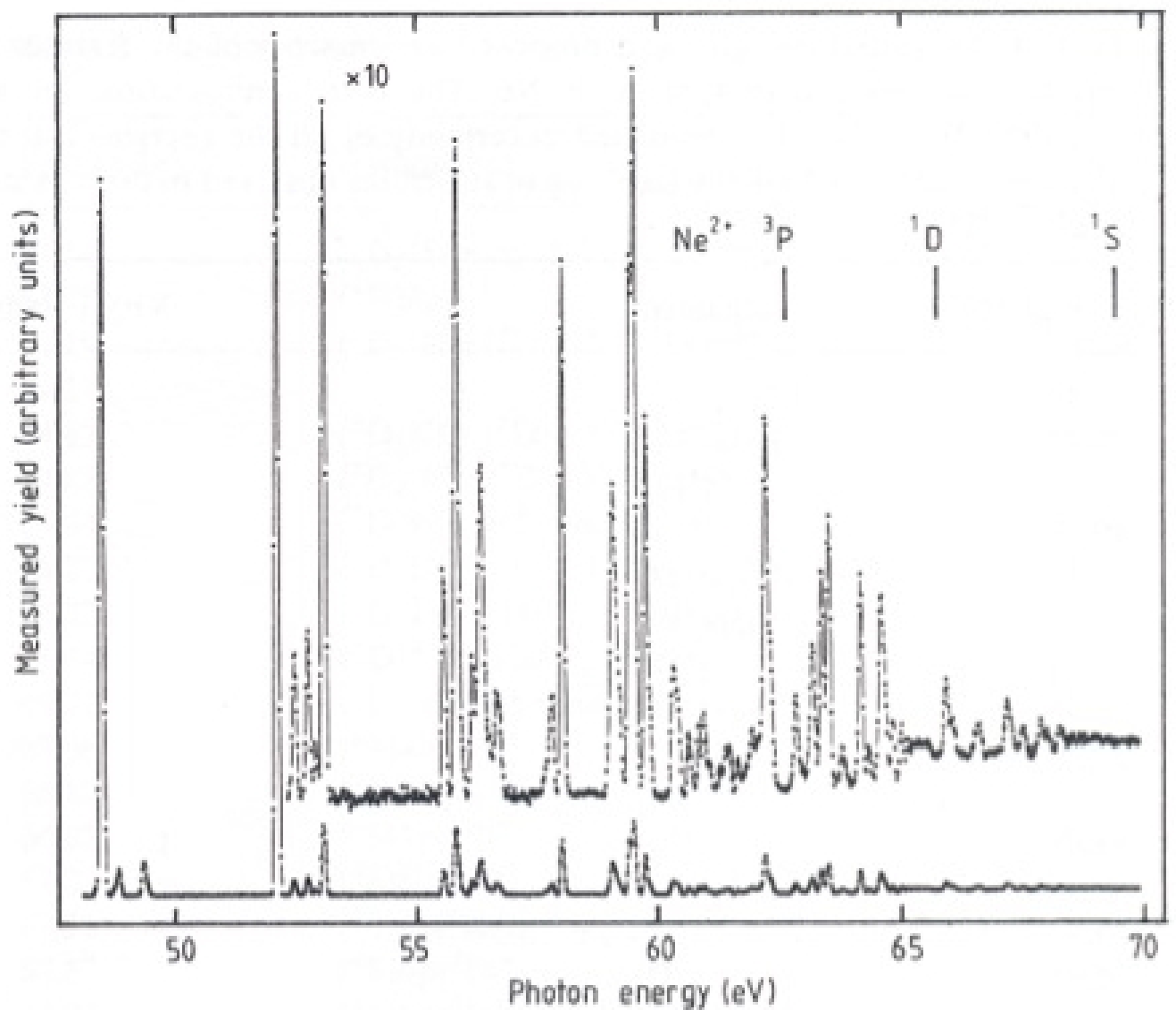
The SRS beam is crossed with the target gas beam that emanates from a narrow capillary tube and the photon energy is scanned across the region of interest. Whenever the photon energy crosses an ionisation threshold of the target species, threshold photoelectrons are produced, which are extracted and detected. The detected yield of threshold electrons, measured as a function of photon energy, is the threshold photoelectron spectrum.

Threshold photoelectron studies

Threshold photoelectron studies of atoms

We conducted comprehensive threshold studies of the rare gases Ne, Ar, Kr and Xe. The aim of the studies was to observe satellite states of the ions, where one electron is ejected and another is raised to an unfilled orbital e.g. Ar^+ , $3s^23p^4nI$. These states are of particular interest because they occur only because of electron correlation. What the threshold measurements demonstrated was that satellite excitation at or near threshold occurs entirely through doubly excited neutral states of the target i.e. via a two-step process.

A threshold photoelectron spectrum obtained in neon over the photon energy range 48 – 70 eV is shown in Figure 4, [3].



The threshold photoelectron spectrum of neon, obtained in helium, is shown in figure 8.

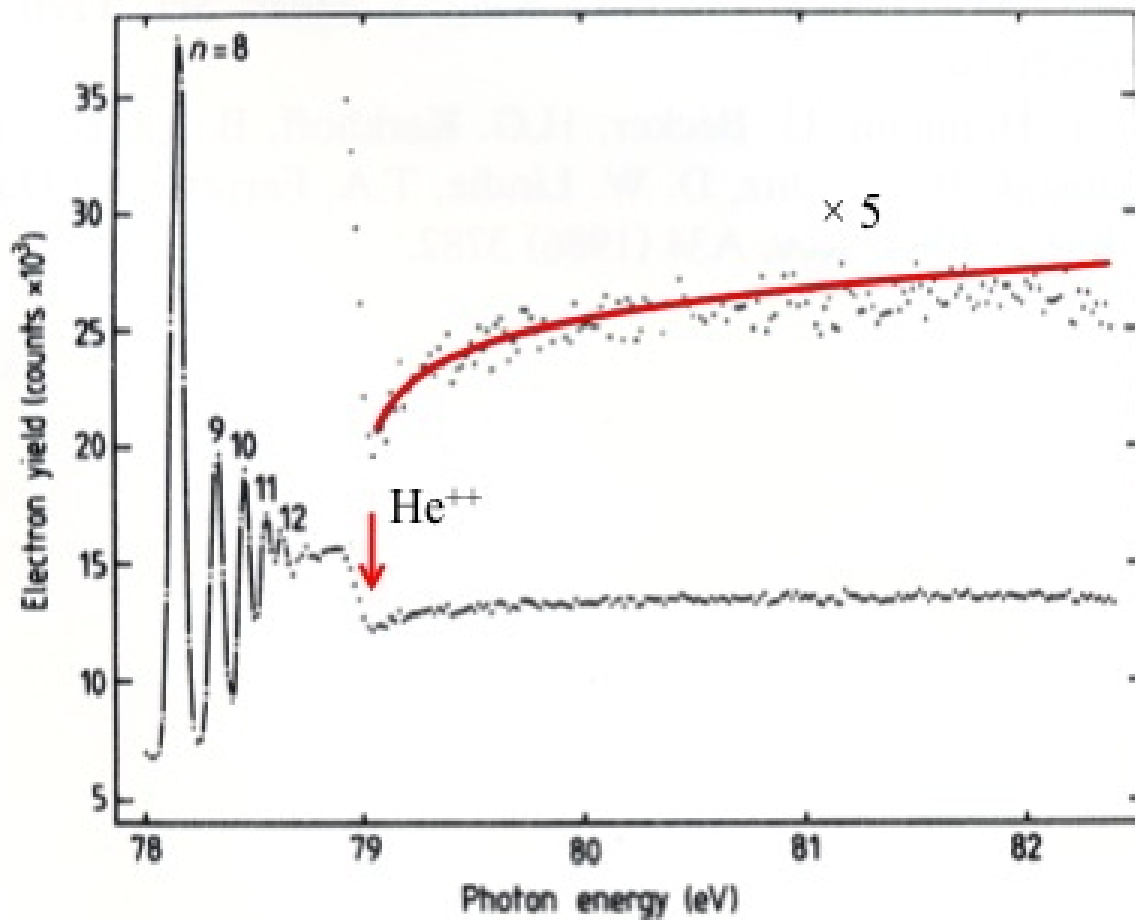


Figure 5. The He II ϵ threshold feature in the photoelectron spectrum of the He II ϵ state. The He II ϵ state is the first excited state of the He II ion, and the He II ϵ state is the first excited state of the He II ion. The He II ϵ state is the first excited state of the He II ion, and the He II ϵ state is the first excited state of the He II ion.

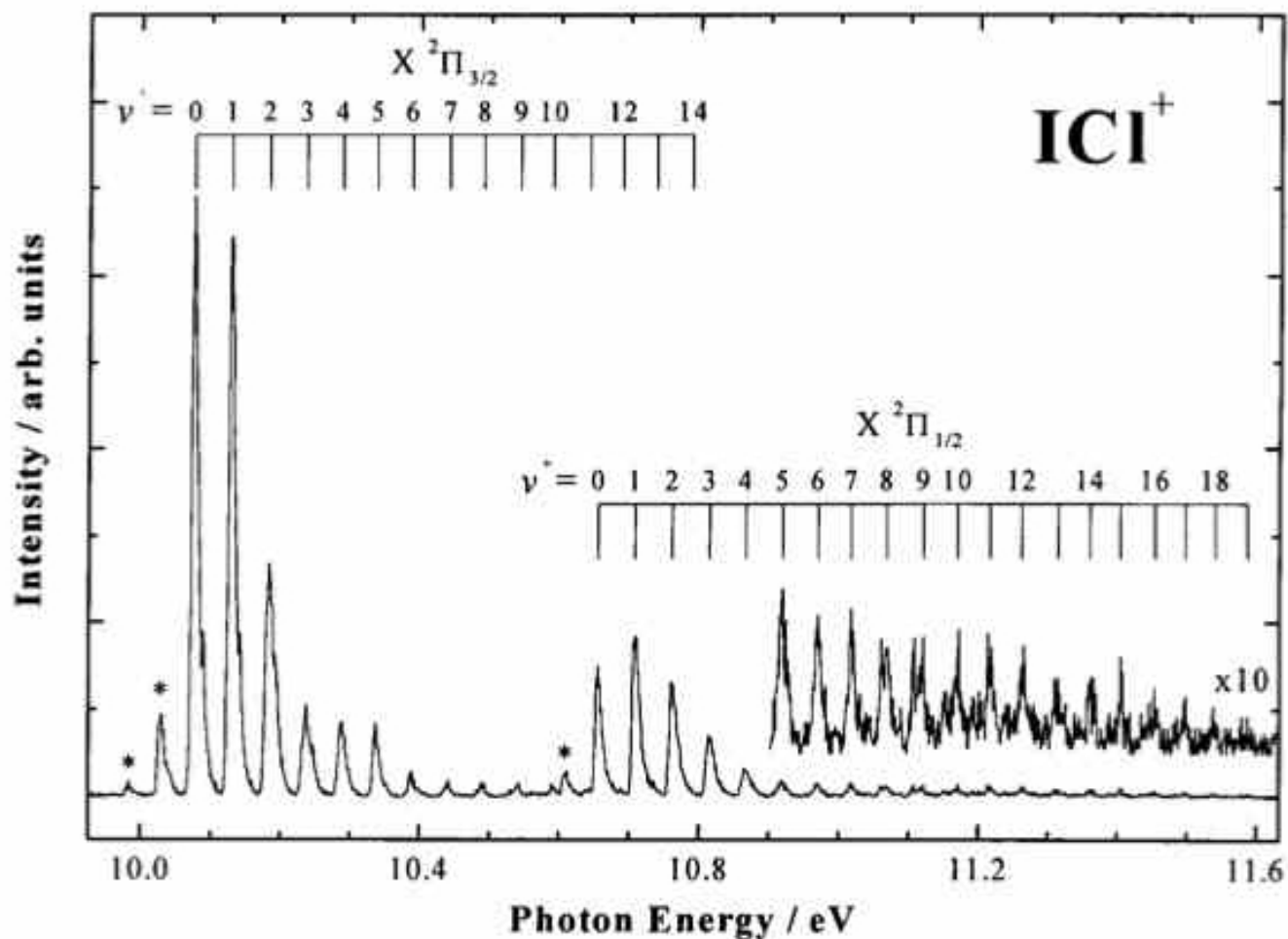


Figure 6. Threshold photoelectron spectrum of the ICI^+ ($X \ ^2\Pi$) vibrational structure in the range 10.0–11.6 eV. The vibrational structure is assigned to the $X \ ^2\Pi_{3/2}$ and $X \ ^2\Pi_{1/2}$ states. The asterisks (*) indicate the peaks assigned to the $X \ ^2\Pi_{3/2}$ state.

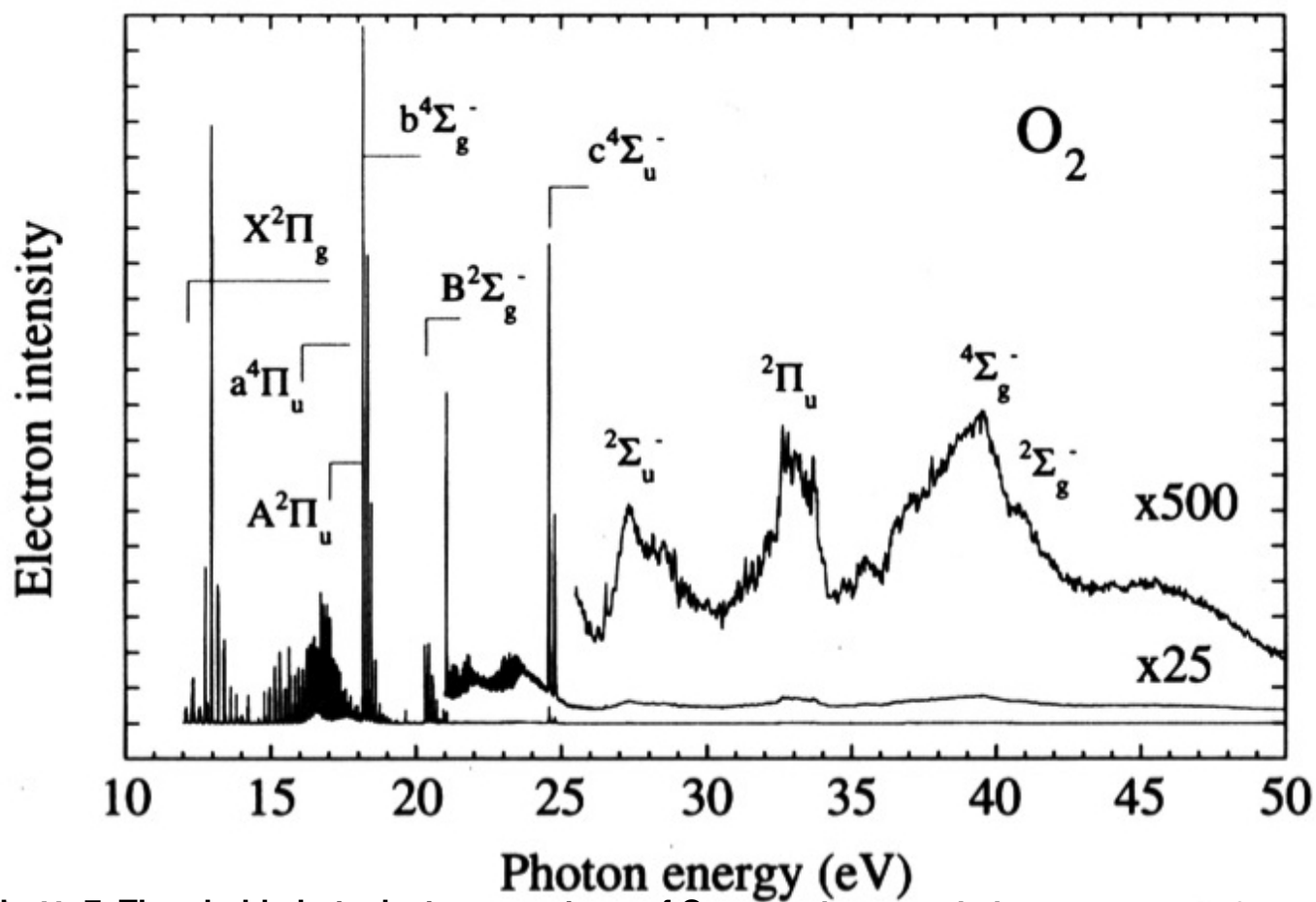


Figure 7. Threshold photoelectron spectrum of O_2 over the extended energy range 12–50 eV. The x500 and x25 traces correspond to the data sets shown in Figure 6.

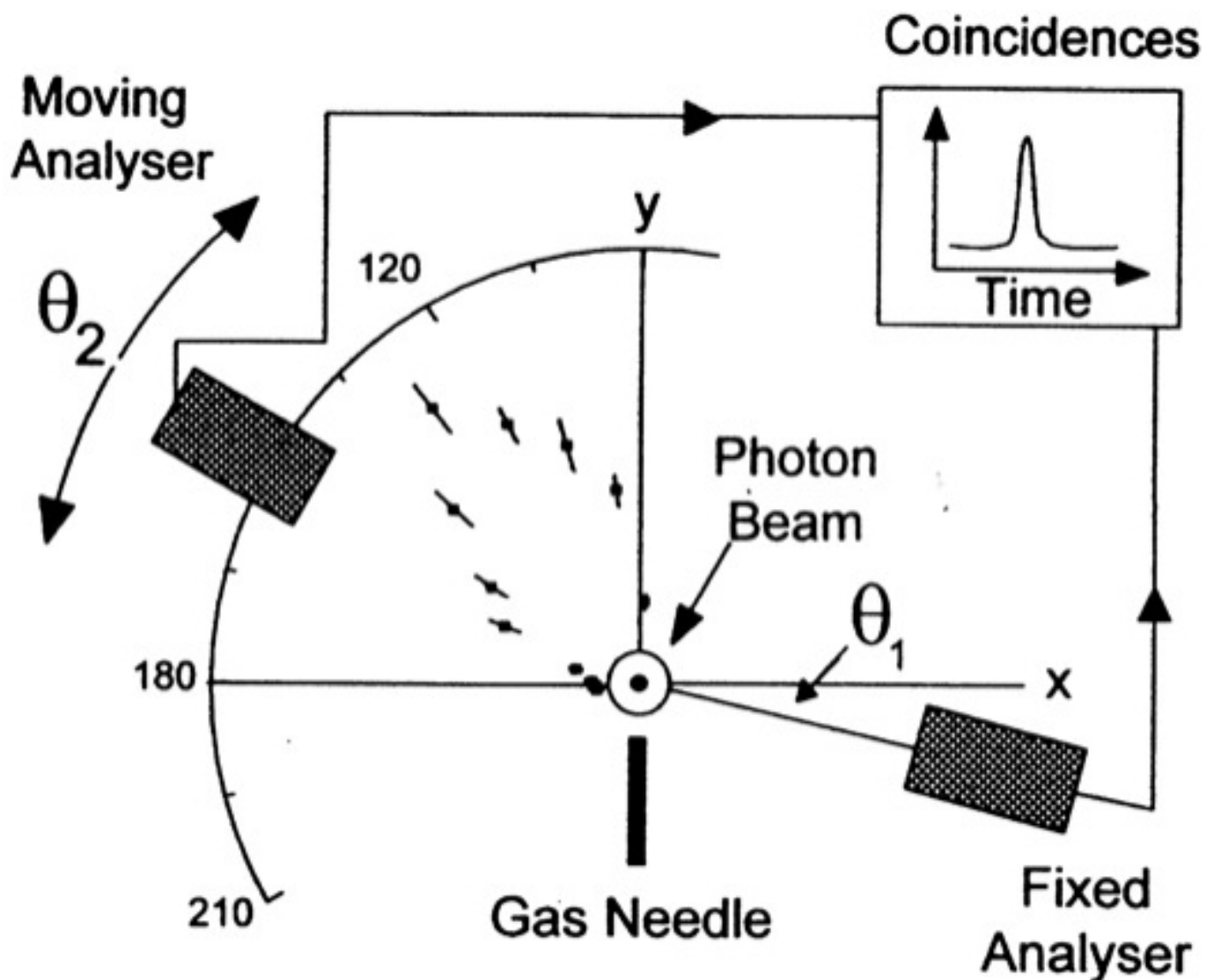


Figure 10.2: Schematic Diagram of the setup for Threshold Electron Spectroscopy (TES) using a Gas Needle and a Photon Beam.

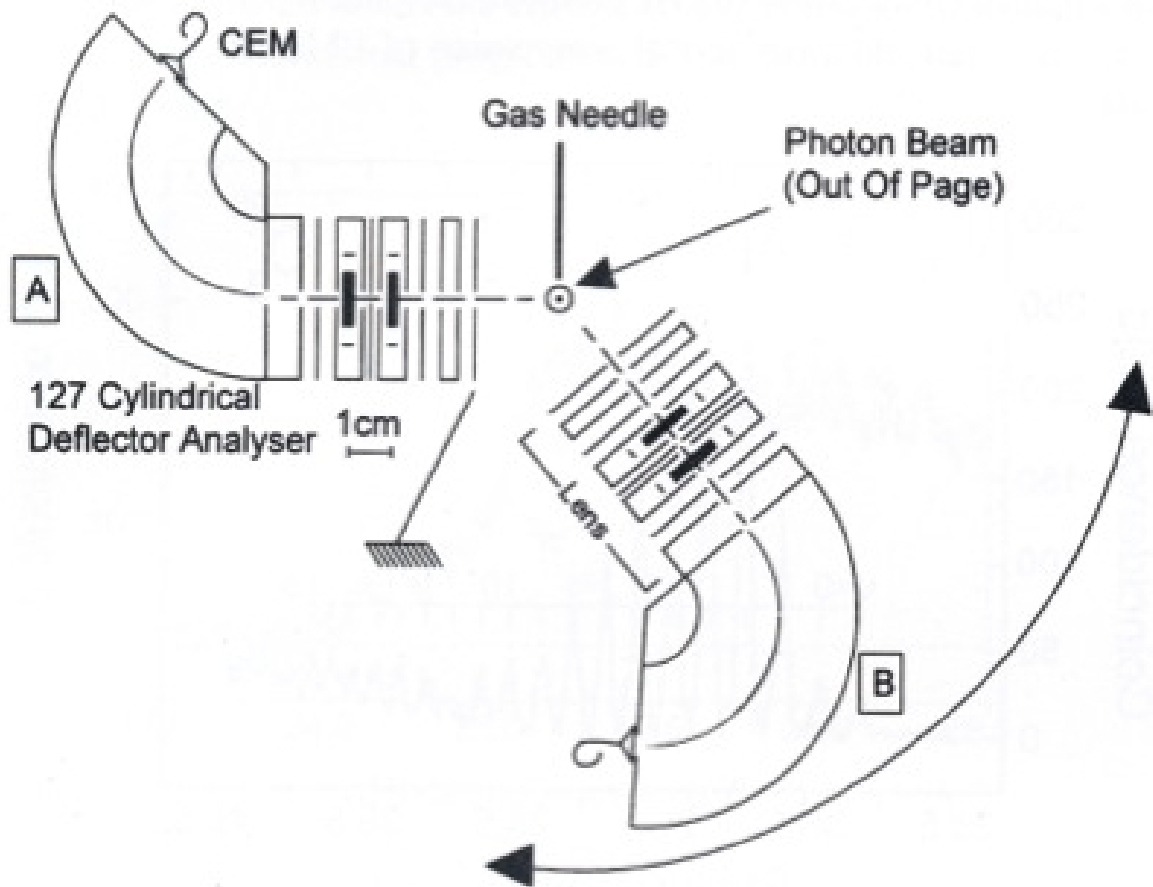


Figure 1: Schematic diagram of the experimental setup for Threshold Electron Spectroscopy (TES). The setup includes a photon beam source, a lens, a series of vertical slits, a gas needle, a 127 cylindrical deflector analyser, and a curved electron multiplier (CEM). The scale bar indicates 1 cm.

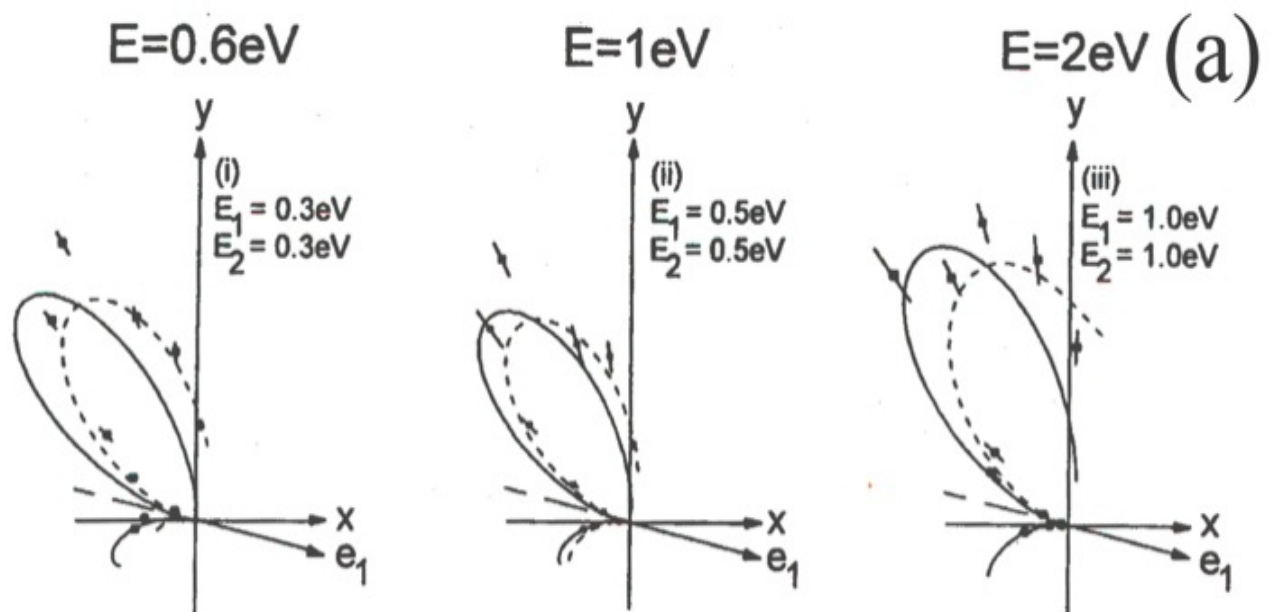


Figure 2: (a) Plot of the electron trajectory in the x-y plane for different incident photon energies. The plots show the electron path (solid line) and the photon path (dashed line) for three different incident photon energies: (i) $E = 0.6 \text{ eV}$, (ii) $E = 1 \text{ eV}$, and (iii) $E = 2 \text{ eV}$. The x-axis is labeled x and the y-axis is labeled y. The electron path is labeled e_1 and the photon path is labeled e_2 .

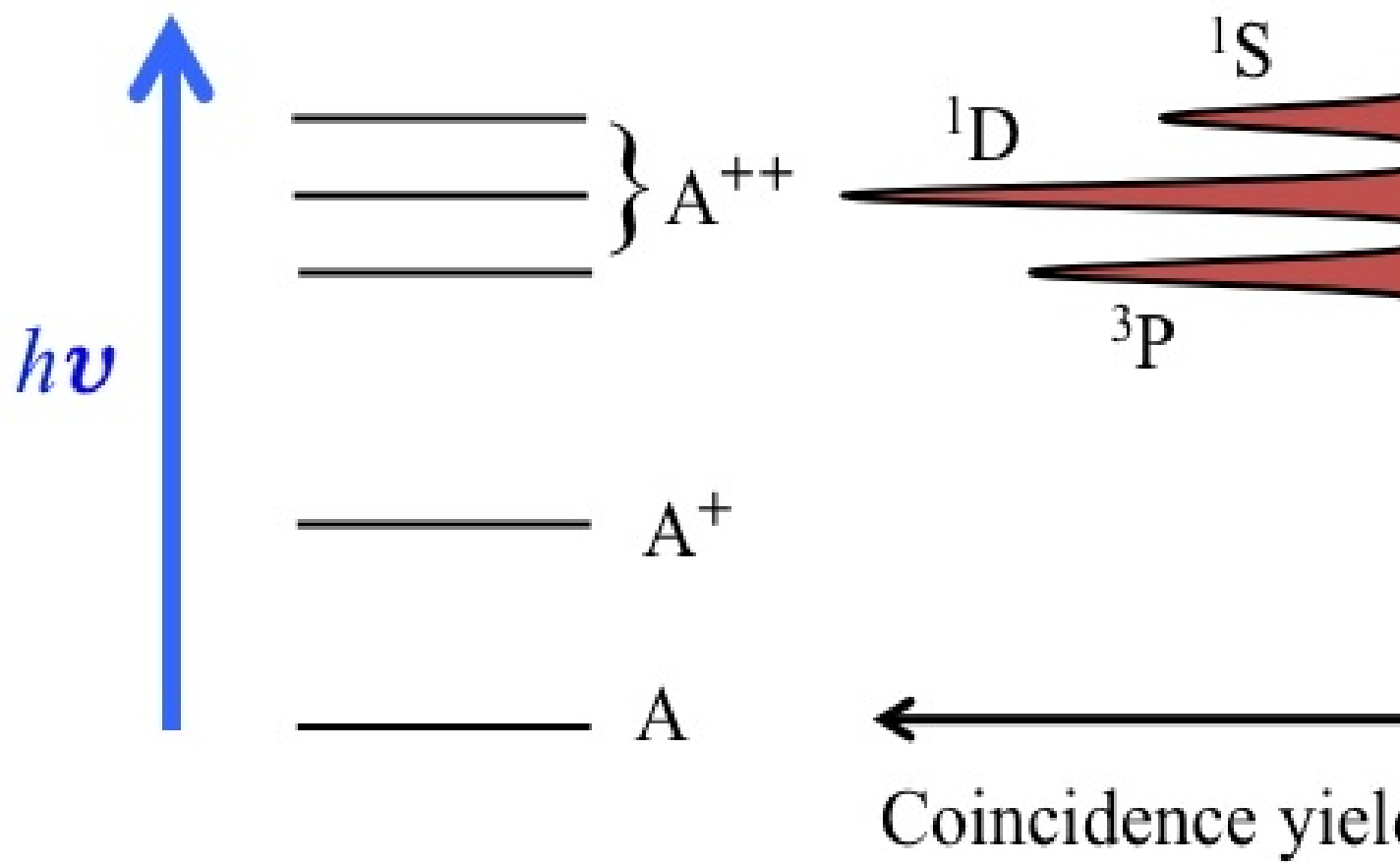


Figure 11.10: Ionization of Fe by Fe^{++} in the Fe^{++} ionization region. The Fe^{++} ionization region is the region where the Fe^{++} ionization cross-section is high and the Fe^{++} ionization cross-section is low. The Fe^{++} ionization region is the region where the Fe^{++} ionization cross-section is high and the Fe^{++} ionization cross-section is low.

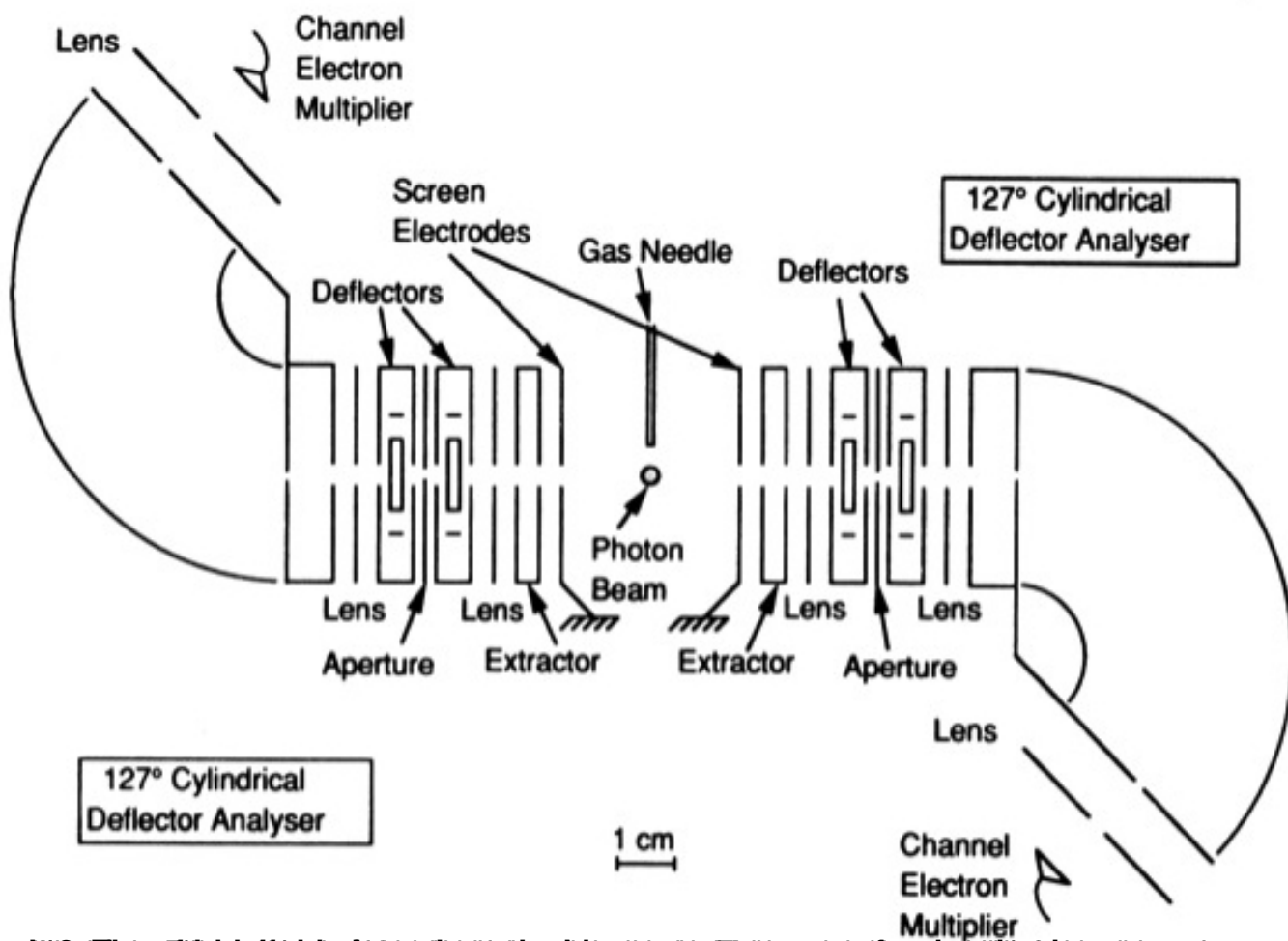


Figure 11.2. Schematic diagram of a Threshold Electron Spectroscopy (TES) instrument. The photon beam and the gas needle intersect in the center of the instrument. The electron paths are directed towards the Channel Electron Multiplier detectors at the ends of the instrument.

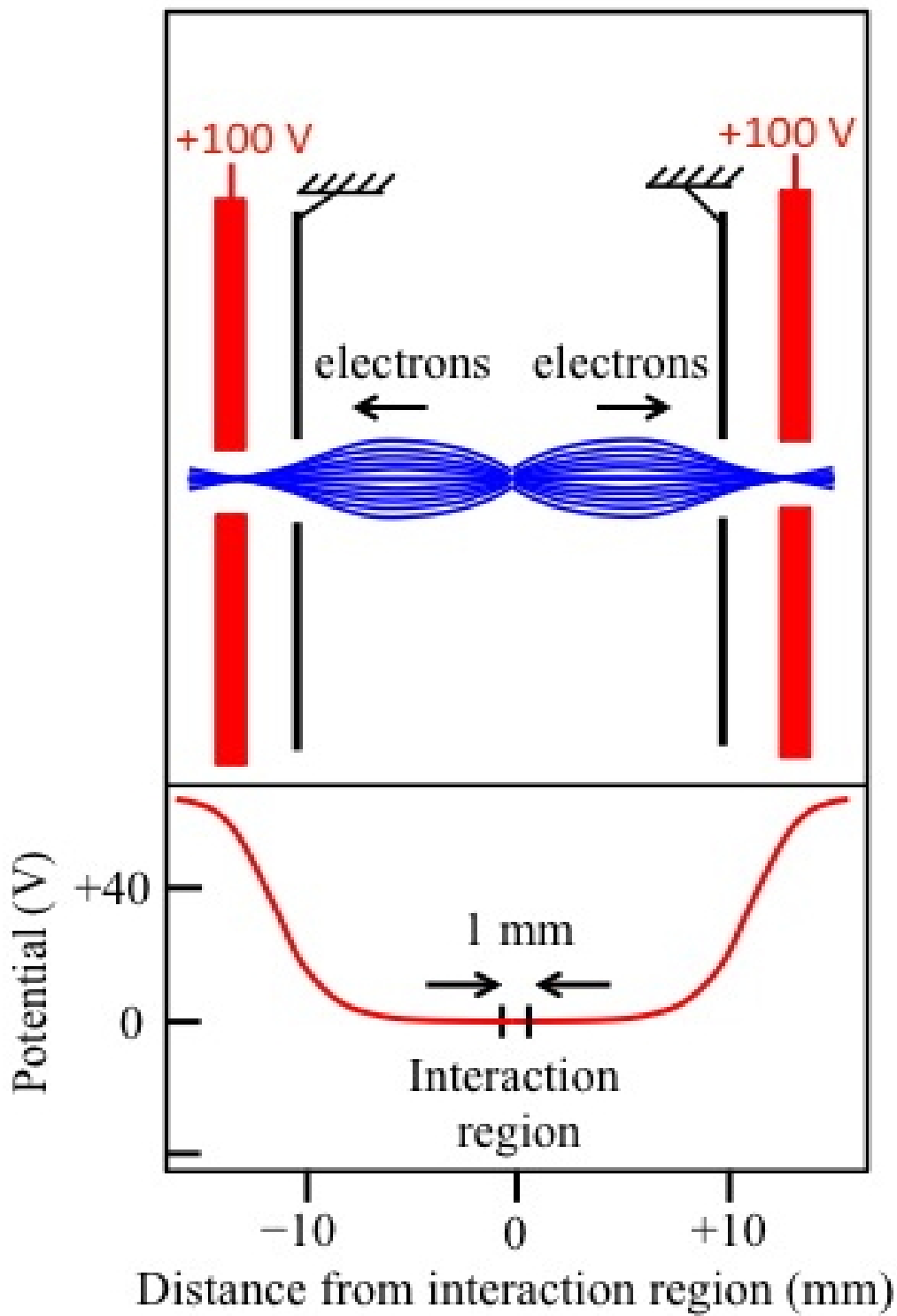


Fig. 10.1. Schematic diagram of the TES setup. The electron beams are produced by the electron gun and the electron detector. The electron beams are directed towards the interaction region. The electron beams are directed towards the interaction region. The electron beams are directed towards the interaction region.

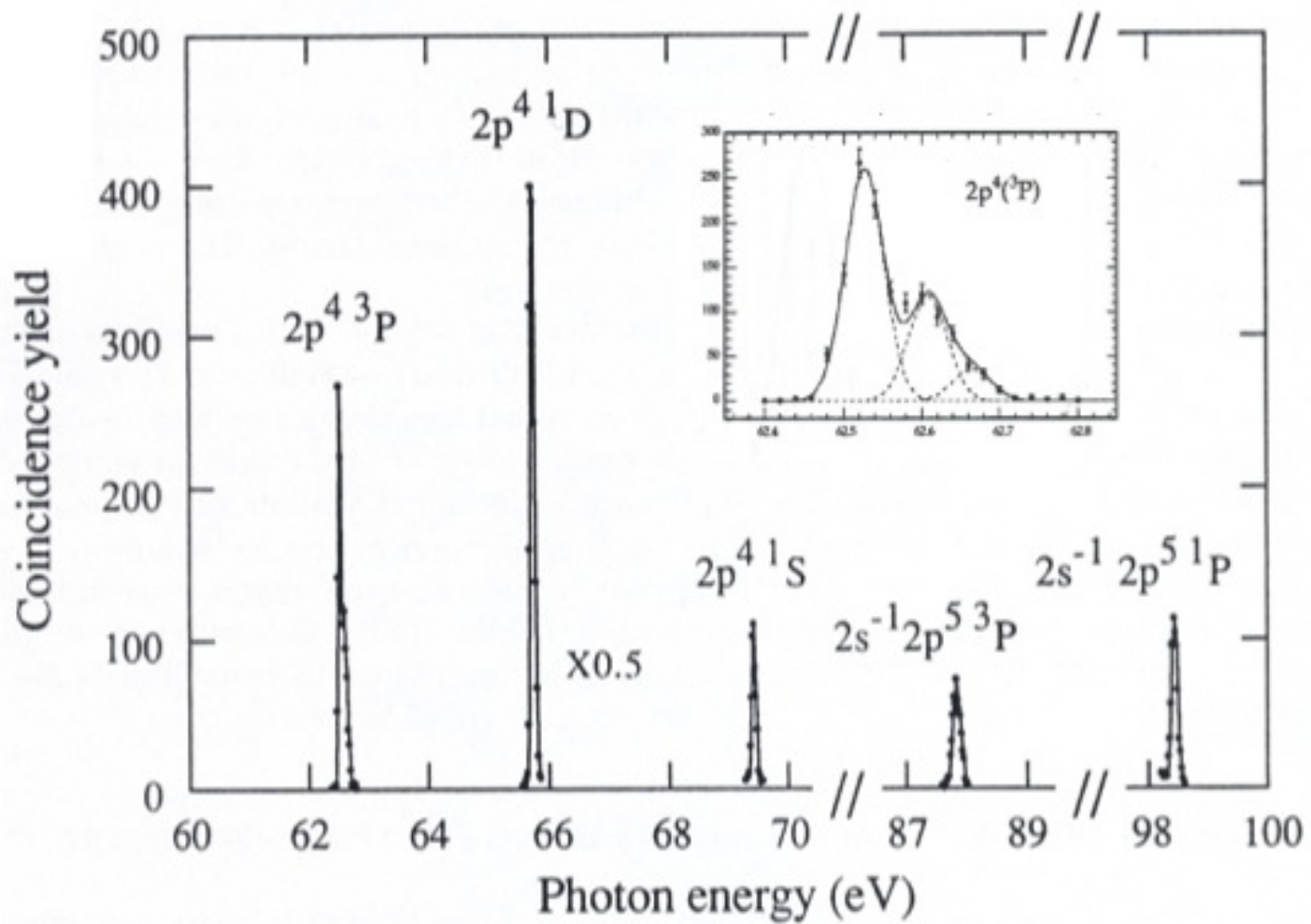


Fig. 14.5 TRES spectrum obtained for Nitrogen in the photon energy range 60 - 100 eV. The inset shows a zoomed-in view of the $2p^4 (3P)$ region. The scale factor is X0.5. The peaks are labeled with their corresponding electronic states.

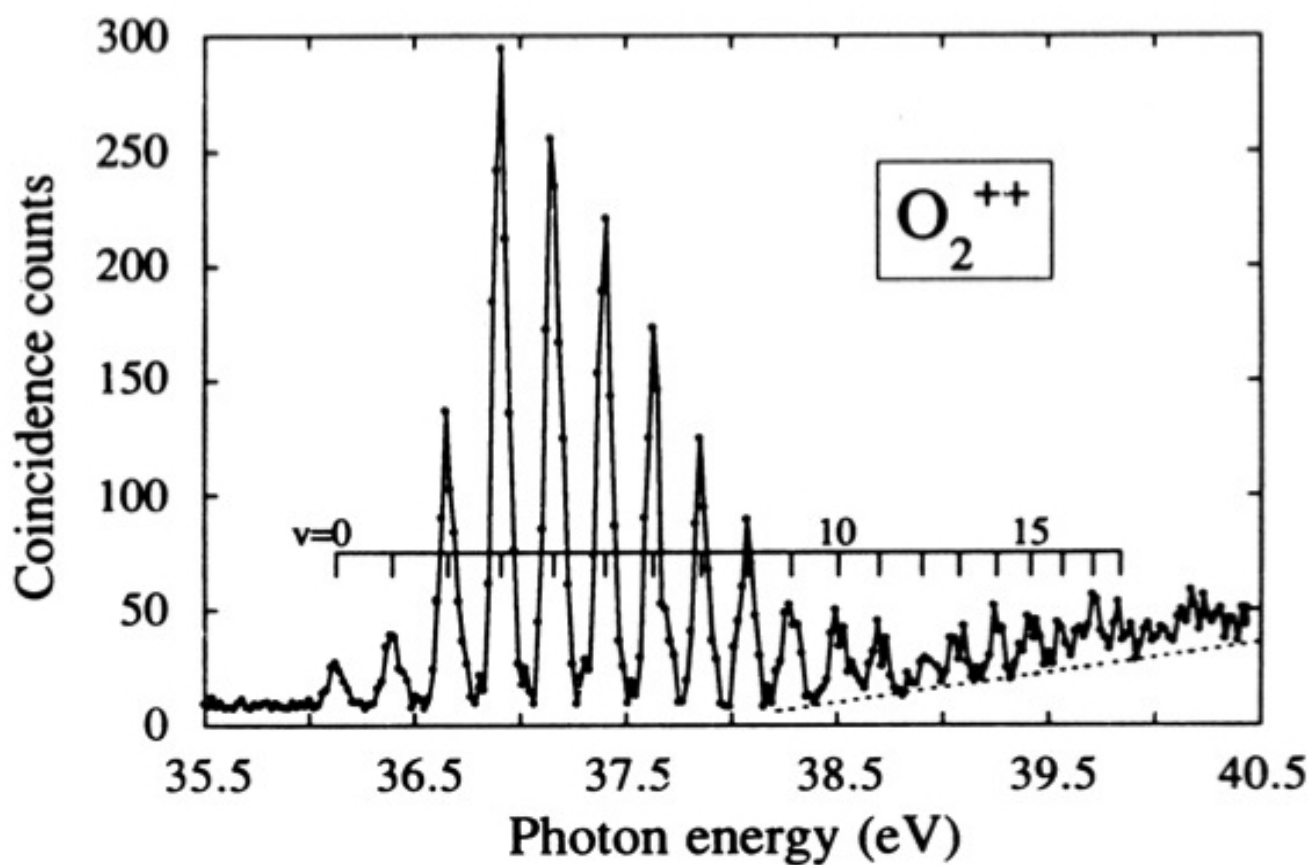


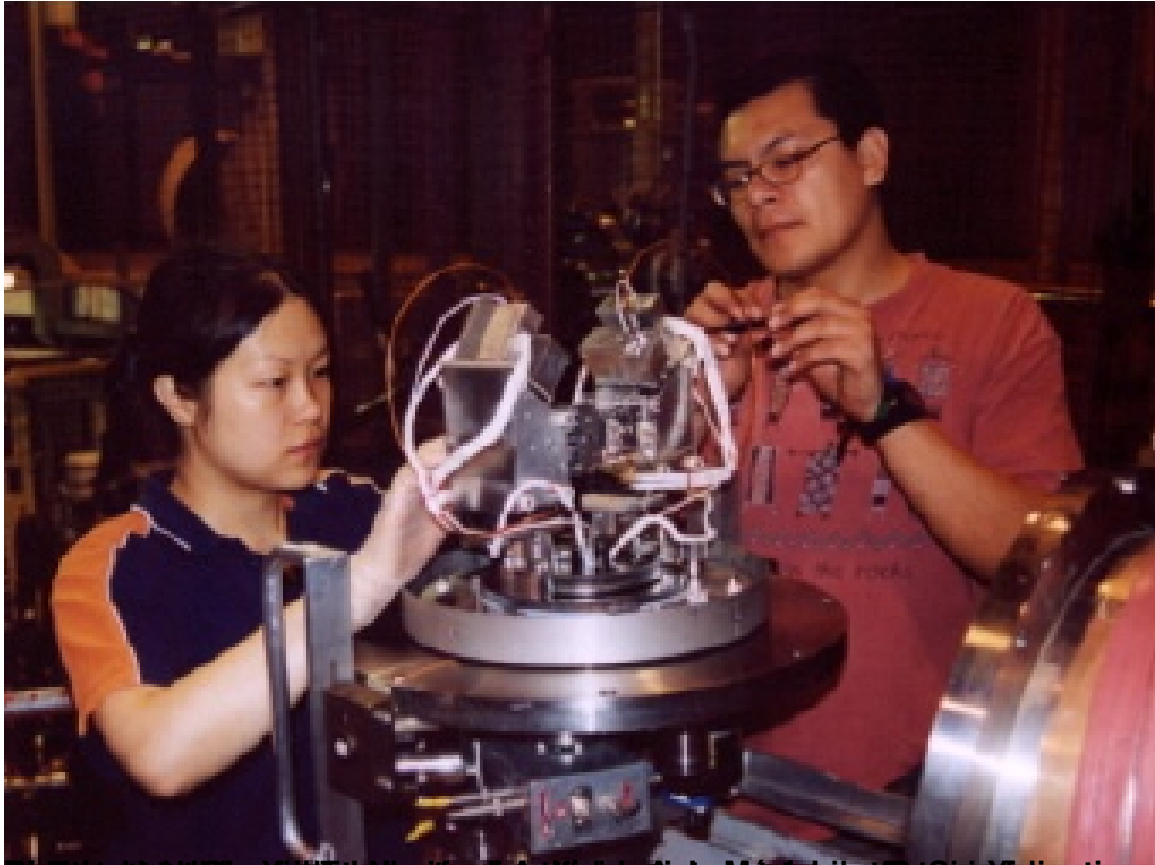
Figure 15. TPE-60 spectrum for the ground electronic state of O_2 showing regular vibrational structure. The inset shows the chemical formula O_2^{++} .



Samuel, David, George, Richard, and Mary. They are the authors of the paper 'Threshold Electron Spectroscopy of O_2 '.



Photo of the author and his wife, taken during a visit to the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, where he worked as a research scientist from 1985 to 1995.



Threshold Electron Spectroscopy (TES) is a technique used to study the electronic structure of materials. It involves measuring the energy of electrons emitted from a material as a function of the incident photon energy. The technique is particularly useful for studying the band structure of semiconductors and the electronic properties of surfaces. The setup shown in the image is a typical TES system, which includes a vacuum chamber, a monochromator, a detector, and a sample stage. The researchers are likely performing a series of measurements to determine the electronic structure of a specific material.