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## ELECTRON COINCIDENCE SPECTROSCOPY OF SODIUM AND POTASSIUM

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### ABSTRACT

The Na 3s and K 4s electron momentum distributions have been obtained using the noncoplanar symmetric (e,2e) reaction at total energies of 800 eV and 1200 eV. They show excellent agreement with the results of plane wave impulse approximation calculations using Roothaan-Hartree-Fock functions, after small corrections are made for the finite angular resolution of the apparatus. The potassium valence s momentum profile is a little narrower than that for sodium, implying a correspondingly slightly larger spatial distribution of the outer valence electrons. The ratio between the (n-1)p and ns cross-sections at their respective maxima in q-space were measured to be  $0.009 \pm 0.003$  and  $0.019 \pm 0.003$  for Na and K respectively. These cross-section ratios are in agreement with the PWIA calculations.

## INTRODUCTION

The electronic structures of alkali atoms are of interest as a testing ground for theoretical models, particularly of valence electron wavefunctions. Photoelectron spectroscopy has been useful in the study of the valence electron separation energies of these atoms. Williams and Potts (1976) studied the valence s-states using HeI (21.2eV) radiation. Some core levels were measured with reduced resolution by Banna et al. (1978) and Martin et al. (1978) using Al K $\alpha$  x-rays. Recent experiments by Slizer et al. (1980) and Krummacher et al. (1980) have investigated the valence p-states of alkali atoms, especially the non-statistical population of multiplet states and presence of satellite lines due to electron correlation effects.

Electron coincidence spectroscopy (McCarthy and Weigold 1976, Weigold and McCarthy 1978) has some advantages over photoelectron spectroscopy in that the electron impact energy can be easily varied and in that the kinematics of the (e,2e) reaction is fully determined. If the incident and outgoing energies are large compared with the electron separation energy and there is a large momentum transfer by the scattered electron, the reaction can be described by the plane wave impulse approximation (McCarthy and Weigold 1976). Under these conditions the momentum of the bound electron prior to knockout can be determined simply by momentum conservation. In the non-coplanar symmetric geometry in which the electrons are emitted with equal energies and equal polar angles relative to the incident direction, the differential cross-section for the (e,2e) reaction is essentially directly proportional to the spherically averaged momentum distribution of the ejected electron. This is defined as the square of the overlap in momentum space between the target in its initial (ground) state and the ion in its final state. In the independent particle model this is simply the momentum probability distribution of the electron in the

selected Hartree-Fock orbital.

All previous (e,2e) coincidence measurements on atoms have been made on the closed shell noble gas atoms, except for the work at Flinders on atomic hydrogen (eg. Lohmann and Weigold, 1981).

In this paper we report the measurement of the momentum distributions of electrons in the Sodium 3s and Potassium 4s states and compare the results with Plane Wave Impulse Approximation calculations using Hartree-Fock wave functions (Clementi and Roetti, 1974) to describe the struck electrons. The intensities of the Sodium 2p and Potassium 3p states were also measured, relative to the s-state peaks. A possible satellite to the main 2p-hole was also investigated in sodium.

#### EXPERIMENTAL APPARATUS AND METHOD

A schematic outline of the apparatus is shown in figure 1. The vacuum system consisted of a large (~ 700ℓ) stainless steel vacuum chamber pumped by a 450ℓ/s turbo-molecular pump, a base pressure of  $10^{-6}$ T being achieved in four hours. It was lined with mu-metal and enclosed by a pair of circular Helmholtz coils to reduce the internal magnetic field to  $\leq 20$ mG.

The electron gun used a directly heated thoriated tungsten hair-pin filament to produce an electron beam (~ 100μA at 1200 volts), which was directed vertically through an aperture in the centre of a pair of concentric horizontal turntables. Mounted on separate turntables were a pair of cylindrical mirror electron energy analysers fitted with five-element retarding electron-lenses. These analysers had a combined resolution of 2.3eV FWHM (for a pass-energy of 100eV) which was adequate to resolve the states of interest. Improved resolution could be achieved at the expense of a reduction in coincidence count rates. The analysers viewed the interaction region at a polar angle  $\theta$  of  $45^\circ$  to the electron beam, through slots in a cylindrical non-magnetic stainless steel cold trap which limited the spread of the target atoms.

Unscattered electrons were collected above the cold trap, using a Faraday Cup, allowing the beam current to be monitored.

The oven was machined from #304 non-magnetic stainless steel. The sample-well was sealed by clamping in place a 19mm diameter steel ball bearing which was lapped into the seat prior to each replenishment of the oven. The oven and the 1.6mm diameter by 2cm long horizontal exit nozzle were separately heated by non-magnetically-wound tungsten wires. A thermocouple in the oven near the nozzle registered the temperature during operation, which was generally close to 360°C.

Samples of sodium (99.99% pure) and potassium (99.999% pure) were cut from the centres of blocks stored in paraffin. They were cut under X-4 petroleum-ether then quickly rinsed in propan-2-ol to leave a clean surface which oxidised immediately in air. The oxides of sodium and potassium have high melting points and did not contaminate the vapour beam. Failure to rinse in propan-2-ol resulted in extended pumping times and carbon residues in the oven. Loading of the oven and evacuation of the chamber to  $10^{-4}$ T required approximately 5 minutes.

The type of electron detection and counting electronics used has been described in detail previously (e.g. McCarthy and Weigold, 1976). Briefly, electrons were detected at the exits of the spectrometers by channeltrons coupled via pulse transformers to fast charge-sensitive pre-amplifiers and shaping amplifiers. Constant-fraction-discriminators provided 'start' and 'stop' pulses for a Time to amplitude converter (TAC). Single-channel analysers were set to select 'coincident' and 'random background' windows from the TAC output. The full width of the actual coincidence peak was approximately 10 ns.

The on-line PDP-11/10 computer summed and recorded the "coincident" and "background" counts from the SCA's for a preset period, then calculated the true signal and standard deviation before advancing to the next point in a programmed scan-table of electron beam energies and spectrometer-

turntable angles. The period spent at each 'point' was normalized to the electron count rate in one channel to correct for short-term drifts in the electron beam or target densities.

Each measurement of momentum profiles contained many scans (to average over long term drifts) and consisted of two parts. First, an energy-loss spectrum was obtained at  $\phi = 0$  ( $q \approx 0$ ) to locate the Na  $3s^{-1}$  or K  $4s^{-1}$  energy-loss peak at 5.1eV and 4.3eV respectively. The peak was found to shift by approximately 2eV in the first few hours of operation of the oven due to coating of the cold trap surrounding the interaction region with a layer of alkali metal. Second, the beam energy was set to select the energy-loss peak and the out-of-plane azimuthal angle  $\phi$  of the spectrometers was varied (e.g. from  $-16^\circ$  to  $+16^\circ$ ). Each scan also contained several points at  $\phi = 0^\circ$  with energies slightly offset from the energy-loss peak, to monitor possible power-supply drifts. These did not exceed 0.5eV and could not affect the shape of the measured profiles. The measurements were carried out at total energies of 1200eV and 800eV to check for possible systematic errors in the analysis of the data which could result from a breakdown of the plane wave approximation.

Measurements of the p-state cross-sections were made slightly differently. Electron count rates in the two analysers were approximately 200 Hz and led to a coincident count rate  $\sim 0.1$  Hz at the peak of the K  $4s^{-1}$  cross-section at 1200eV. Since the non-coplanar symmetric (e,2e) cross-section for knockout of a (n-1)p-electron is approximately 100 times smaller than that for a valence ns electron (due to the greater diffuseness of the p orbitals in momentum space), it was not feasible to measure the entire (n-1)p momentum profiles. Instead, the peak of the  $p^{-1}$  profile was measured relative to the  $s^{-1}$  profile peak for each atom. A new oven providing a greater intensity of atoms in the collision region with less frequent refills would make measurements of the (n-1)p cross-

sections possible. Each experimental scan contained points at  $\phi = 0^\circ$  at the energy-loss peak for the  $ns^{-1}$  transition and also at  $\phi = 10^\circ$  or  $12^\circ$  (near the peaks in the calculated  $(n-1)p^{-1}$  cross-sections) at a small range of energies around the  $(n-1)p^{-1}$  separation energy peaks of 38eV for sodium and 24.5 to 25eV for potassium. The change in electron beam current for the different energy-loss peaks was negligible and the focusing conditions in the analysers were not changed so that relative normalizations were preserved. Measurements were made at a total energy (in the exit channels) of 800eV for potassium and 1200eV for sodium.

The angular resolution of these experiments was limited by dispersion in the electron beam, the width of slits in the two analysers, aberration in the retarding lenses and backlash in the turntable drives. The resultant resolution was estimated in three ways:

- (1) a momentum profile for the  $3p^{-1}$  transition of argon was measured and compared with a profile measured on other equipment which had a resolution better than  $\pm 0.5^\circ$ ;
- (2) the argon momentum profile was compared to calculated cross-sections convoluted with several different resolution functions;
- (3) the sodium  $3s^{-1}$  profile (at 1200eV) was compared to variously convoluted calculated cross-sections.

All methods indicated a resolution of  $\pm 1.5^\circ$  in  $\phi$ , with the third method detecting noticeably worse agreement for  $\Delta\phi = \pm 1.3^\circ$  or  $\pm 1.7^\circ$ . All data, for potassium and sodium at 800eV and 1200eV, was best fitted using resolution functions within this range.

The shape of the convoluted cross-section was not sensitive to the width of the window in the polar angle  $\theta$  for  $\Delta\theta < 2^\circ$ . Therefore a value of  $\Delta\theta = \pm 0.5^\circ$ , consistent with the experimental geometry, was chosen.

For each target atom data was measured at total energies of 800eV and 1200eV. The measured coincidence signal at the s-state energy-loss

peak was accumulated over a range of positive and negative out-of-plane azimuthal angles, then folded about the axis of symmetry at  $0^\circ$  and summed.

The (e,2e) cross-section for the state was then calculated for these angles using the PWIA model and Hartree-Fock wavefunctions discussed above. The finite experimental resolution was included by calculating the cross-section at a mesh of points in the range  $\Delta\phi = \pm 1.5^\circ$ ,  $\Delta\theta = \pm 0.5^\circ$  about each angle and then performing an arithmetic average to find the convoluted cross-section. The measured data and convoluted cross-sections were then normalized to each other using a least-squares fitting program. The resulting overlap was found to be excellent for both target atoms at both total energies. An example of a measured angular correlation, with both the calculated ( $\Delta\phi = \Delta\theta = 0$ ) and convoluted cross-sections, is shown in Figure 2.

However, this analysis does not allow direct comparison of the measured cross-section to other theoretical calculations, at different energies. Therefore the final step in the analysis was to deconvolute the data by multiplying the signal at each point  $\phi$  by the ratio of the PWIA model cross-section at  $\phi$  to the convoluted cross-section at that point. The deconvoluted data and PWIA cross-section were then scaled to a peak height of unity and plotted as a function of the magnitude of the ion recoil momentum  $q$ , instead of  $\phi$ , the momentum  $q$  in the plane wave limit being simply the momentum of the struck electron.

This deconvolution procedure assumes that the calculated cross-section and true cross-section are closely proportional to each other over each range of  $\Delta\phi$ ,  $\Delta\theta$ . This is supported by the excellent agreement obtained between the raw data and the convoluted cross-section. The deconvolution procedure is in any case not sensitive to small variations in the cross-section shape.

The (n-1)p : ns cross-section ratio measurements for potassium at 800eV and sodium at 1200eV were deconvoluted in the same way as the s-state

momentum profiles.

### RESULTS AND DISCUSSION

The outer electronic structure of the alkalis consists of a filled (n-1)p shell below the loosely bound outermost open ns shell. The separation energy for the outermost ns electron is 5.14eV for Na and 4.34eV for K, the ion being in a closed shell  $^1S$  configuration. Ionization from the (n-1)p shell gives rise to multiplet structures, namely the  $^3P(J=2,1,0)$  and  $^1P(J=1)$  states, due to the interaction of two open shells (n-1)p<sup>5</sup> ns. For Na the separation energies for these states are respectively 37.98, 38.07, 38.14 and 38.45eV and for K they are 24.48, 24.57, 24.81 and 24.97eV. The  $^3P$  and  $^1P$  states can therefore not be resolved with the present energy resolution.

The (deconvoluted) momentum distributions for the ns transitions in Na and K obtained at 800 and 1200eV are shown in Figure 3, where the solid curves are the distributions obtained using the H-F wavefunctions at Clementi and Roetti (1974). The 800eV and 1200eV momentum profiles have the same shapes in both cases. Agreement between the calculated and measured momentum distributions is excellent at both energies. For ease of comparison the cross-sections have been arbitrarily normalized to a value of unity at  $q = 0$ , since absolute measurements were not obtained.

Both momentum distributions are very narrow with  $q$  (half max) being 0.20 a.u. for Na and 0.17 a.u. for K whereas, for example, in neon and argon the figures are 0.7 and 0.6 respectively (Weinold and McCarthy 1978). This means that these valence orbitals are very diffuse in coordinate space, and in fact the calculated radial expectation values  $\langle r \rangle$  and  $\langle r^2 \rangle$  are 4.21 a.u. and 20.70 au<sup>2</sup> for Na and 5.24 a.u. and 31.54 au<sup>2</sup> for K. By comparison, for the (n-1)p orbitals these radial expectation values are 0.80 and 0.82 for Na and 1.44 and 2.44 for K, showing that the p orbitals are much more localized about the nuclei than the outer s

orbitals. The p orbitals should therefore be significantly more extended in momentum space than the s orbitals.

In figure 4 the calculated (n-1)p orbital momentum distributions for Na and K are shown. The differential cross-sections have been normalized relative to the maximum in the corresponding ns cross-section at  $\phi = 0^\circ$ . The peaks in the calculated (n-1)p cross-sections are much smaller than those for the outer valence ns transitions for both K and Na, despite the fact that there are six electrons in the p shell and only one in the s shell. This is due to the diffuseness of the (n-1)p wave functions in momentum space, which of course must be normalized when integrating over the whole of momentum space.

Due to the relative smallness of the (n-1)p<sup>-1</sup> cross-sections, and the constant need to replenish the Na or K supply in the oven, only one measurement was made close to the peaks in the expected momentum distributions. The measured deconvoluted cross-section ratios for the transitions leading to the (n-1)p<sup>5</sup> ns ion states relative to those leading to the (n-1)p<sup>6</sup> 1S ground state are  $0.009 \pm 0.003$  and  $0.019 \pm 0.003$  for Na and K respectively. The quoted errors include an estimation of the maximum noise background which might have accumulated during the 150 hours required for these measurements. These measured cross-section ratios are in good agreement with the PWIA calculations (fig. 4).

Electron correlation effects in the ground or final states could give rise to other transitions. Since the ns cross-section is much larger than the (n-1)p shell cross-section, it would be much easier to see correlation effects in the s shell. In Na, configuration interaction (CI) calculations of the ground state of the atom and ion show negligible CI mixing in this case [Glass, 1982]. Krummacher et al. (1980) detect a peak in their photoelectron spectrum at a separation energy of 45.1eV, which they attribute to excitation of either the 2p<sup>5</sup> 3d or 2p<sup>5</sup> 4s ion states arising from final state CI interaction in the 2p shell. The

intensity of this peak relative to the main  $2p$  peak is about 0.2. We have carried out a search at a separation energy  $\epsilon$  of 45eV and find little evidence for this peak, the cross-section ratio for the 45eV transition at  $q = 1.0$  a.u. to the  $3s^{-1}$  transition at  $q \sim 0.07$  a.u. is  $0.002 \pm 0.002$ , compared with the value of  $0.009 \pm 0.003$  for the main  $2p^{-1}$  transition. Gruzdev and Loginov (1973), in a multi-configuration calculation of radiation lifetimes of levels of the NaII ion, find little evidence for configuration interaction in the  $2p^5 3s$  levels. For instance in the  $^3P_0$  state the "purity" of the  $2p^5$  configuration was approximately 99%. They did find substantial superposition between the  $2p^5 3d$  and  $2p^5 4s$  configurations ( $2p^5 4s \sim 0.89 2p^5 4s + 0.11 2p^5 3d$ ).

More recently Glass (1982) carried out a detailed CI calculation on NaII in the LS coupling scheme for the  $2p^5 3d$ ,  $2p^5 4s$  and  $2p^5 3s$  multiplet configurations. Although he finds considerable coupling between the  $^1P$  and  $^3P$  configurations within each multiplet, he finds no ( $< 0.1\%$ ) configuration interaction between the  $2p^5 3s$  configuration and the other configurations. Again substantial superposition is predicted between the  $2p^5 4s$  and  $2p^5 3d$  configurations. Since the measured cross-section for the  $2p^5 3s$  transition at 38eV is already somewhat larger than the PWIA cross sections, and any satellite strength must be added to the measured cross sections for comparison with the PWIA cross section, the present data can be regarded as supporting these calculations which suggest negligible satellite strength.

In potassium, Süzer et al. (1980) see excitation of the  $3p^5 3d \ ^3P$  levels with 40.8eV HeII radiation, the intensity being 0.16 relative to that of the  $3p^5 4s \ ^3P$  transitions. However, since the  $3p^5 3d$  and  $3p^5 4s$  ion states all lie extremely close to each other (in the range 24.5 to 25.0eV), they cannot be resolved in the present experiment, which therefore sums over all the satellite structure. The total (summed) cross section is in good agreement with the expected cross section

10.

given by the PWIA calculation (fig. 4).

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FIGURE CAPTIONS

- Figure 1. Experimental Apparatus:- CMA-Cylindrical Mirror Analyser;  
CEM-Channeltron Electron Multiplier; FC-Faraday Cup;  
EL-Electron Lens; CT-Cold Trap; OV-Oven; TT-Turntable;  
EG-Electron Gun.
- Figure 2. The 800eV noncoplanar symmetric angular correlation for the ground state ( $3s^{-1}$ ) transition in sodium. The dotted curve is the shape of the calculated cross-section without allowing for angular resolution. The solid line shows the calculated cross-section convoluted with the experimental resolution of  $\Delta\phi = \pm 1.5^\circ$ ,  $\Delta\theta = \pm 0.5^\circ$ , and normalized to the data.
- Figure 3. The 800eV and 1200eV noncoplanar symmetric momentum profiles for the 3s and 4s orbitals of sodium and potassium respectively, compared with the PWIA using the H-F wave functions of Clementi and Roetti (1974).
- Figure 4. Momentum Distributions for the sodium 2p and potassium 3p orbitals, normalized relative to the maximum in the corresponding ns cross-sections at  $\phi = 0^\circ$ .

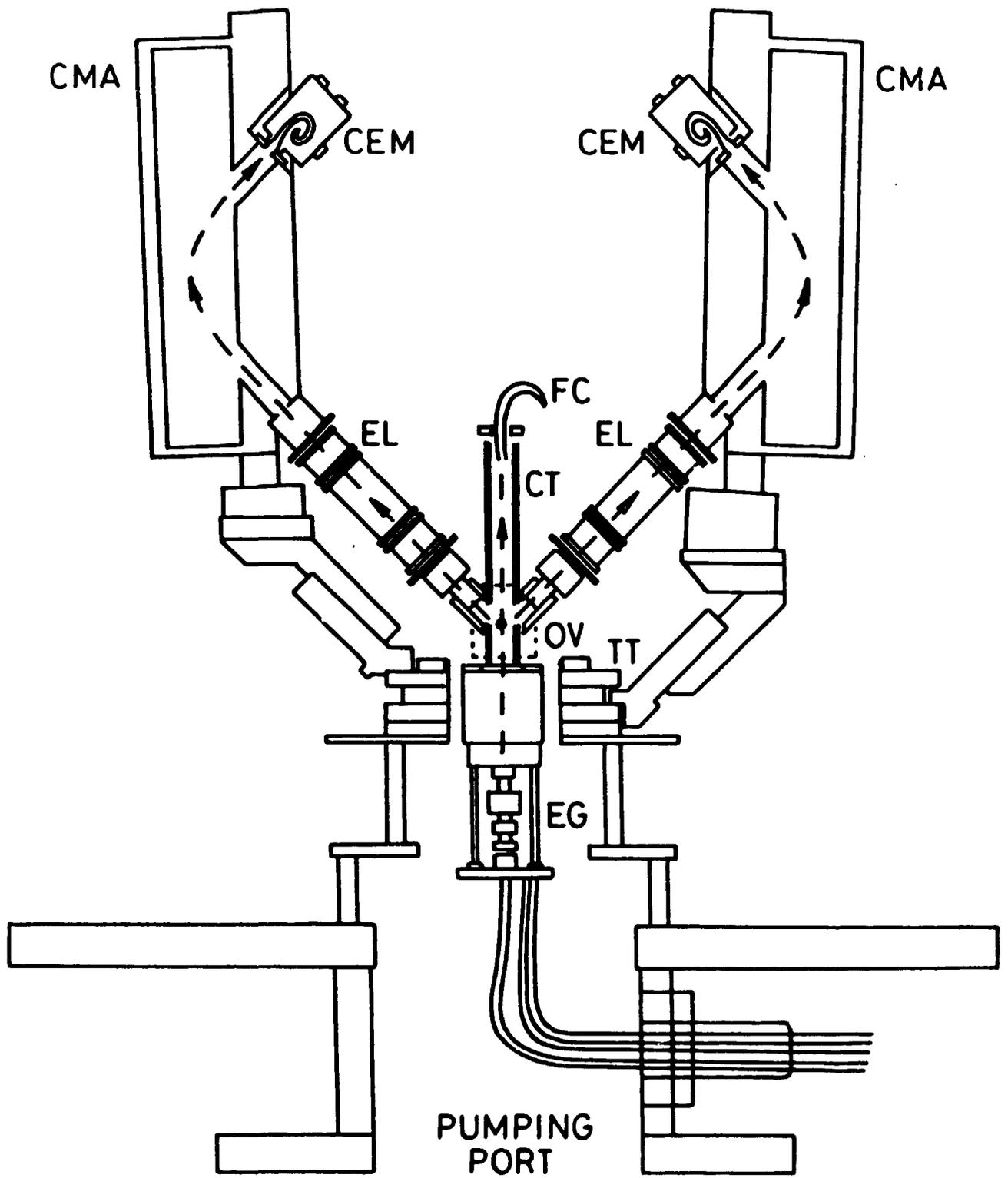


Figure 1

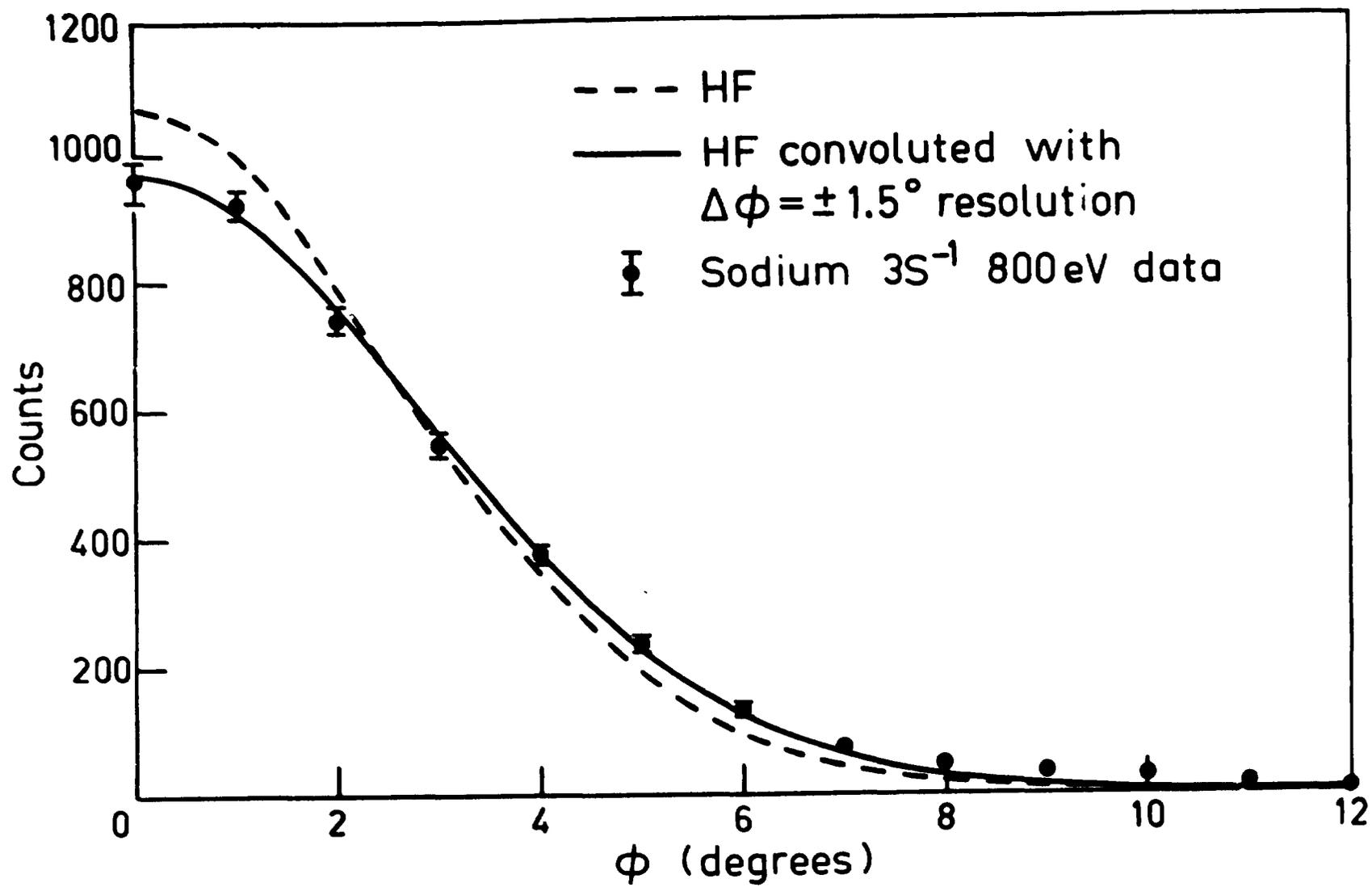


Figure 2

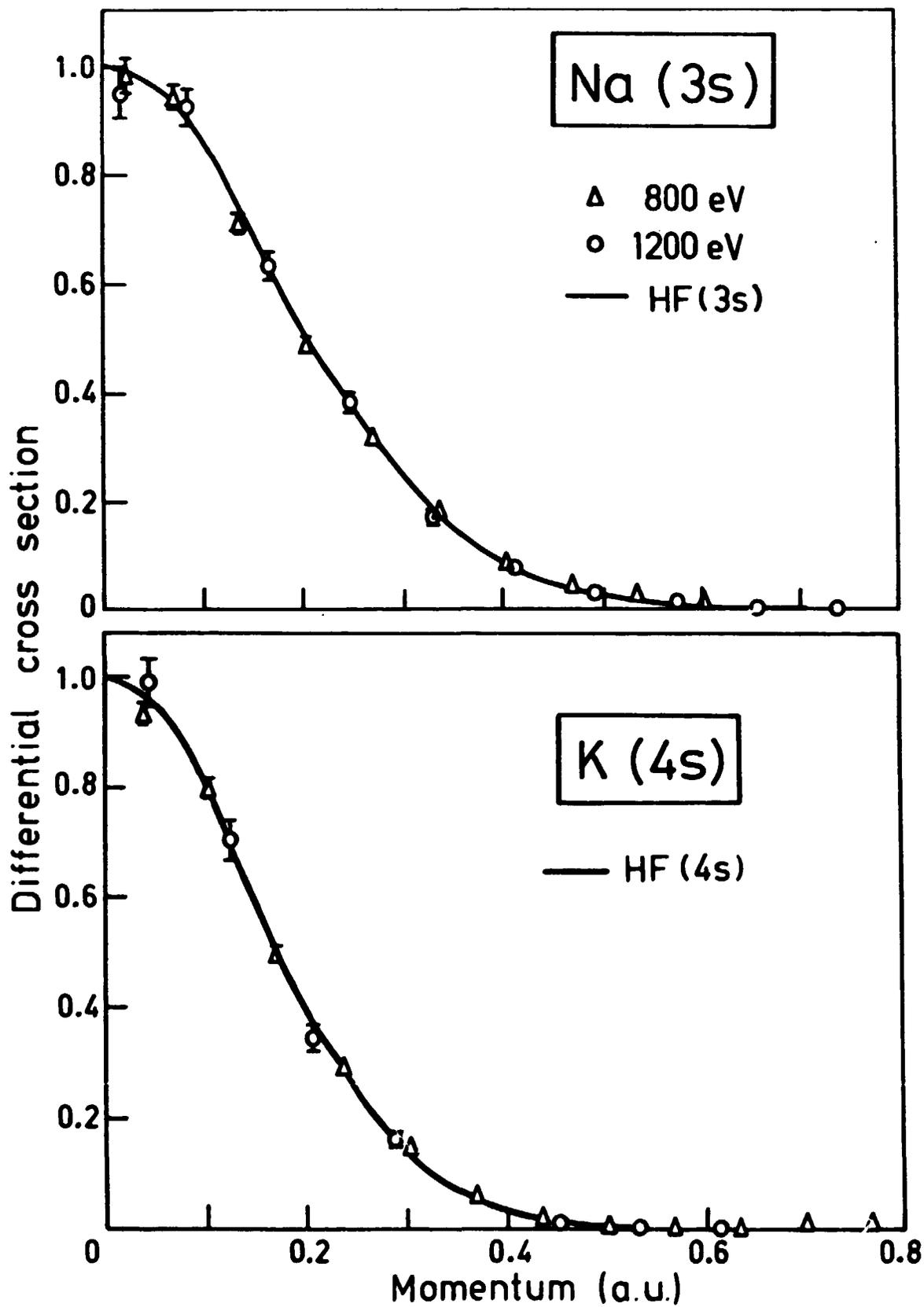


Figure 3

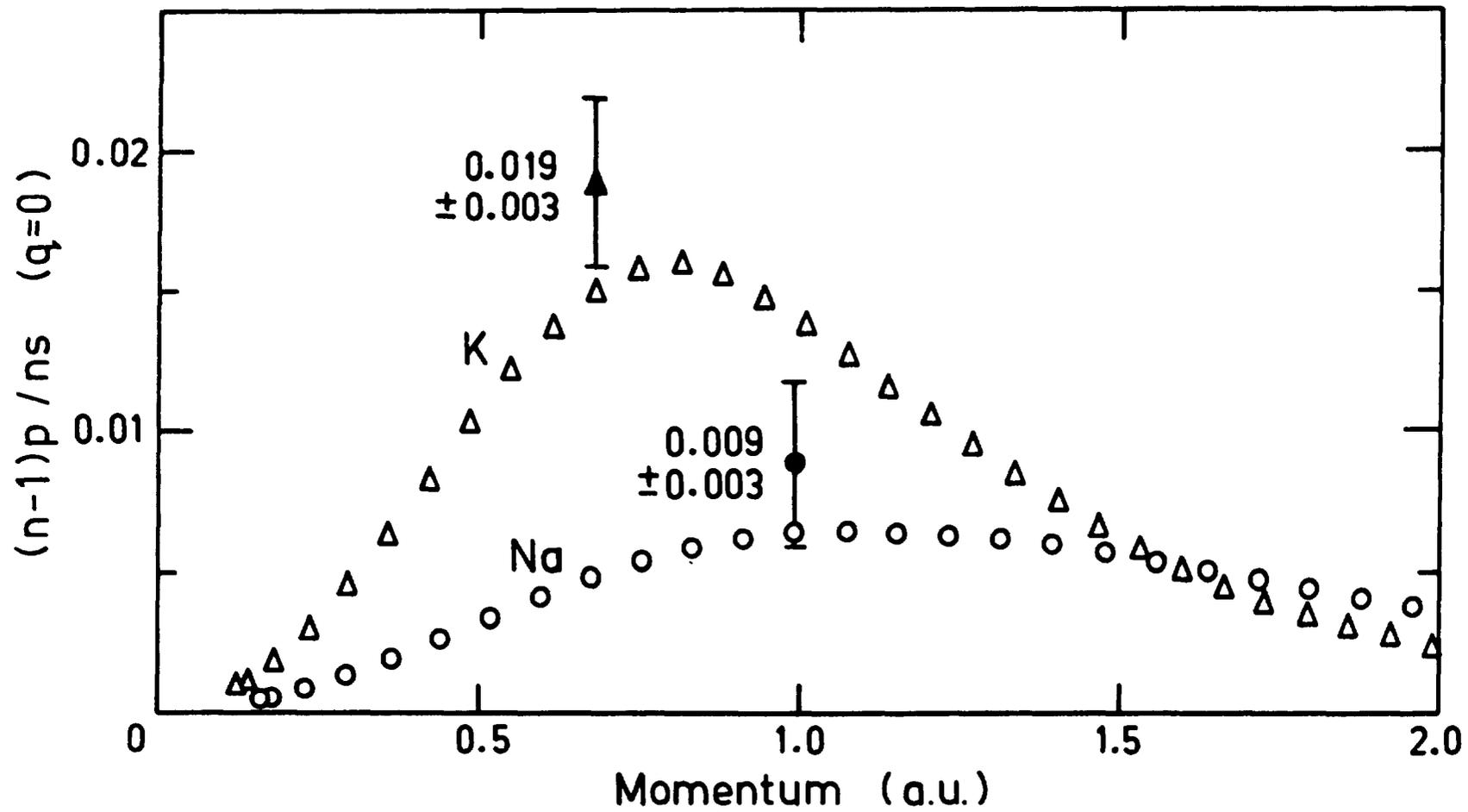


Figure 4