Threshold Photoionisation of Atoms and Molecules

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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 monochronomator (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 Yencha (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 (~ few meV) photoelectrons, i.e. *threshold photoelectrons*. This technique employs the penetrating field technique [1], which is illustrated schematically in Figure 1.

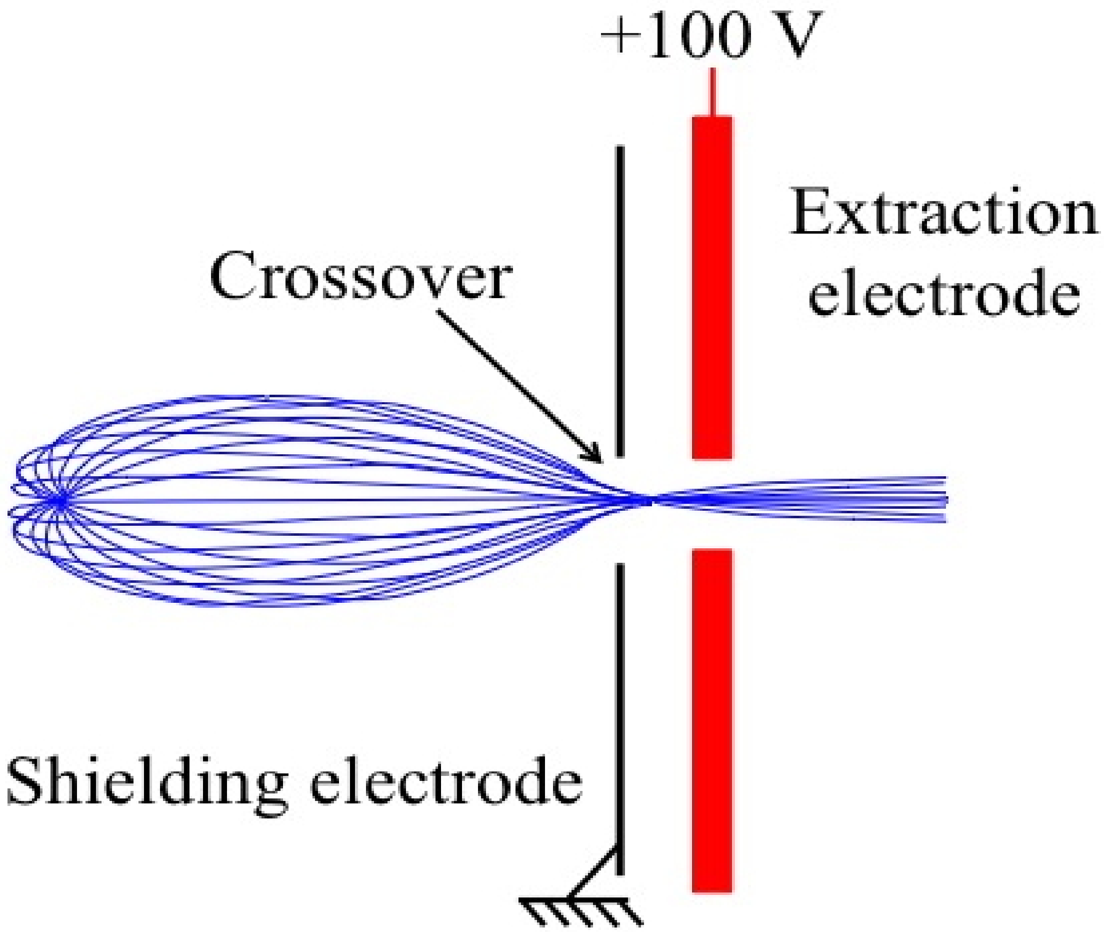


Figure 1. A computer simulation of the trajectories of 2 meV photoelectrons, illustrating the principle of the penetrating field technique.

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 ~ 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].

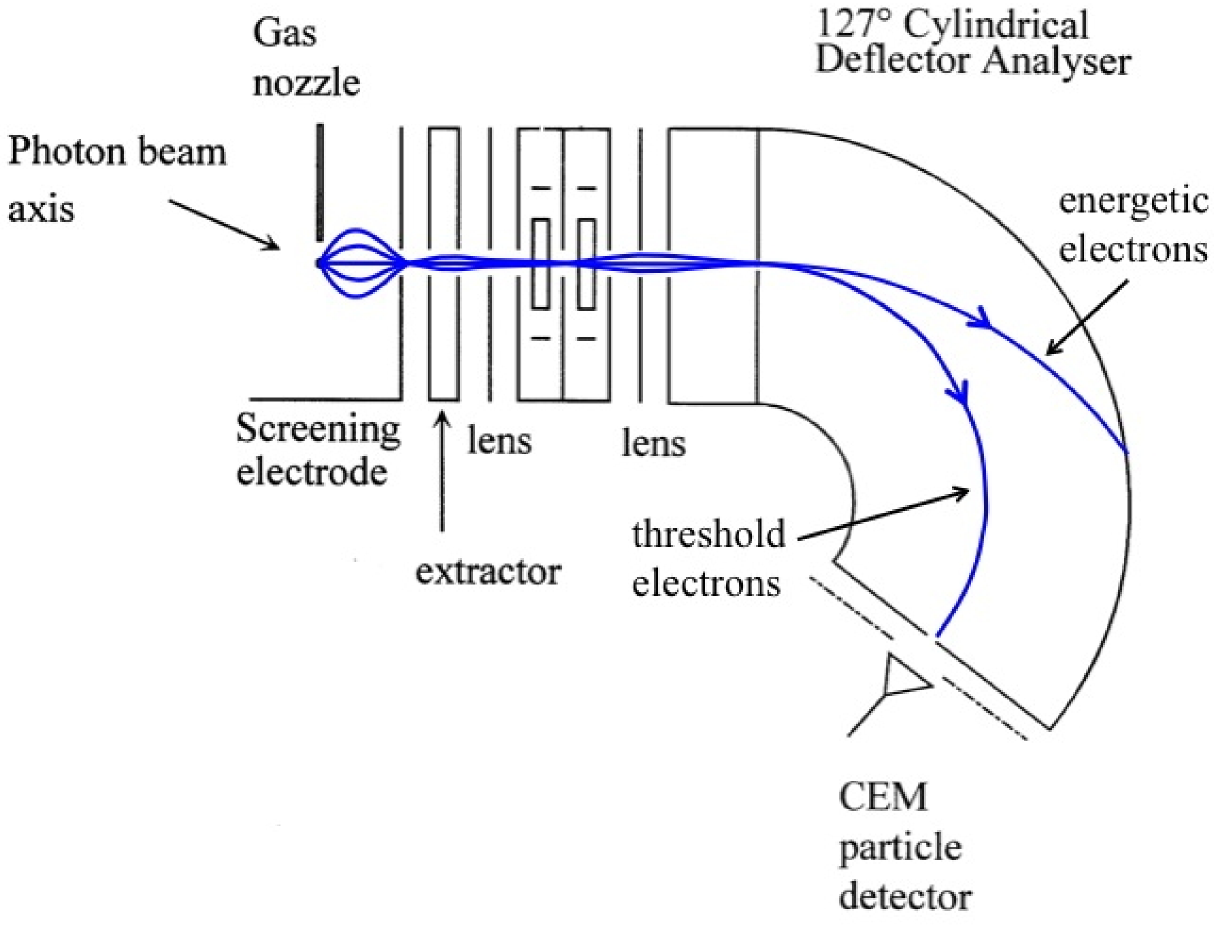


Figure 2. A threshold photoelectron spectrometer. The purpose of the 127° cylindrical deflector analyser is to filter out energetic photoelectrons that are emitted within the solid angle subtended by the aperture in the shielding electrode.

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.

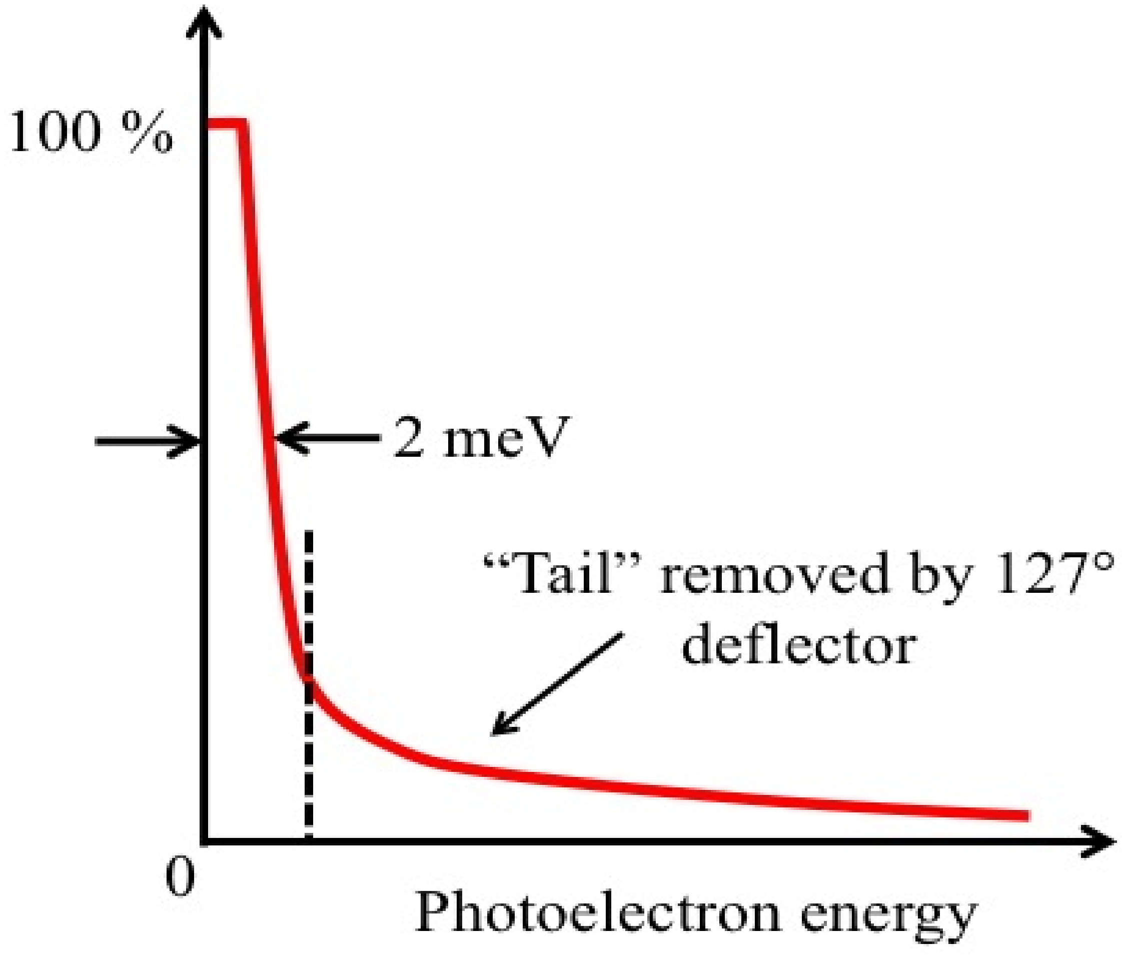


Figure 3. Transmission function of the threshold analyser. The width of the function is ~ 2 meV and photoelectrons of energy less than this value are collected with ~ 100 % efficiency.

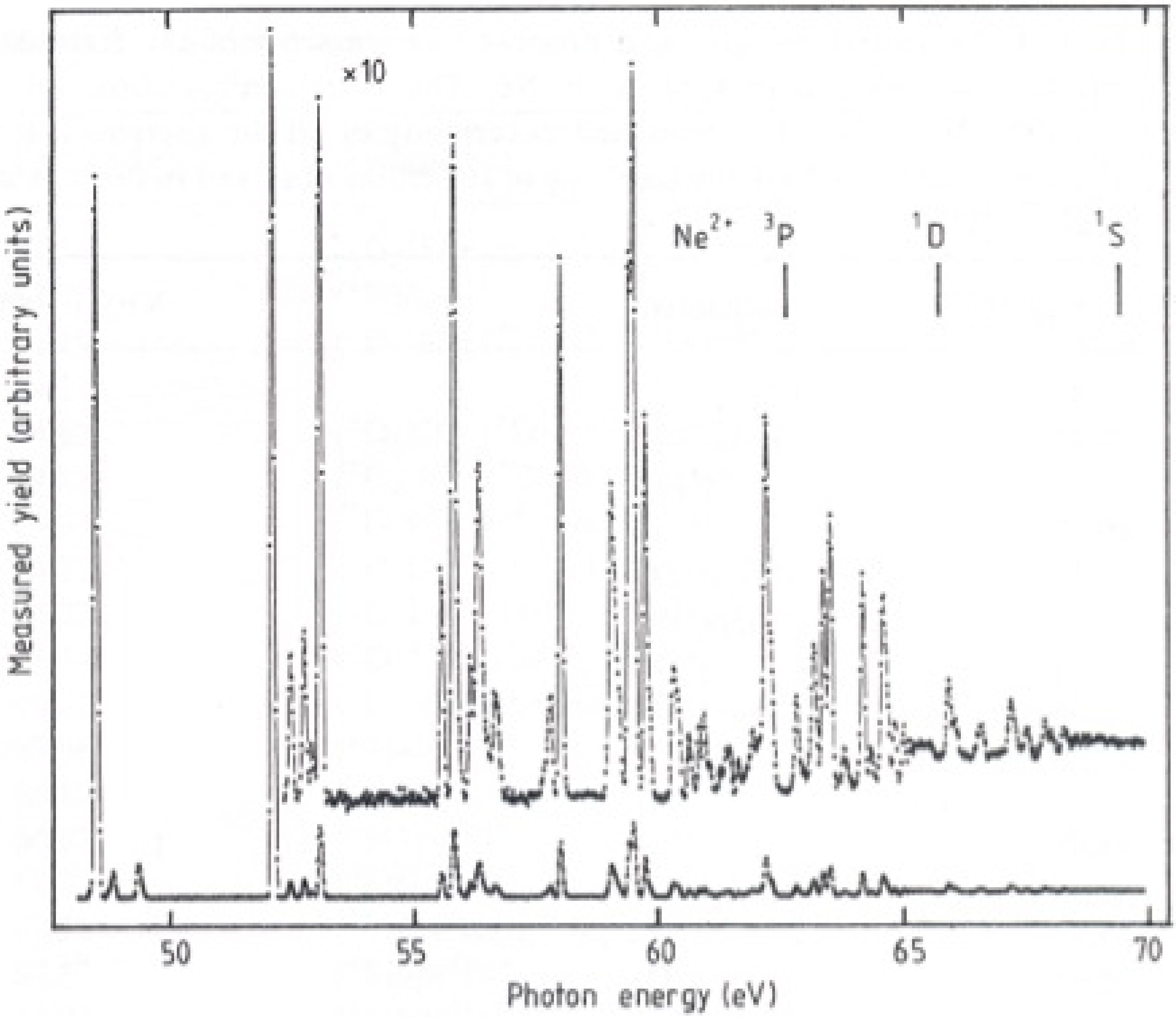
The SRS beam is crossed with the target gas beam that emanates from a narrow capillary tube and the photon energy is scanned across the region of interest. Whenever the photon energy crosses an ionisation threshold of the target species, threshold photoelectrons are produced, which are extracted and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

Threshold photoelectron studies

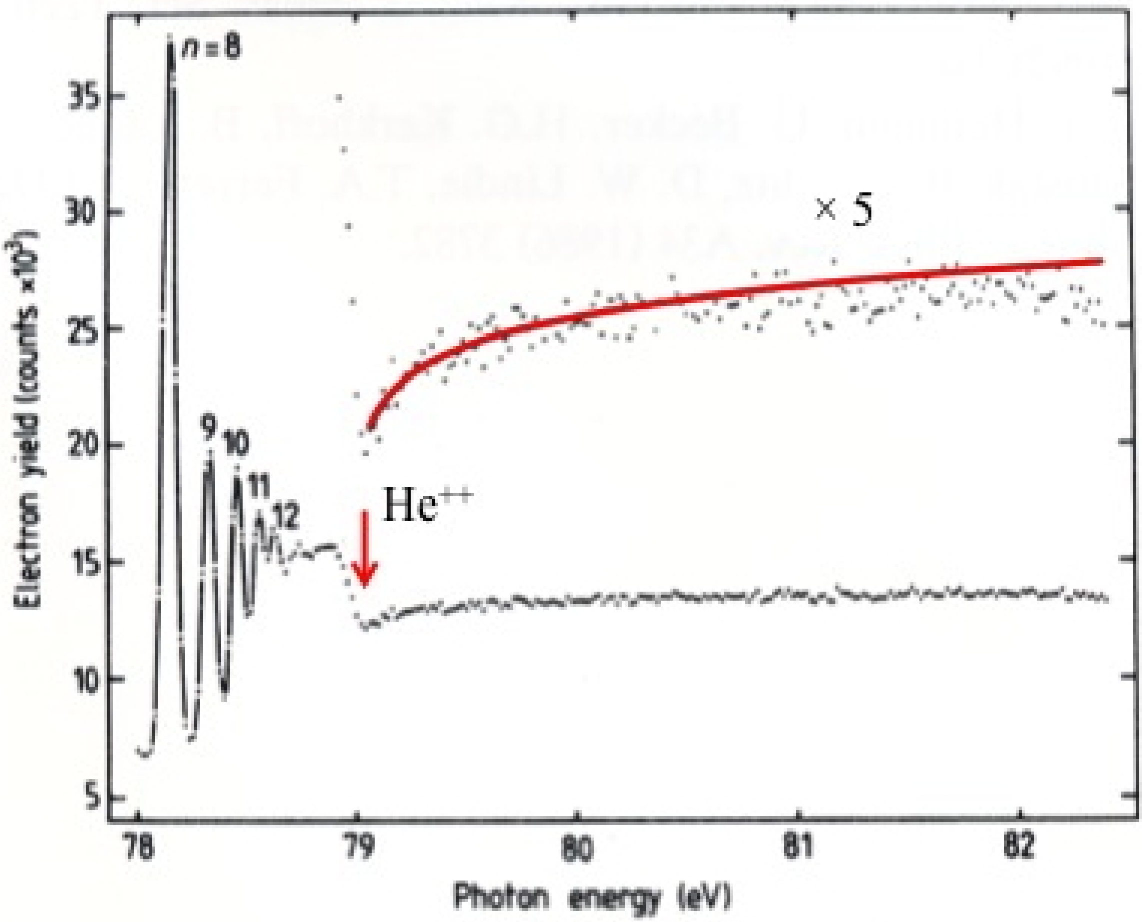
Threshold photoelectron studies of atoms

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^+, $3s^2 3p^4 nl$. 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 we obtained in helium [5] is shown in Figure 6.


n = 8
9
10
11
12
× 5
He++
Electron yield (counts ×10³)
Photon energy (eV)
5
10
15
20
25
30
35
78
79
80
81
82

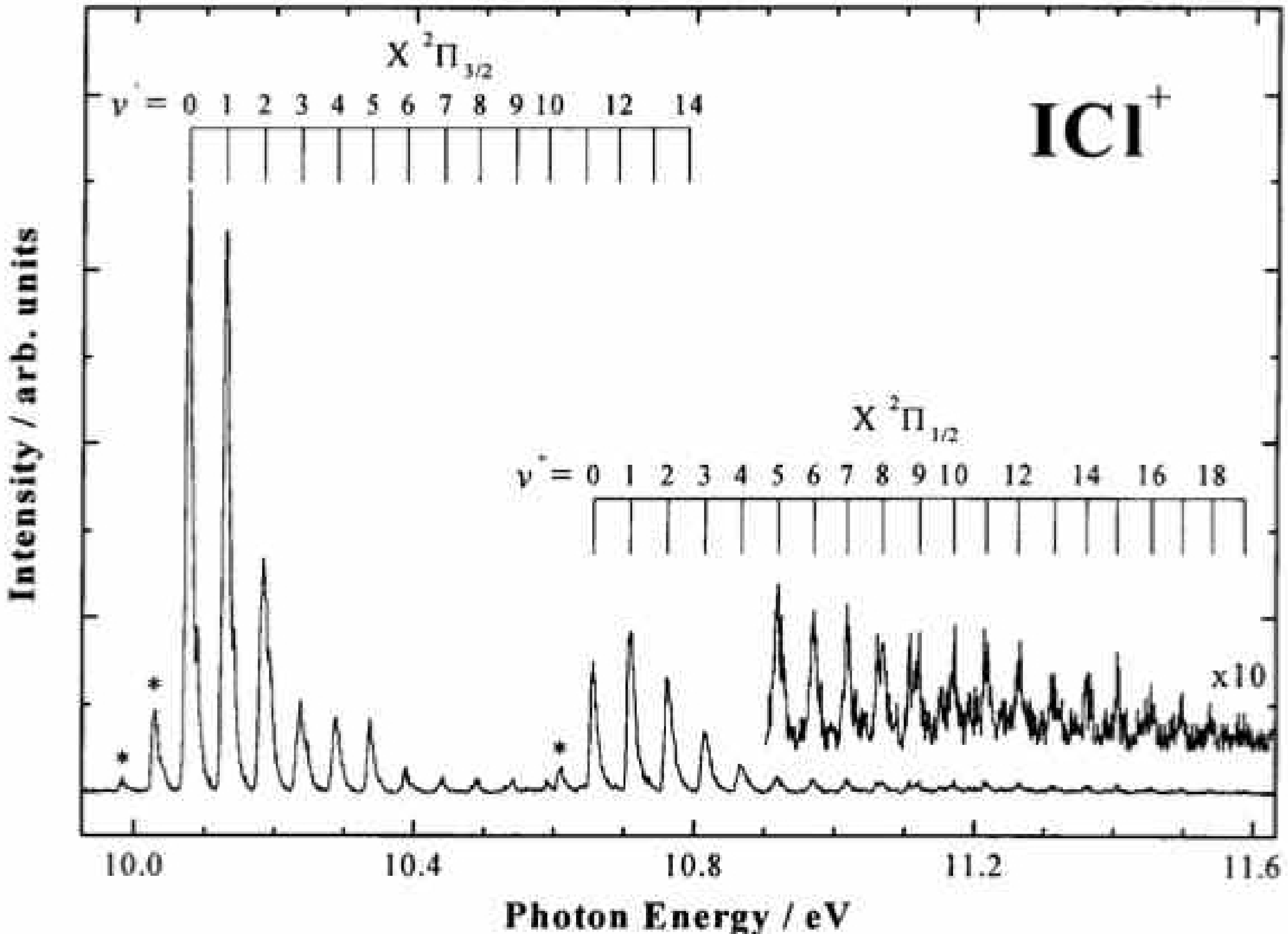


Figure 6. Threshold photoelectron spectrum of the ICl^+ ($X\ ^2\Pi$ [illegible]

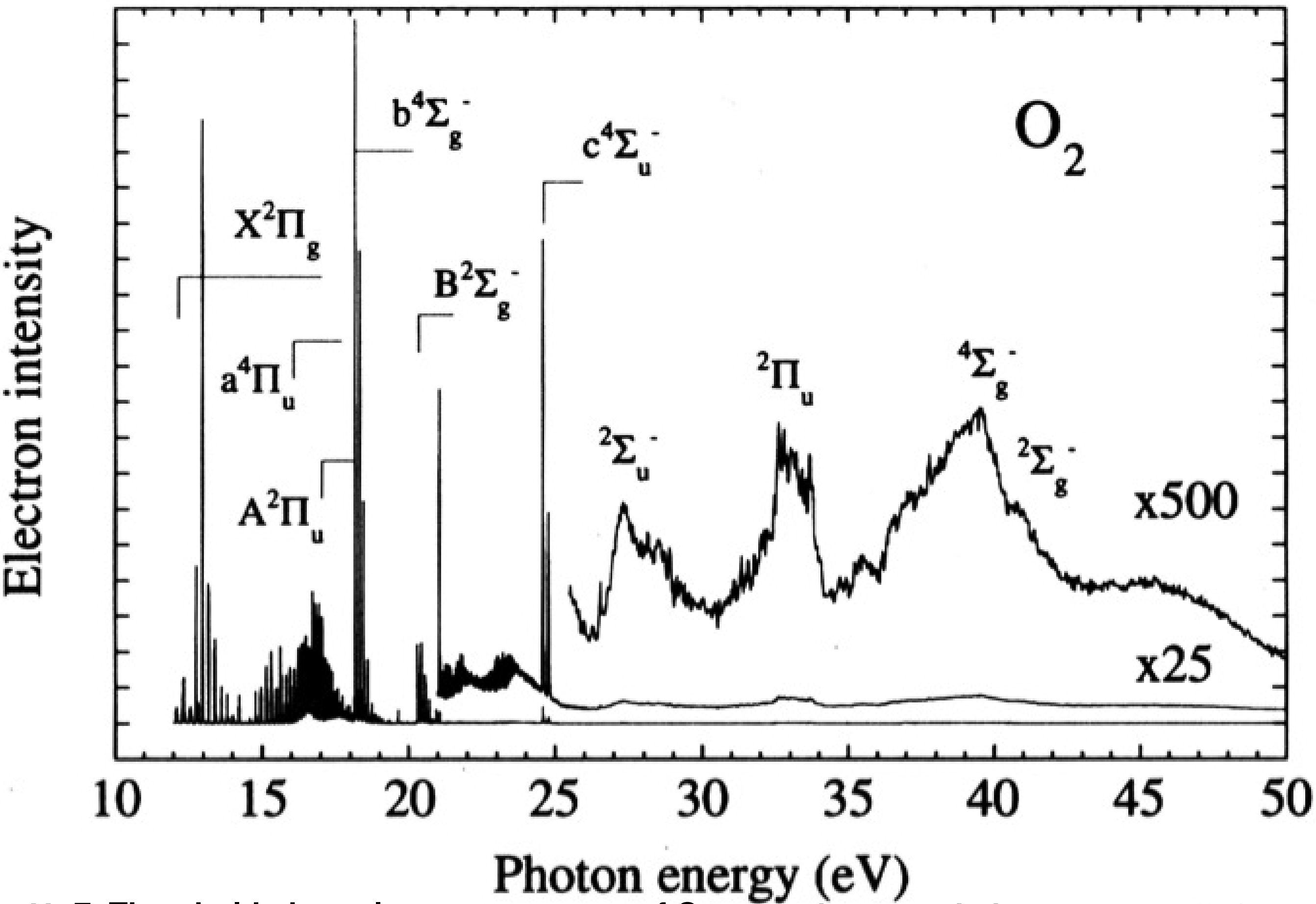
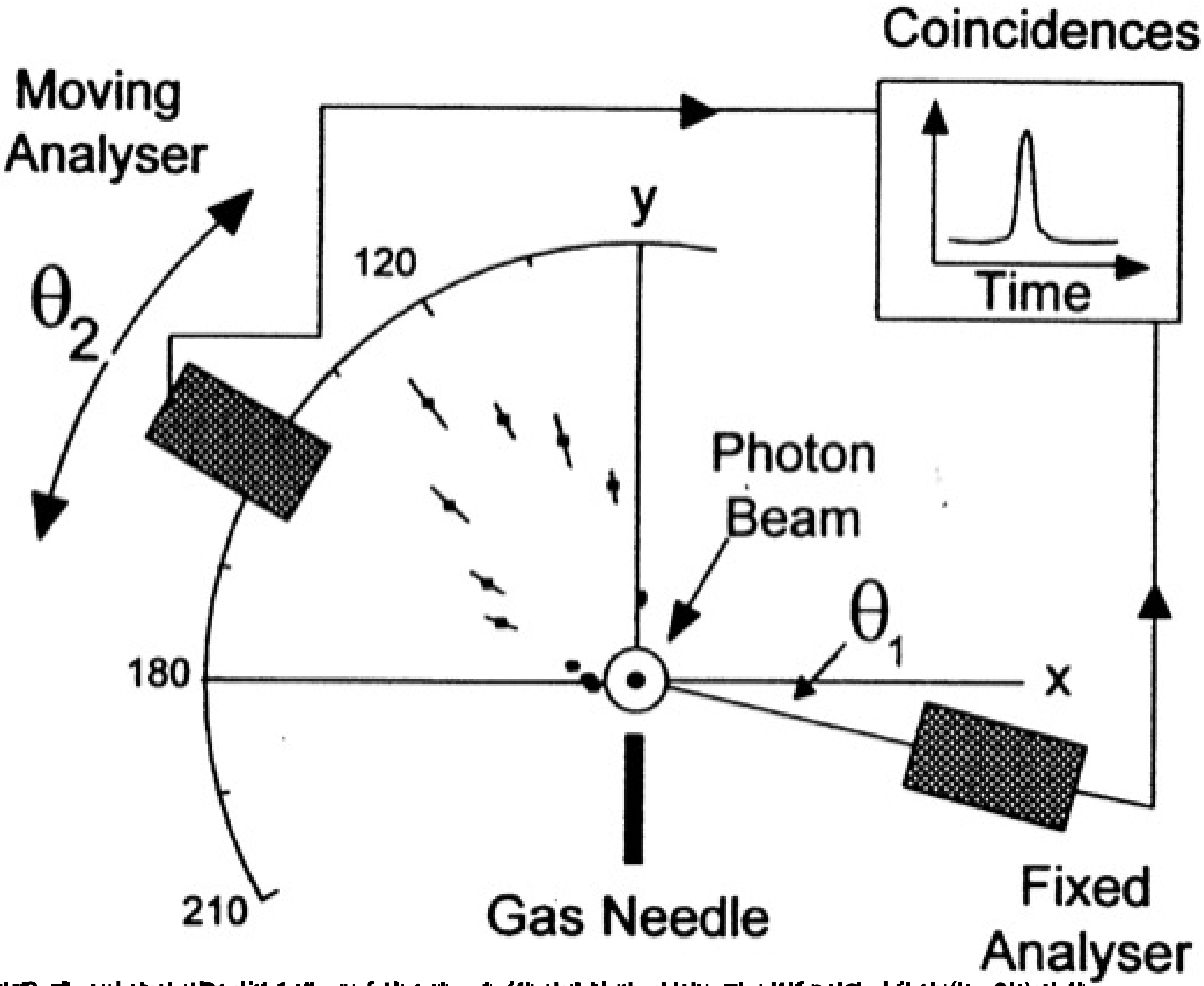
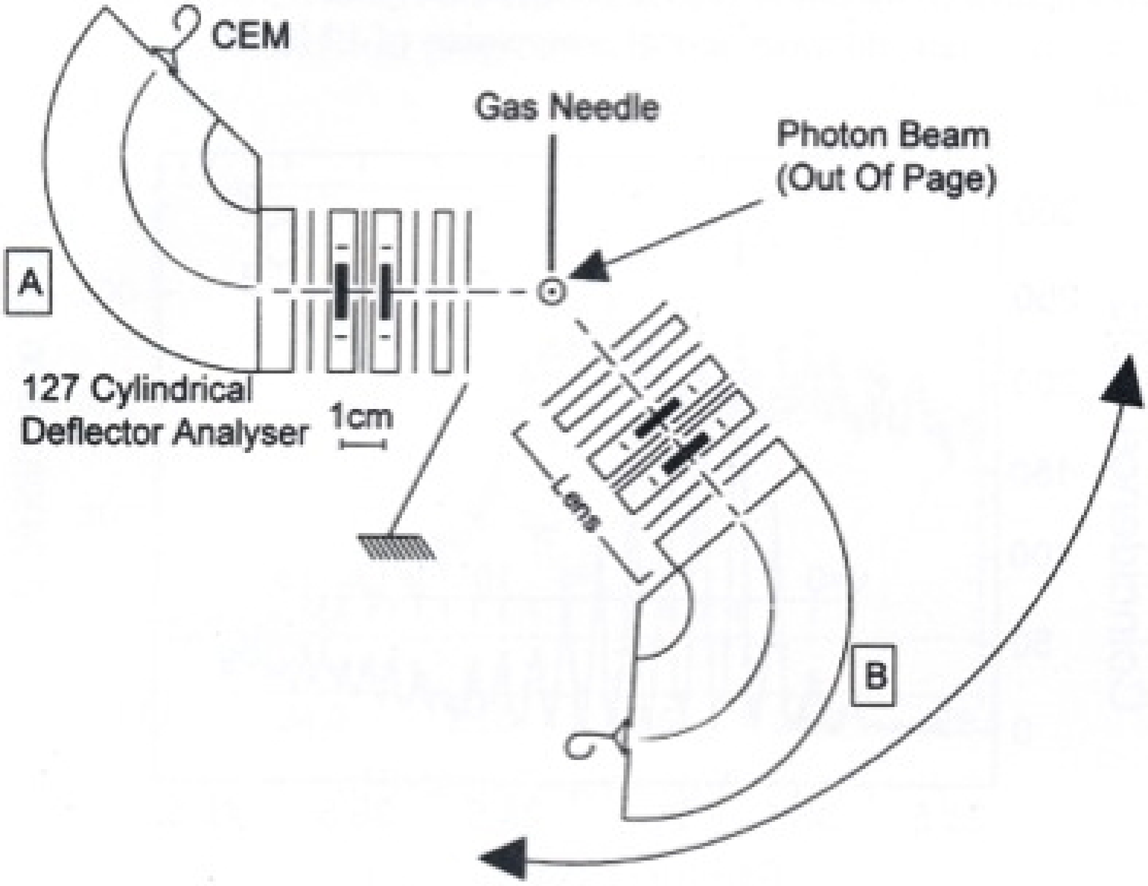


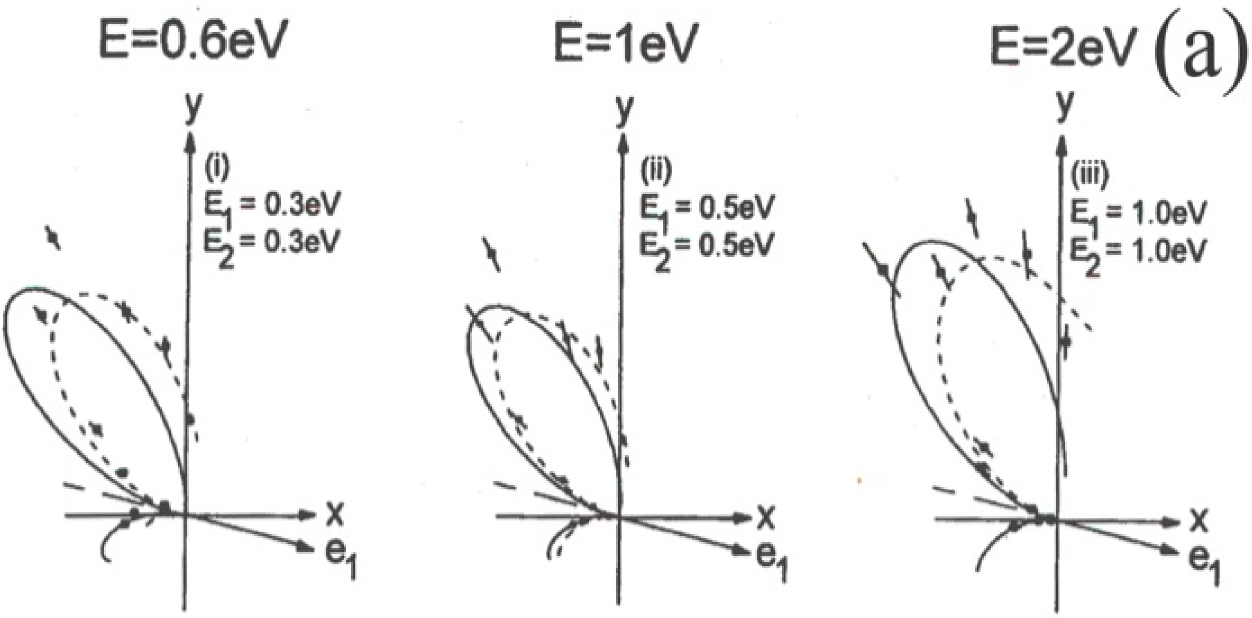
Figure 7: Threshold photoelectron spectrum of O_2 over the extended energy range 12


Coincidences
Moving
Analyser
Time
y
120
θ2
Photon
Beam
θ1
180
x
210
Gas Needle
Fixed
Analyser

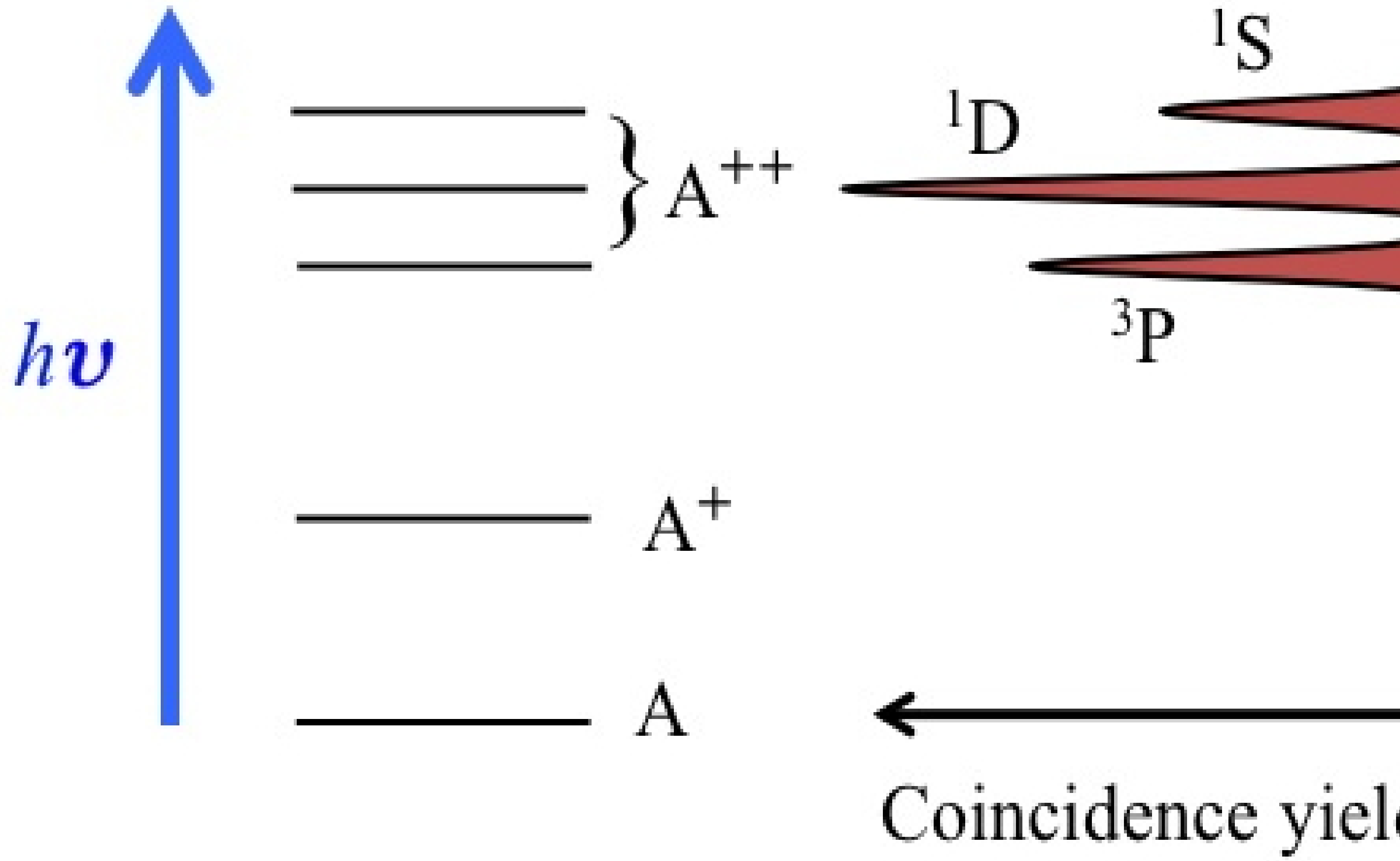
[illegible]


CEM
Gas Needle
Photon Beam
(Out Of Page)
A
127 Cylindrical
Deflector Analyser
1cm
Lens
B

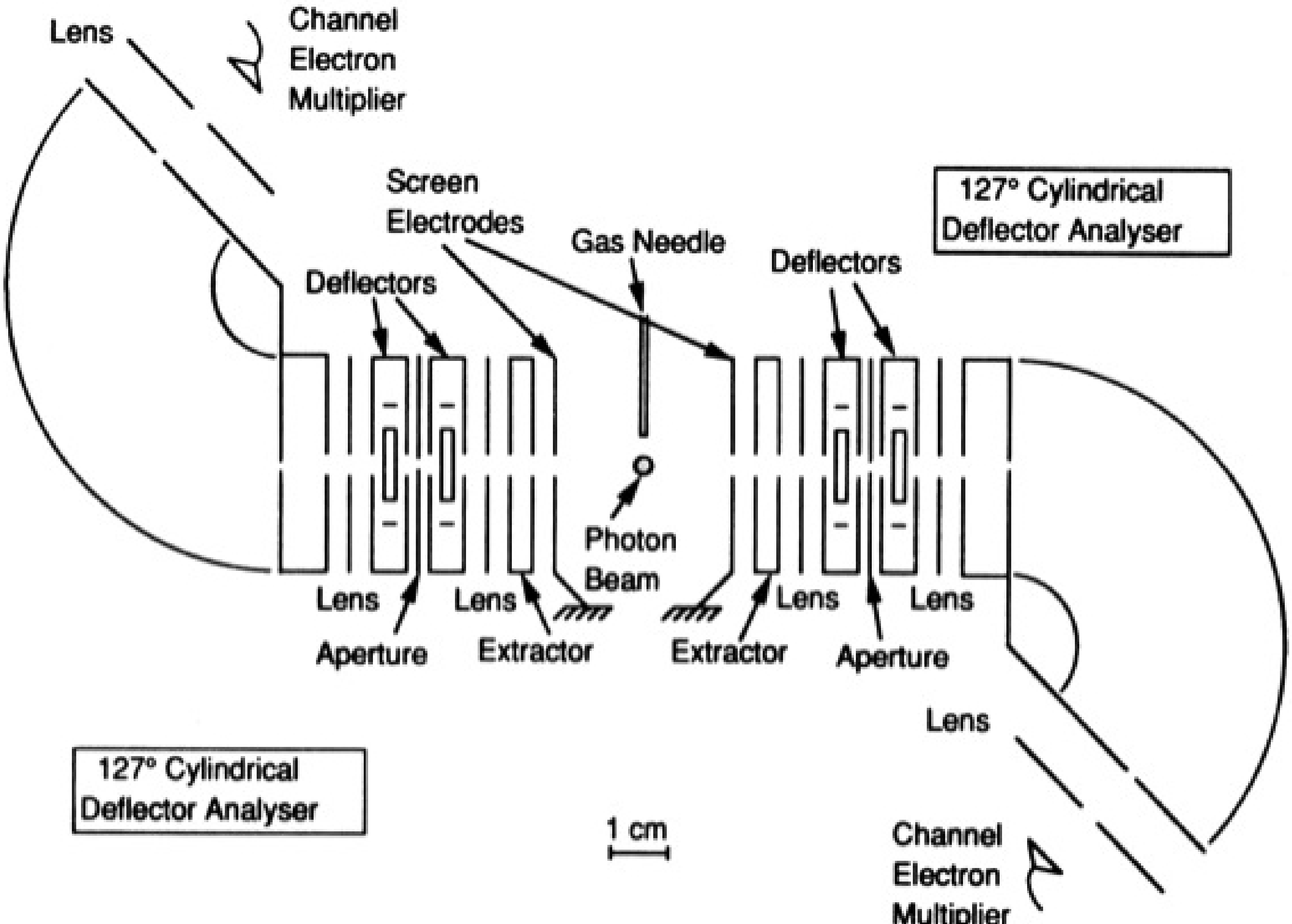
[illegible]


E=0.6eV
E=1eV
E=2eV
(a)
y
x
e_1
(i)
E_1 = 0.3eV
E_2 = 0.3eV
(ii)
E_1 = 0.5eV
E_2 = 0.5eV
(iii)
E_1 = 1.0eV
E_2 = 1.0eV

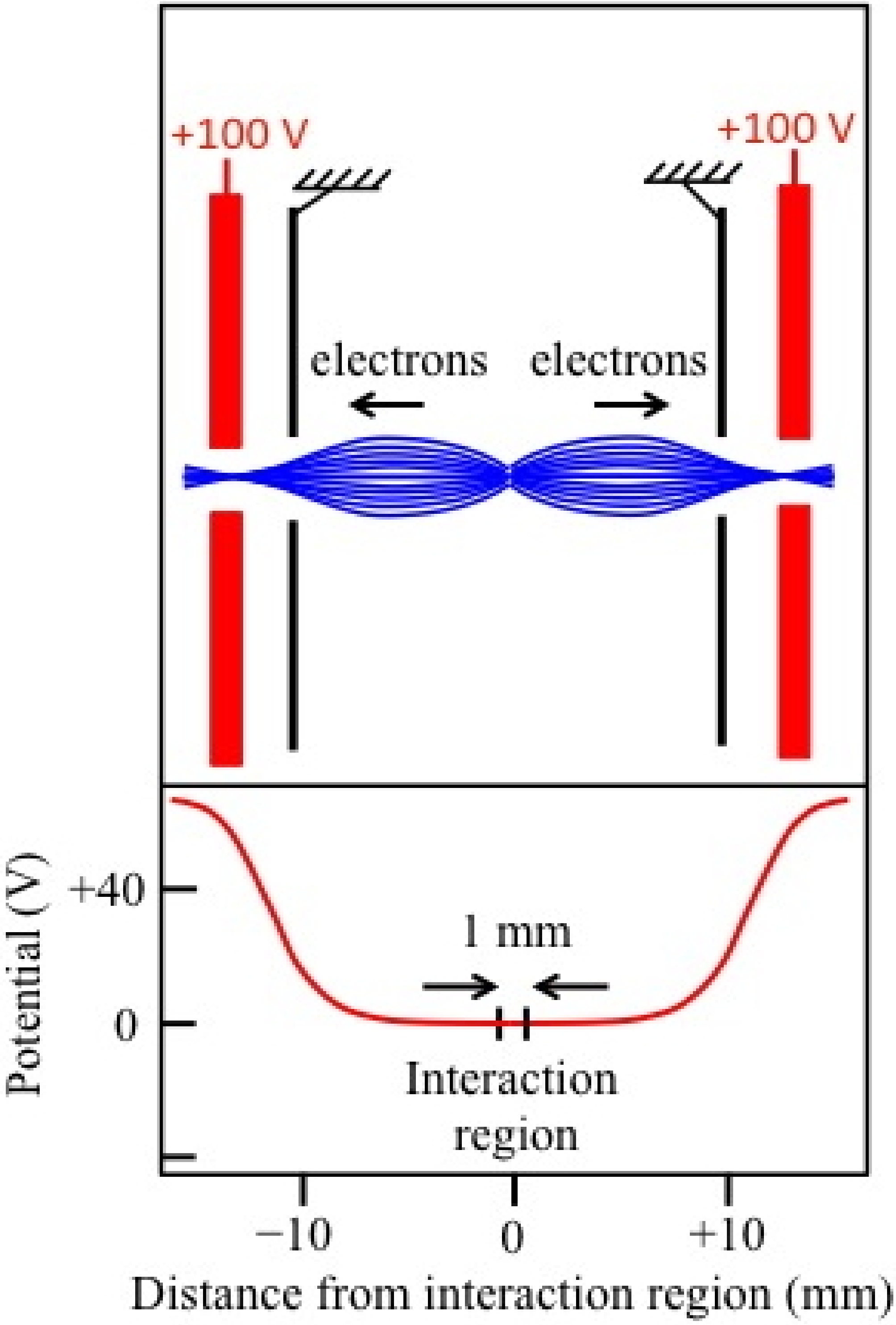
[illegible]


hv
A++
A+
A
1S
1D
3P
Coincidence yiel

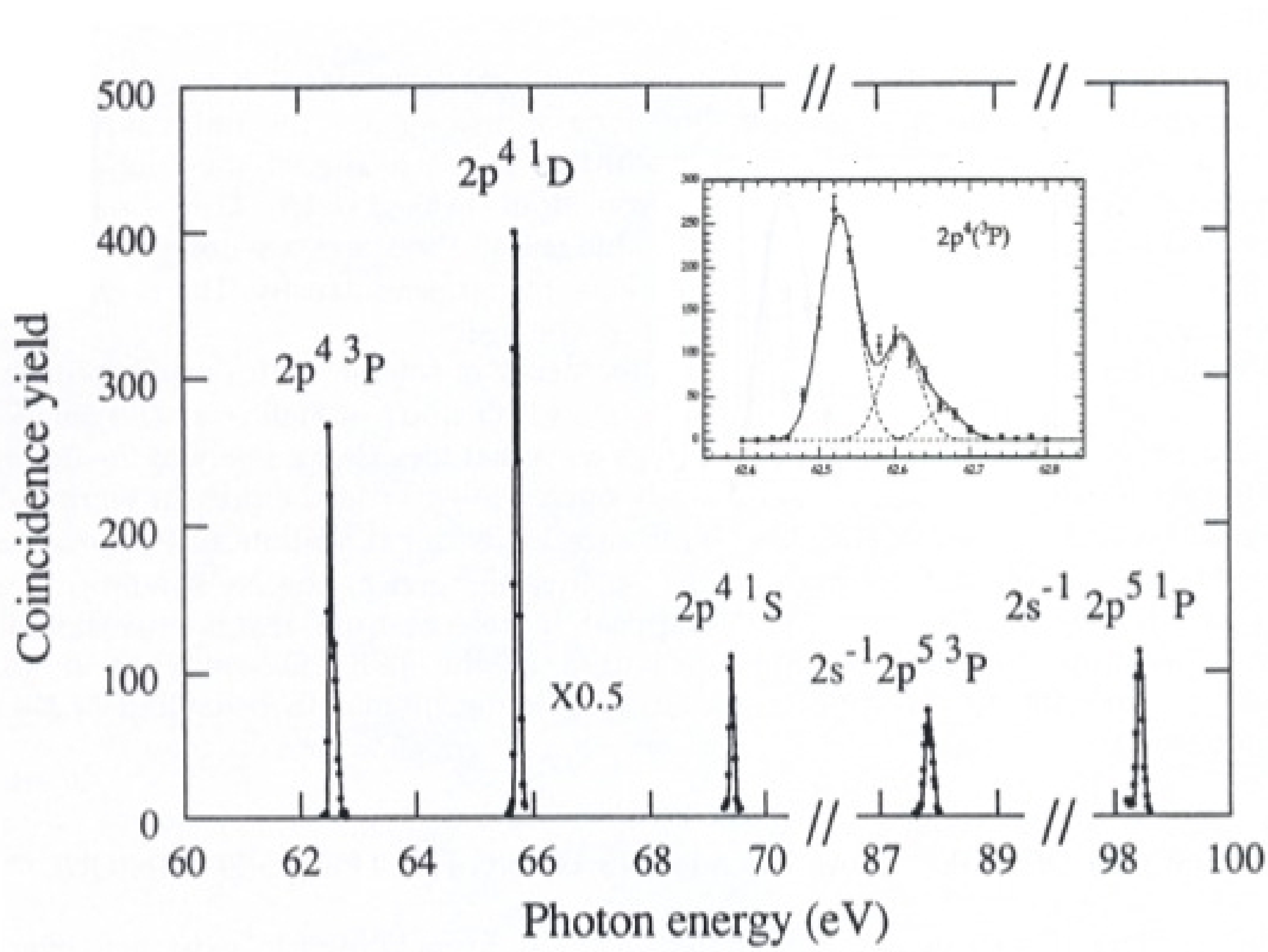
[illegible]


Lens
Channel
Electron
Multiplier
Screen
Electrodes
Gas Needle
127° Cylindrical
Deflector Analyser
Deflectors
Deflectors
Photon
Beam
Lens
Lens
Lens
Lens
Aperture
Extractor
Extractor
Aperture
Lens
127° Cylindrical
Deflector Analyser
1 cm
Channel
Electron
Multiplier

[illegible]


+100 V
+100 V
electrons
electrons
Potential (V)
+40
0
1 mm
Interaction region
−10
0
+10
Distance from interaction region (mm)

[illegible]



[illegible] photon energy range 60 - 100 [illegible]

[illegible] vibrational levels can be seen in the spectrum.

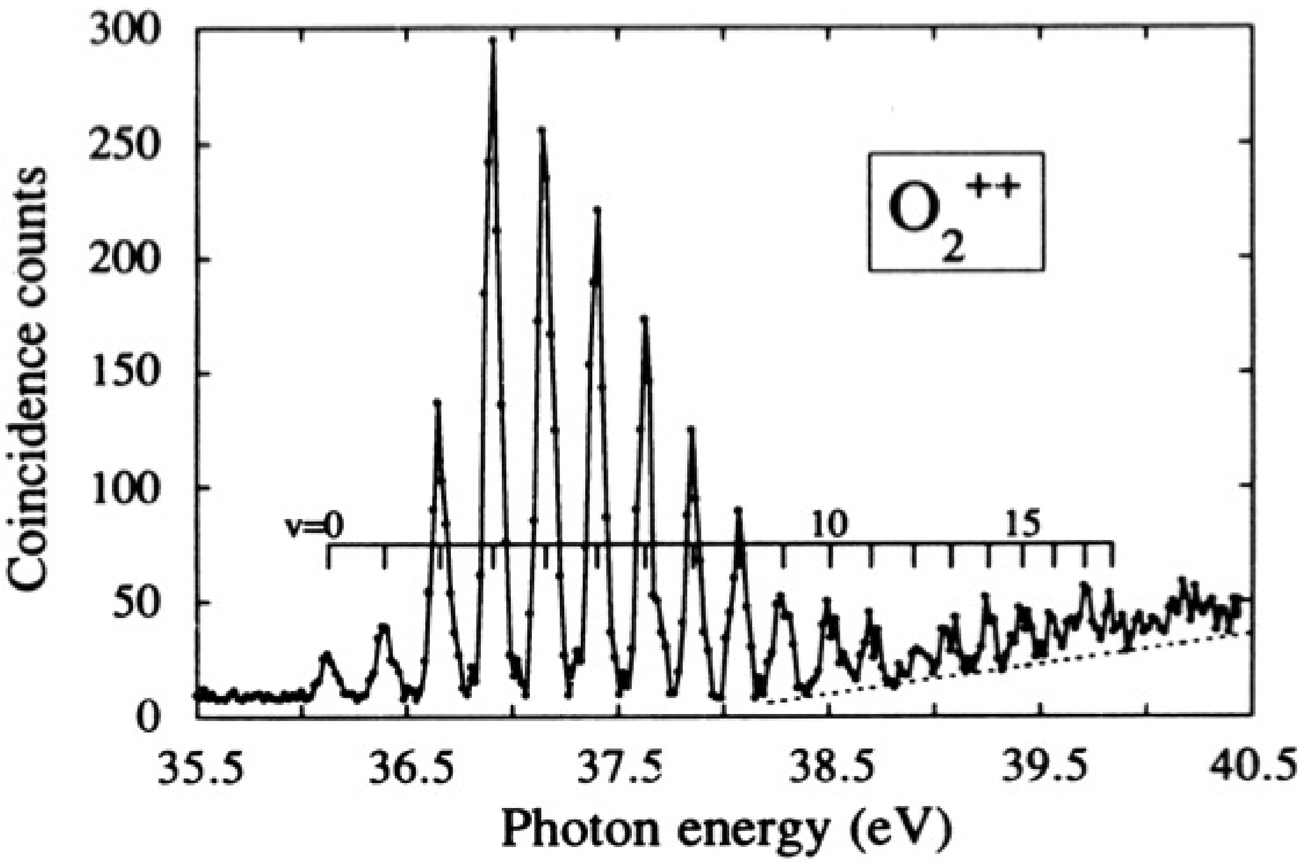


Figure 15: TPEsCO spectrum for the ground electronic state of O_2^{++} showing 19

[illegible]