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ENERGY- AND ANGLED-RESOLVED PHOTOELECTRON SPECTROSCOPY OF NEGATIVE IONS

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Abstract

Energy- and angle-resolved photoelectron detachment spectroscopy is currently being used to investigate the structure of negative ions and their interaction with radiation. Measurements of the electron affinity of the Ca atom and the partial cross sections for photodetachment of the metastable negative ion, $He^-(1s2s2p\,^4P)$, are reported.

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1. Introduction

The formation of an atomic negative ion involves a delicate balance between attractive forces supplied by the nucleus and interelectronic repulsive forces. Shielding of the nucleus by the atomic electrons and correlations between the motions and spins of the electrons both play important roles in determining whether a negative ion will exist. The net force binding the attached electron arises from polarization and exchange effects. This relatively weak and short-ranged force results in negative ions being fragile and easily destroyed. Over 80% of the naturally occuring elements are able however, under appropriate conditions, to attach an additional electron to form a stable negative ion. Other elements are able to form metastable negative ions. Figure 1 shows the electron affinities of elements in the first half of the periodic table. Stable ions have positive electron affinities. The electron affinity an atom is numerically equivalent to the binding energy of the least tightly bound electron of the negative ion. With the noticeable exceptions of the halogens, the electron affinities of most elements are seen to be less than ~1 eV.

In this paper we describe how the technique of energy- and angle-resolved photoelectron detachment spectroscopy from a fast moving negative ion beam is being used to determine the structure of negative ions and to investigate the interaction between negative ions and radiation. The method involves measuring photoelectron energies, yields and angular distributions.

2. Experimental Considerations

Figure 2 shows a schematic of the apparatus in which a fast beam of negative ions is crossed by an energy-resolved photon beam from a laser. As a result of the interaction, precisely known amounts of energy and angular momentum can be transferred to the ions. The fast-moving and tenuous beam of negative ions is produced by double charge transfer when a momentum-selected positive ion beam

from an accelerator is passed through a Li vapor charge-exchange cell. Details of the apparatus can be found in a paper by Pegg et al. [1].

Since the source used in these experiments is a fast beam of ions, the reference frame in which the "physics" occurs is moving with respect to the laboratory frame in which the measurements are made. As a result there will be kinematic modifications of the kinetic energies, yields, energy distributions and angular distributions of the photoelectrons ejected from the moving ions. Some of these effects can be exploited. In Section 3.1, for example, we show how electrons ejected with very low energies relative to 60 keV Ca^- ions have their energies kinematically increased in the laboratory frame by a factor of ~70. This kinematic "magnification" is also used, as described in Section 3.2, to arrange for the photoelectron peaks of He^- to coincide in energy with that of the reference ion, D^-. This allows for the cancellation of unknown efficiency factors. Another kinematic effect that is often used to advantage is peak doubling. In Section 3.1 we describe how this phenomenon is used in the analysis of photoelectron spectra. Analysis based on the measurement of the separation of a kinematically-doubled pair of peaks is particularly useful since only energy differences between peaks of a photoelectron spectrum can be measured with confidence due to unknown offsets such as contact and surface potentials. The kinematically-shifted energy of a forward-directed ($\theta_L = 0$) electron in the laboratory frame, E_L, is related to its energy in the ion frame, E_c, by the relationship $E_L = E_c + \varepsilon \pm 2\sqrt{\varepsilon E_c}$. Here ε is the energy of an electron moving at the same velocity as the ions of the beam. The positive sign corresponds to emission of electrons in the forward direction ($\theta_c = 0$) in the ion frame and the negative sign corresponds to backward-directed emission ($\theta_c = \pi$) in this frame. If the ion beam velocity is greater than the velocity of the electrons in the ion frame, it becomes possible for both the forward- and backward-directed electrons to be swept forward in the laboratory frame. Peak doubling in the

laboratory frame will then occur since E_L becomes double valued. The separation of these peaks will be $\Delta E_L = 4\sqrt{\epsilon E_c}$.

Figure 3 shows a spectrum of photoelectrons ejected from a fast-moving beam of He^- ions. The backward-directed peak 1 and the forward-directed peak 2 are a kinematically-doubled pair, both being associated with the photodetachment process that leaves the He atom in the $(1s2p)^3P$ state. Peak 3 is due to the forward-directed electrons associated with the exit channel that leaves the He atom in the $(1s2s)^3S$ state. The laboratory-frame separation of the two forward-directed peaks can be written as

$$\Delta E_L(23) = E_e + 2\sqrt{\epsilon}\ \left[\ \sqrt{E_c(2) + E_e} - \sqrt{E_c(2)}\ \right] \qquad (1)$$

where E_e corresponds to the known $(1s2s)^3S - (1s2p)^3P$ separation. The separation of the kinematically-doubled pair of peaks 1 and 2 can be written as

$$\Delta E_L(12) = 4\sqrt{\epsilon\ E_c(2)} \qquad (2)$$

The reduced ion beam energy, ϵ, and the kinetic energy of the photoelectron in the ion frame, $E_c(2)$, can be determined by simultaneously solving equations (1) and (2). The electron affinity of the He $(1s2s^3S)$ atom can now be determined using the Einstein energy balance equation. The result is in excellent agreement with the currently accepted value and this test case gives us confidence in applying a similar analysis to the photoelectron spectrum of Ca^-, an ion whose electron affinity was previously unmeasured.

3. Results

In this section we describe experiments that illustrate the use of photoelectron detachment spectroscopy in the determination of electron affinities and photodetachment cross sections.

3.1 The structure of Ca^-

The existence of a long-lived Ca^- ion has been known for some time [2] yet, until recently, calculations failed to predict a stable ion. Prior to our

recent measurement [1] and the concurrent calculation by Froese Fischer et. al. [3] this ion was thought to exist in a metastable state, the prime candidate being the core-excited $(4s4p^2)^4P$ state. We have shown that, contrary to earlier theoretical predictions, the Ca^- ion is stable.

An energy spectrum of electrons photodetachment from a beam of Ca^- ions is shown in Figure 4. The relative intensities and spacing of the peaks in this photoelectron spectrum show unambiguously that $Ca^-(4s^24p^2P)$ is bound. Peaks 1 and 2 are a kinematically-doubled pair associated with the photodetachment exit channel that leaves the Ca atom in the $(4s4p)^3P$ excited state. Peak 3 arises when the residual atom is left in the $(4s^2)^1S$ ground state. In the ion frame, the difference in energies between electrons associated with peak 2 and 3 is equal to the excitation energy of the $(4s4p)^3P$ state, a quantity well known from photon spectroscopy. Analysis of the spectra is based on the measurement of the separations of peaks 1 and 2 and peaks 2 and 3 as described in Section 2. The details of the analysis of photoelectron spectra taken at several different ion- and photon-beam energies can be found in the paper by Pegg et. al. [1]. The final result for the electron affinity of Ca is 0.043 ± 0.007 eV. Correlation effects, which are associated with the relative motions and spins of the electrons, are an important consideration in the calculation of electron affinities. Correlation is the "glue" that helps keep negative ions intact. Two recent calculations employing extensive correlation are essentially in agreement with our measurement. The revised multiconfigurational Hartree-Fock result of Froese Fischer et al. [3] is 0.062 eV. Krylstedt et al. [4] report a value of 0.055 eV.

3.2 Photodetachment of He^-

In an earlier paper by Compton et al. [5] we reported measurements of the total cross sections for photodetaching He^- $(1s2s2p^4P)$. In this work two unresolved exit channels, corresponding to the He atom being left in either the

$(1s2s)^3S$ or $(1s2p)^3P$ state, were open. We report here on the use of photoelectron spectroscopy to resolve these channels and describe ongoing measurements of the partial cross sections for each of these competing processes. Figure 3 shows a spectrum of electrons photodetached from a beam of He^- ions. The two forward-directed peaks, 2 and 3, are associated with the $(1s2p)^3P$ and $(1s2s)^3S$ exit channels, respectively. To determine the partial cross sections we measure the yields of photoelectrons in each of the He^- peaks relative to the photoelectron yield produced when D^- (H^-) ions in a reference beam are photodetached under conditions which differ only in the ion beam energies. By multiplying these yield ratios by measured factors which take account of the different frame-transformed solid angles and ion densities associated with the two beams, one obtains the ratio of the differential cross sections of He^- to D^-. The correction factors, which depend on the velocities of the ions in each beam, can be determined, as described in Section 2, by measuring in situ the separations of the peaks in the He^- and D^- spectra. In this work we arrange, by appropriate choice of beam energies, that the photoelectron peaks in each spectrum are kinematically shifted so that they coincide in energy in the laboratory frame. The electron spectrometer efficiency factors associated with the transmission and detection of photoelectrons of the same energy will then be the same for He^- and D^- ions. Similarly, the geometric source volume, the collection solid angle and the photon flux remain unchanged in going from He^- to the D^- reference ions.

Total (partial) cross sections are obtained from the differential cross sections in the usual manner by independently measuring the angular distributions of the photoelectrons. These angle-resolved measurements determine the asymmetry parameter, β, which characterizes the shape of the emission pattern. The measurements are made by determining the yield of a photoelectron peak as a function of the angle, θ, between a fixed collection direction (in our case, the direction of motion of the ion beam) and the variable direction defined by

the electric field vector of the linearly polarized laser beam. A typical measurement is shown in Figure 5. For the case of plane polarized radiation in the electric dipole approximation and an independent electron model, the shape of the angular distribution should take the form of $1 + \beta P_2(\cos\theta)$, where $P_2(\cos\theta)$ is the second-order Legendre polynomial. Multiphoton absorption or an anisotropic ion state prior to photoabsorption would produce higher (even) order polynomials in the fit. The apparatus was first tested on beams of D^- and Li^- ions where the expected $\cos^2\theta$ ($\beta = 2$) distribution was obtained in each case.

Measurements of the He^- photodetachment cross sections are presently in progress and the preliminary results are encouraging. These results will permit us, using detailed balance arguments, to indirectly determine the cross sections for the far more improbable inverse process of radiative attachment.

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References

[1] D. J. Pegg, J. S. Thompson, R. N. Compton and G. D. Alton, Phys. Rev. Lett. 59 (1987) 2267.

[2] G. D. Alton, T. J. Kvale, R. N. Compton, D. J. Pegg and J. S. Thompson, Nucl. Instr. and Methods A244 (1986) 142; E. Heinicke, H. Kaiser, R. Rackwitz and D. Feldmann, Phys. Lett 50A (1974) 265.

[3] C. Froese Fischer, J. B. Lagowski and S. H. Vosko, Phys. Rev. Lett. 59 (1987) 2263.

[4] P. Krylstedt, N. Elander and E. Brändas, J. Phys. B. (to be published).

[5] R. N. Compton, G. D. Alton and D. J. Pegg, J. Phys. B13, (1980) L651.

Figure Captions

Figure 1. Electron affinities of elements in the first half of the periodic table. The open circles represent measured quantitites and the dots represent calculated values.

Figure 2. Schematic of the crossed laser-ion beams apparatus used in photoelectron detachment spectroscopy.

Figure 3. Spectrum of electrons photodetached from a 40 keV beam of He^- ions. The photon wavelength was 689.5 nm.

Figure 4. Spectrum of electron photodetached from a 60 keV beam of Ca^- ions. The photon wavelength was 635.2 nm.

Figure 5. The angular distribution of photoelectrons detached from a 30 keV beam of He^- ions. The photon wavelength was 638.4 nm.

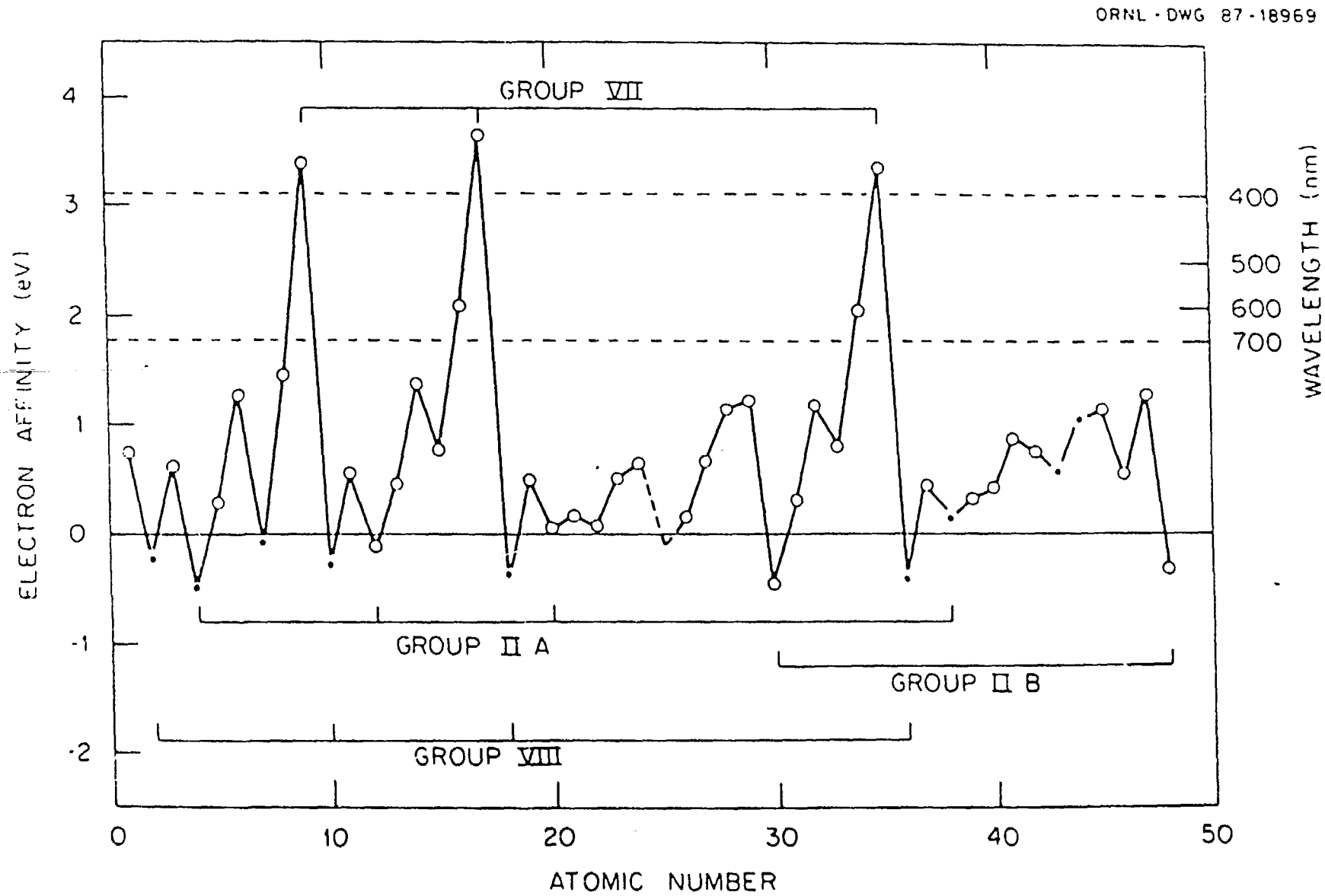

ORNL - DWG 87-18969
GROUP VII
GROUP II A
GROUP II B
GROUP VIII
ELECTRON AFFINITY (eV)
WAVELENGTH (nm)
400
500
600
700
4
3
2
1
0
-1
-2
0
10
20
30
40
50
ATOMIC NUMBER

FIGURE 1

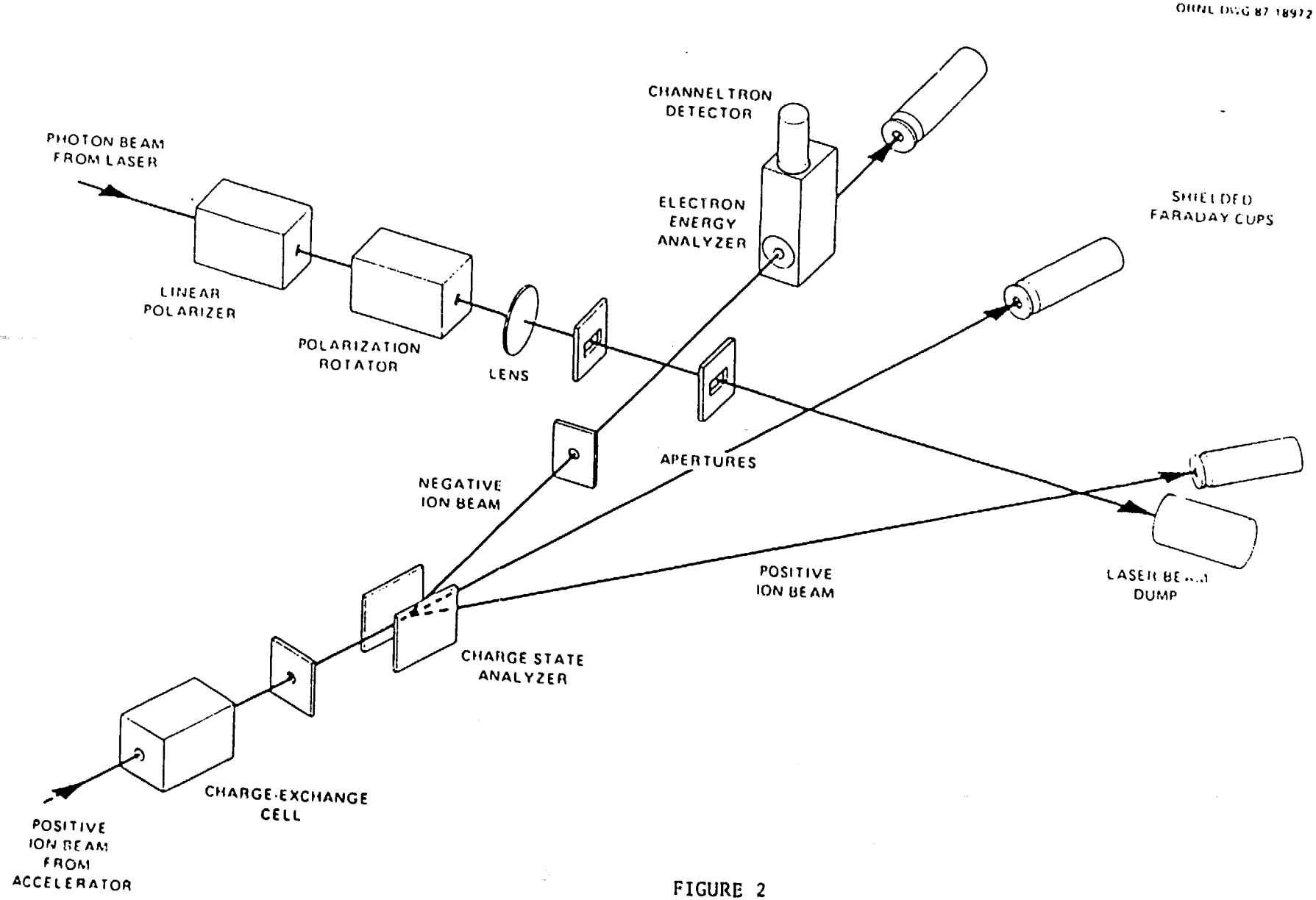

ORNL DWG 87 18972
PHOTON BEAM FROM LASER
LINEAR POLARIZER
POLARIZATION ROTATOR
LENS
CHANNELTRON DETECTOR
ELECTRON ENERGY ANALYZER
SHIELDED FARADAY CUPS
APERTURES
NEGATIVE ION BEAM
POSITIVE ION BEAM
LASER BEAM DUMP
CHARGE STATE ANALYZER
CHARGE-EXCHANGE CELL
POSITIVE ION BEAM FROM ACCELERATOR

FIGURE 2

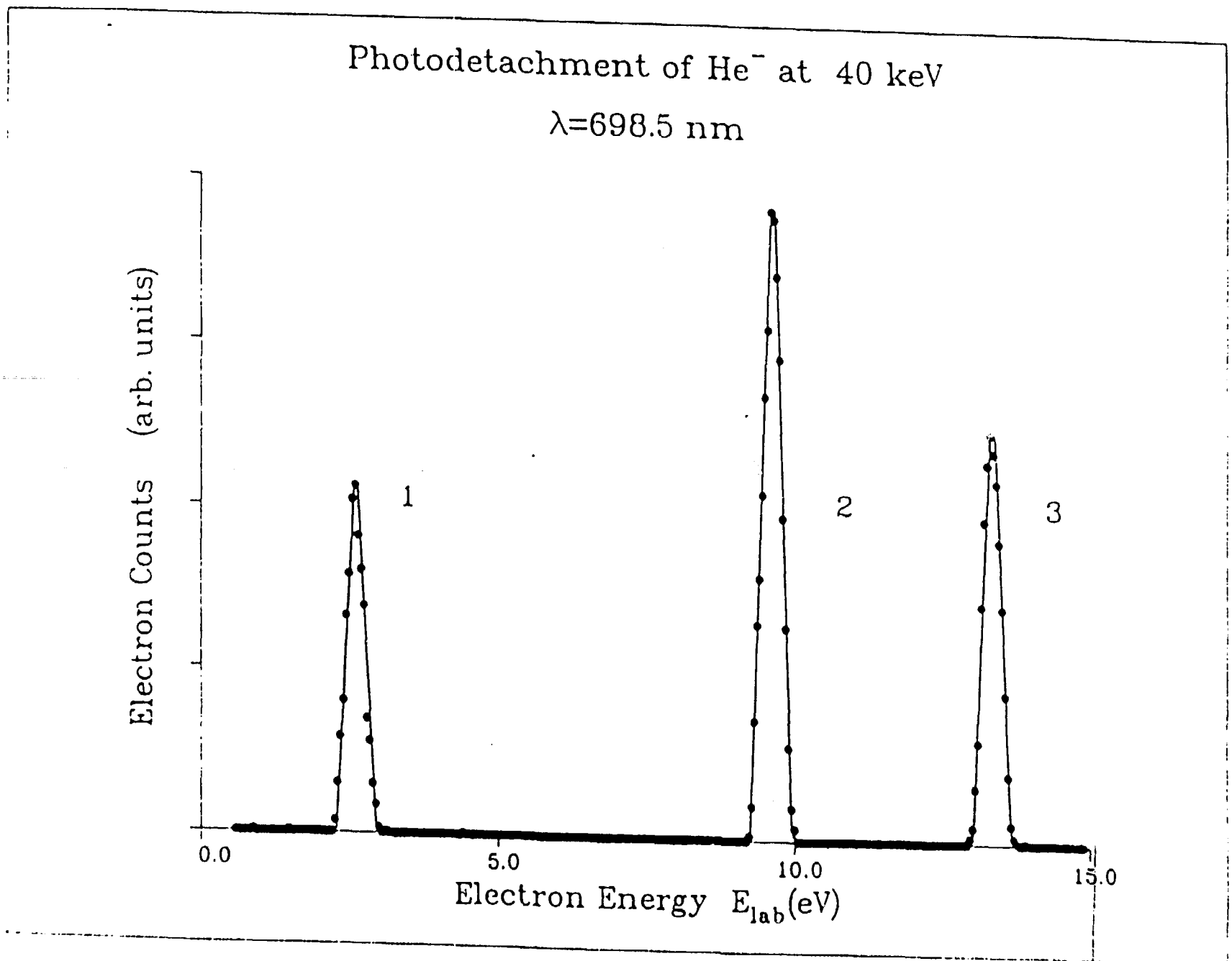
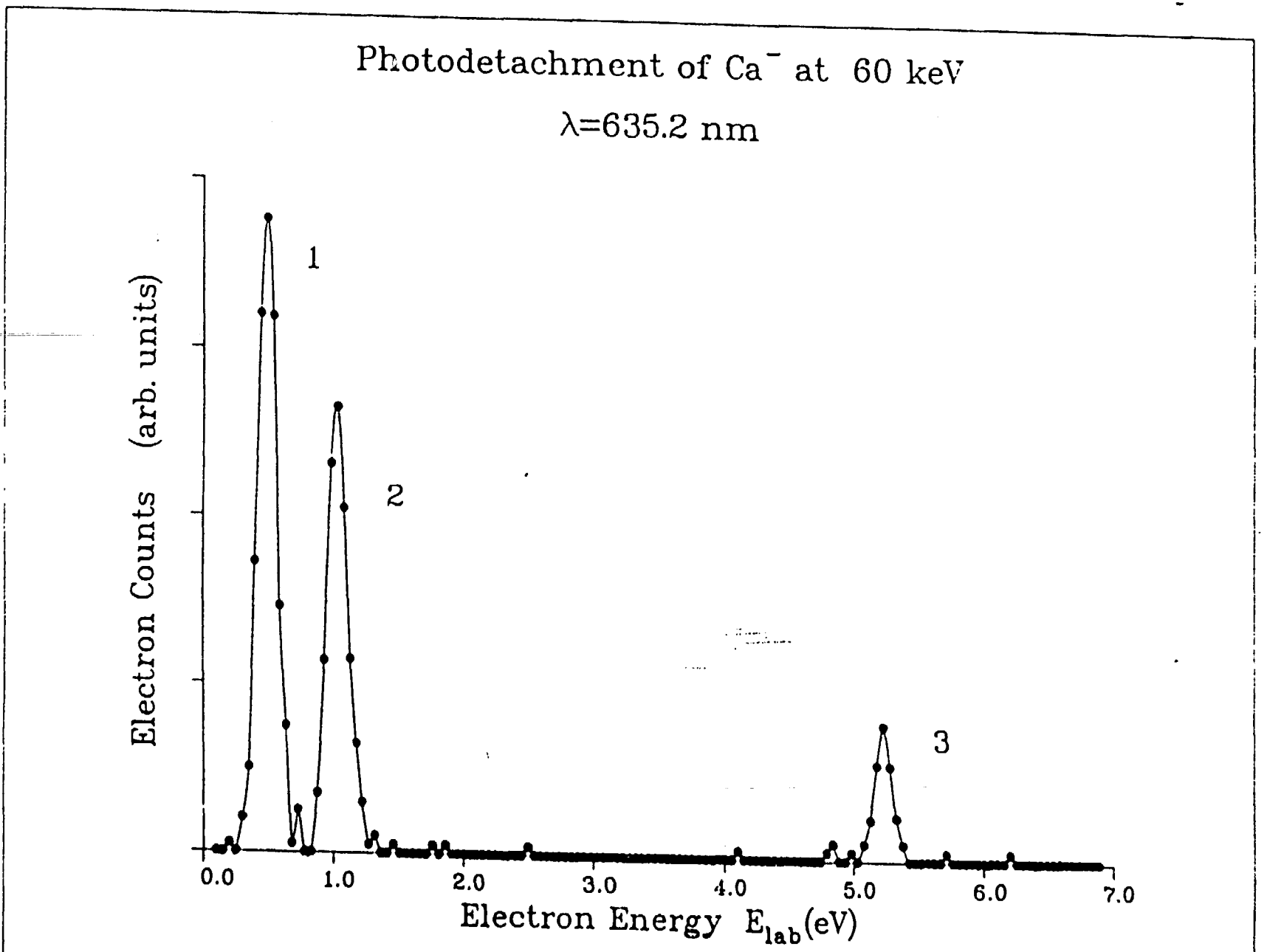
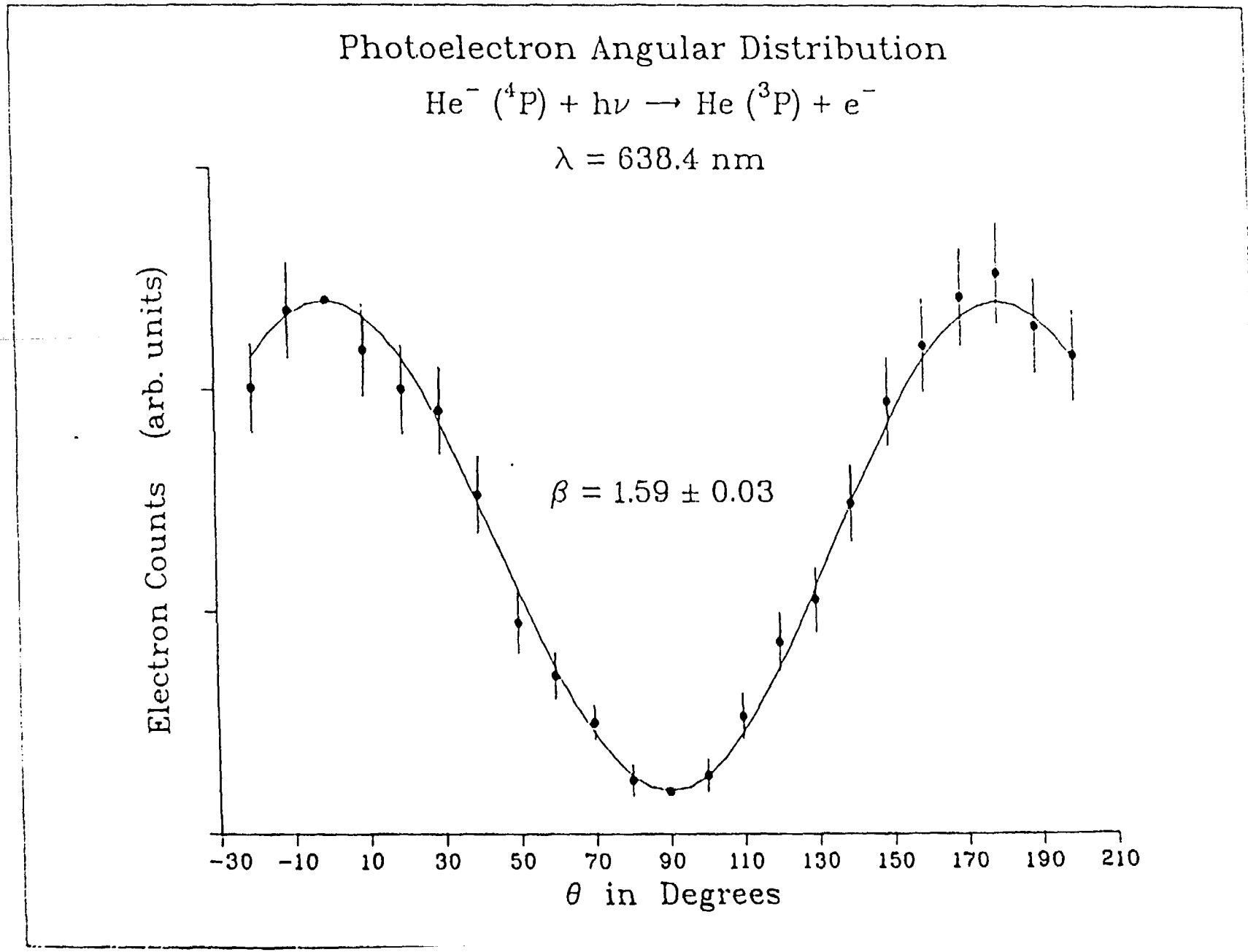

Photodetachment of He^- at 40 keV
λ=698.5 nm
Electron Counts (arb. units)
1
2
3
0.0
5.0
10.0
15.0
Electron Energy E_{lab}(eV)

FIGURE 3


Photodetachment of Ca^- at 60 keV
λ=635.2 nm
Electron Counts (arb. units)
1
2
3
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
Electron Energy E_{lab}(eV)


Photoelectron Angular Distribution
$He^- (^4P) + h\nu \rightarrow He (^3P) + e^-$
$\lambda = 638.4$ nm
Electron Counts (arb. units)
$\beta = 1.59 \pm 0.03$
-30 -10 10 30 50 70 90 110 130 150 170 190 210
θ in Degrees