



ANGULAR DISTRIBUTION OF PHOTOELECTRONS
FROM GASES AND A DESIGN FOR A ROCKET-
BORNE EUV SPECTROPHOTOMETER

By

David A. M. Gigney, B.Sc.(Hons)

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SPELLING MISTAKES AND TYPOGRAPHICAL ERRORS

- Page 9 Equation 1.13 should read
- $$\psi_{nlms}(r, \theta, \phi) = u_{nl}(r) H_{lm}(\theta) \bar{\phi}_m(\phi) \sigma_{ms}$$
- Page 15, line 6: "... θ is between the electron *direction* and ..
- Page 23, Equation 1.31: replace j_t with j_t .
- Page 34, line 9: "transition" misspelt.
- Page 60, line 16: "grids" misspelt.
- Page 66, line 17: replace "Kev" with "keV".
- Page 66, line 18: replace "in" with "is".
- Page 70, line 8: replace " θ_y " with " θ_z ".
- Page 70, Equation 2.12: replace "cos" with "sin".
- Page 102, line 6: "adequately" misspelt.
- Page 114, line 5: should read "Sections 2.9.2 and 2.9.3".
- Page 148, line 3: insert "of" before "Figures ...".
- Page 155, line 10: "analysers" misspelt.
- Page 164, line 13: "proportional" misspelt.
- Page 179, line 8: replace "Rimothy" with "Timothy".

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SUMMARY

The material presented in this thesis is primarily concerned with the measurement of the angular distribution of photoelectrons from gases. A second and much smaller part, describes the design and construction of a rocket-borne instrument to measure extreme ultraviolet airglow.

A review has been made of the various processes involved in the photoionization of gaseous atoms and molecules by extreme ultraviolet radiation. In particular, the review concentrates on the subset of the photoionization process applicable to the angular distribution of photoelectrons. The emphasis is on a comparison between theory and experiment.

An instrument was constructed to measure the angular distribution of photoelectrons from the photoionization of gases by unpolarized extreme ultraviolet radiation. A simple plane grid retarding analyser, rotated in the plane of the light beam, was used. To provide an adequate signal, the analyser had a large entrance half angle of 10 degrees. The description is given of a computer program that numerically calculated the expected signal at each angle. This was used to investigate the effect of this large field of view on the measured distribution and to evaluate the volume correction factor.

The asymmetry parameter was measured for photoelectrons from the outer p subshells of the inert gases helium, neon, argon, krypton and xenon using 30.4 nm radiation, and for argon, krypton and xenon with 58.4 nm radiation. For krypton and xenon, photoelectrons corresponding to the $^2P_{1/2}$, $^2P_{3/2}$ states of the ion were

resolved.

The measurement of β for the helium photoelectrons was used to test the equipment. The value of $2.01 \pm .05$ obtained compared well with the known value of 2 providing assurance that the experimental method was reliable. A comparison of the present results for the inert gases photoionized by 58.4 nm radiation with those of other experimenters, strengthened the confidence in the method.

The results have been compared with other measurements using both resonance sources and synchrotron radiation. A comparison is also made with theoretical calculations.

The asymmetry parameter was measured for photoelectrons produced by the photoionization of oxygen, nitrogen, carbon monoxide and carbon dioxide by 30.4 nm radiation. Photoelectrons corresponding to the following ionic states were analysed : $O_2^+(X^2\Pi_g)$, $N_2^+(X^2\Sigma_g^+, A^2\Pi_u, B^2\Sigma_u^+)$, $CO^+(X^2\Sigma_g^+, A^2\Pi_u, B^2\Sigma_u)$, $CO_2^+(X^2\Pi_g, A^2\Pi_u, A^2\Pi_u + B^2\Sigma_u^+, C^2\Sigma_g^+)$. The results are compared where possible with other measurements, in particular the wavelength dependent results from synchrotron radiation.

The second part of the thesis describes a rocket-borne extreme ultraviolet spectrophotometer. It was designed to measure 58.4 nm and 30.4 nm airglow which arises from the scattering of solar radiation from atmospheric and extraterrestrial atomic and singly ionized helium. A brief review of the occurrence of these radiations is given. The instrument was based on the photoelectric effect. The emitted electrons were analysed with a cylindrical mirror analyser to

provide wavelength discrimination. The design and construction of the instrument are described and a preliminary calibration is given. This is the limit of the discussion as the instrument was destroyed because of rocket failure.

P R E F A C E

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University. To the best of the author's knowledge and belief it contains no material previously published or written by another person, except where due reference is made in the text.

D. GIGNEY.

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CHAPTER 1 : REVIEW OF PHOTOELECTRON ANGULAR DISTRIBUTION PROCESSES1.1 INTRODUCTION

Photoionization is the interaction of a photon with an atom or molecule which results in a positively charged ion and a free electron. The process can most easily be visualised by reference to the hypothetical atomic energy level diagram in Figure 1.1. The lowest energy level is called the ground state of the atom while the upper levels of increasing energy are excited states. These converge to a fixed level.

Radiation incident on the atom has an energy which is related to its wavelength λ by,

$$\text{Energy} = hc/\lambda \quad 1.1$$

where h is Planck's constant and c the speed of light. If this energy is equal to the energy difference between the state the atom is in and one of the upper states, the radiation may be absorbed with the energy causing the atom to undergo a transition to the upper state. This occurs by the movement of an electron to an outer orbital as illustrated by transition A in Figure 1.1

However, if the energy is sufficient, the electron may reach the continuum as shown by transition B. For this to occur, the energy must be at least equal to the energy difference between, in this case, the ground state and the series limit. This difference is called the ionization potential. A transition to the continuum leaves the electron unbound and hence free.

Since the continuum does not contain any discrete energy levels, all photons of energy greater than the ionization potential will result in photoionization. The excess energy appears as kinetic energy which is

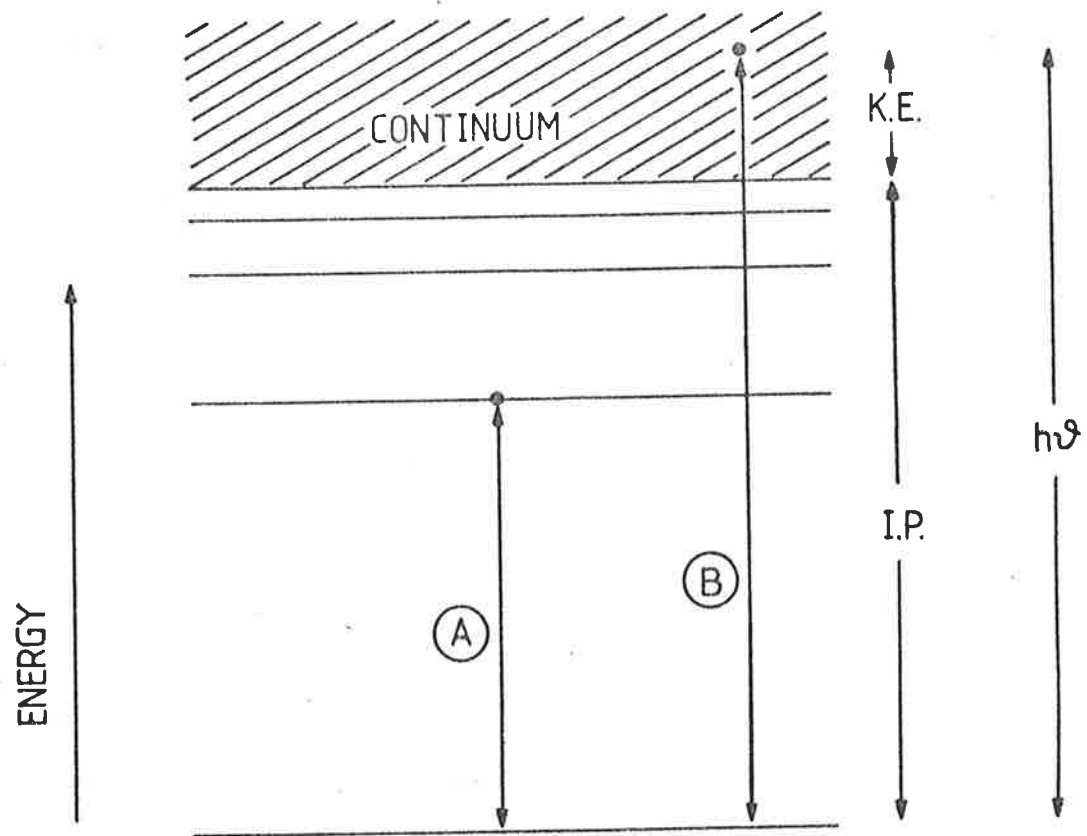


FIG. 1.1 Atomic energy levels.

mostly carried away by the electron due to its mass being much less than that of the ion. The picture presented thus far only applies to an atom. A molecule has a more complicated energy distribution with some of the photon energy contributing to vibration and rotation of the molecule.

The energy of the emitted electron depends on the wavelength of the light, while the number of electrons depends on the intensity. Thus if the wavelength is known, a measurement of the energy of the electron allows a calculation of the ionization potential by Equation 1.1, while a measurement of the number of photoelectrons emitted per absorbed photon gives the total photoionization yield. For atoms such as helium, xenon, neon etc., this has the value one, but for molecules it is generally less than one since there are alternate processes such as photodissociation.

In many cases, electrons of more than one energy are produced corresponding to the ion being left in different states. A measurable quantity here is the branching ratio which is the fraction of ions in a particular state. If this is multiplied by the photoionization cross-section, the result is the partial photoionization cross section for that particular photoionization channel. Measurements of these have been continuing for a number of years (e.g. Blake and Carver, 1967; Bahr *et al*, 1969; Samson and Gardner, 1976) and the information can be used for example, to examine competing photoionization processes (Wuilleumier *et al*, 1977).

A further measurement which is the one of concern here is of the angular distribution of the emitted electron. For radiation from a fixed direction incident on a random array of atoms or molecules, the electrons are emitted in preferred directions relative to the photon beam.

The angular distribution depends partly on the polarization of the beam, but more importantly is linked with the orbital from which the electron originated and the interaction between the field of the ion and the electron as it escapes. As such it has proved a useful probe of electron/ion dynamics and a test bed for a theoretical understanding of the properties of atoms and molecules and of the process of photo-ionization.

A consequence of the measurement of angular distributions was the discovery that different photoionization channels had different distributions. Thus early measurements of branching ratios (e.g. Blake, 1966) are in error because of this and their correction requires accurate measurements of the photoelectron angular distributions (Reilman *et al*, 1976). Branching ratio measurements are now made with equipment which is independent of the angular distribution of the emitted photoelectrons (Samson and Gardner, 1976; Lindemans *et al*, 1979).

Of chemical interest, angular distribution measurements can be used in the identification of different orbitals. At any one wavelength, complex organic molecules emit a range of overlapping energies. It is sometimes difficult to assign these to particular orbitals and a correlation between the angular distribution and the orbital type has been used to assist in this (Kobayashi, 1978 (a), (b); Kobayashi and Nagakura, 1975). However at present, the rules are largely empirical and a better theoretical understanding is required (Sell *et al*, 1978).

A final example is an application of angular distribution measurements to upper atmosphere investigations. In the region where the gas density is low, the mean free path of the photoelectrons produced can be long enough for them to spiral along the earth's magnetic field and deposit their energy in a region other than where they were formed. The initial angular distribution of the photoelectrons is then important

since this determines the angle of injection into the magnetic field (Manson *et al*, 1974).

Photoelectron angular distribution measurements thus have the ability to aid the understanding of a wide range of photoionization processes. The object of this review chapter is to concentrate on the interplay between experimental results and theory. The importance of this is that most theoretical results necessarily involve various assumptions and approximations and it is only by comparison with experiments that their validity can be ascertained. Conversely, experimental measurements also depend on theory, since it is often through this comparison that the purpose and direction of the work is established.

In the following review, a number of publications have provided somewhat more guidance to the author than is evident from the references. These are; the two part review of atomic photoelectron spectroscopy of Manson (1976, 1977), the angular distribution review of Dehmer (1978), the Daresbury Synchrotron radiation lecture notes of Marr (1975, 1976) and parts of the review entitled "Spectral Distribution of Atomic Oscillation Strengths" by Fano and Cooper (1968).

The review breaks naturally into two parts, atoms and molecules. Atoms will be considered first and in slightly more detail than molecules. This is partly due to them being simpler and hence more widely studied, but also because atoms provide a good starting point for the discussion on molecules.

The review begins in Section 1.2 with a brief discussion of some of the basic techniques for theoretically describing atomic photoionization. This carries into Section 1.3 which concentrates on the part

of the theory concerned with angular distributions. The theoretical discussion will be qualitative, being concerned mainly with describing the background to the calculations and some of the results as they affect an understanding of the process of photoelectron angular distributions. As well, Section 1.3 is concerned with the special cases of spin orbit coupling and autoionization.

Section 1.4 introduces molecules with a short discussion on their properties which differ from atoms, namely the possibility of rotation of the molecule and vibration of the internuclear bond. This considerably complicates the picture and the approximations that are introduced to reduce the theory to a manageable form are discussed. Section 1.5 briefly outlines the theoretical techniques used to investigate molecular photoelectron angular distributions and compares the calculated results with the experimental data.

A basic assumption in the majority of this work is that the photoionization is an electric dipole interaction. Section 1.6 explores the effect of the inclusion of terms other than the electric dipole.

1.2 ATOMIC PHOTOIONIZATION

Before addressing the question of the form of the photoelectron angular distribution, it is necessary to provide a preliminary discussion of the physics relevant to this subset of atomic photoionization. This will begin with a statement of the form of the photoionization cross section and continue with a discussion of the electric dipole approximation and the central field approximation. This is followed by a brief resumé of the use of the Hartree self-consistent-field potential.

The cross section for the photoionization of an atom in state i by unpolarized photons, resulting in a final state f consisting of a photoelectron of energy E and an ion in state j , is given by (Manson, 1976),

$$\sigma_{ij}(E) = (4\pi^2 \alpha a_0^2 / 3g_i)(E + I_{ij}) |M_{if}|^2 \quad 1.2$$

where α is the fine structure constant, a_0 the Bohr radius and g_i the statistical weight of the initial discrete state, that is the number of degenerate sublevels at the energy of the initial state. I_{ij} is the ionization energy and E the photoelectron energy both expressed in Rydberg units.

It is apparent that any angle dependence must be contained within the matrix element $|M_{if}|^2$. Expressed in Rydberg units, this is given by (Manson, 1976),

$$|M_{if}|^2 = \frac{4}{(I_{ij} + E)^2} \left| \sum_f \langle \psi_f | \sum_{\mu} \exp(i \underline{k}_{\nu} \cdot \underline{r}_{\mu}) \nabla_{\mu} | \psi_i \rangle \right|^2 \quad 1.3$$

where $\underline{k}_{\nu}$ is the propagation vector of the photon, $\underline{r}_{\mu}$ the position vector of the μ th electron and the summation is over all degenerate

initial and final states. The functions ψ_i and ψ_f are the wavefunctions for the initial and final states respectively. These wavefunctions are normalised such that (Cooper, 1962)

$$\int |\psi_i|^2 dr = 1 \quad 1.4(a)$$

and

$$\int \psi_f(E) \psi_f(E') dr = \delta(E - E') \quad 1.4(b)$$

The form of the wavefunctions and the methods of evaluating them will be discussed in Sections 1.2.2 and 1.2.3. However, firstly Section 1.2.1 is concerned with a simplification to the matrix element by assuming the interaction to be electric dipole. This is an important assumption and a large part of the information that follows in later sections relies upon it.

1.2.1 ELECTRIC DIPOLE APPROXIMATION

For photoionization with extreme ultraviolet radiation, the matrix element given by Equation 1.3 can be grossly simplified by using the electric dipole approximation.

This begins by expanding the exponential term in a series expansion,

$$\exp(i \underline{k} \cdot \underline{r}) = 1 + i \underline{k} \cdot \underline{r} + \frac{1}{2}(i \underline{k} \cdot \underline{r})^2 + \dots \quad 1.5$$

For the extreme ultraviolet, the wave number k is of the order of 10^6 cm^{-1} . The value of r is of the order of the Bohr radius since the wave function is mostly concentrated at this distance from the nucleus (Manson, 1976). This has a value of about 10^{-8} for an atom of low atomic number. Thus the product $\underline{k} \cdot \underline{r}$ is very much less than one, and the exponential can be approximated by just the first term. This is

called the electric dipole approximation and physically corresponds to the wavelength of the radiation being large compared with the radius of the orbital.

The matrix element now becomes

$$|M_{if}|^2 = \frac{4}{(I_{ij} + E)} \sum_{i,f} | \langle \psi_f | \sum_{\mu} \nabla_{\mu} | \psi_i \rangle |^2 \quad 1.6$$

which is referred to as the dipole velocity matrix element. An alternate form is the dipole length matrix element (Manson, 1976),

$$|M_{if}|^2 = \sum_{i,f} | \langle \psi_f | \sum_{\mu} r_{\mu} | \psi_i \rangle |^2 \quad 1.7$$

and a third is the dipole acceleration form (Manson, 1976),

$$|M_{if}|^2 = \frac{16Z^2}{(I_{ij} + E)^4} \sum_{i,f} | \langle \psi_f | \frac{\sum_{\mu} r_{\mu}}{r_{\mu}^3} | \psi_i \rangle |^2 \quad 1.8$$

These three alternate forms have been generated using exact wave functions. In any calculation the wave functions used are generally only approximate and the three forms will not necessarily give the same result (Fano and Cooper, 1968). However, if the calculations with the different forms agree, this does not necessarily imply exactness of the wavefunctions (Manson, 1976).

1.2.2 CENTRAL FIELD APPROXIMATION

It is now necessary to consider in more detail the wavefunctions for the initial and final states. In general they can be found by solving the wave equations

$$H \psi_i = E_i \psi_i \quad 1.9(a)$$

and

$$H \psi_f = E_f \psi_f \quad 1.9(b)$$

where E_i and E_f are the energies of the initial and final states which have wavefunctions ψ_i and ψ_f respectively. H is the Hamiltonian which in the non-relativistic coulomb approximation has the form,

$$H = \sum_{\mu} \frac{p_{\mu}^2}{2m} + V(r_1, r_2, \dots) \quad 1.10$$

where p_{μ} is the momentum of the μ th electron and V the potential of the system.

However, an exact solution is only possible for hydrogen, and a starting point for handling more complex atoms is to assume that each electron moves in a potential that depends only on its distance from the nucleus. This is called the central field approximation and the approximate Hamiltonian used is (Manson, 1976).

$$H_o = \sum_{\mu} \left[\frac{p_{\mu}^2}{2m} + U'(r_{\mu}) \right] \quad 1.11$$

where the potential $U'(r_{\mu})$ depends only on the scalar r_{μ} . The Schrödinger equation can then be written,

$$\frac{-\hbar^2}{2m} \sum_{\mu=1}^Z \nabla_{\mu}^2 \psi + \sum_{\mu=1}^Z U'(r_{\mu}) \psi = E\psi \quad 1.12$$

where the wavefunction ψ applies to either the initial or final state.

Consider firstly the bound state of the electron. Solutions of the Schrödinger equation are antisymmetric combinations of one electron wavefunctions of the form,

$$\psi_{n\ell m s}(r, \theta, \phi) = u_{n\ell}(r) \Theta_{\ell m}(\theta) \Phi_m(\phi) \sigma_{ms} \quad 1.13$$

where r , θ and ϕ are the spherical polar coordinates of the electron from the nuclear origin. The eigenfunctions are characterised by four

quantum numbers n, ℓ, m and m_s which have the values,

$$n = 1, 2, 3, 4, \dots$$

$$\ell = 0, 1, 2, \dots, n-1$$

$$m = -\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell$$

$$m_s = +\frac{1}{2}, -\frac{1}{2}$$

The quantum number n is called the principal quantum number. The quantum number ℓ is the azimuthal quantum number and gives the orbital angular momentum of the electron which is a vector of magnitude,

$$|\mathbf{L}_i| = \sqrt{\ell(\ell+1)} \hbar \quad 1.14$$

The quantum number m is the magnetic quantum number and gives the component of the orbital angular momentum in a given direction as for example that of a magnetic field. Finally, m_s is the spin quantum number and gives the component of the spin of the electron which is a vector of magnitude,

$$|\mathbf{S}_i| = \sqrt{m_s(m_s+1)} \hbar \quad 1.15$$

Each single particle state is therefore specified by these quantum numbers. Furthermore, the Pauli exclusion principle states that in any one atom, no two electrons can have the same combination of these quantum numbers. From this principle and a knowledge of the quantum numbers, it is therefore possible to construct the electronic configuration.

Returning to Equation 1.13, the function $U_{n\ell}(r)$ is called the radial wave function and,

$$U_{n\ell}(r) = P_{n\ell}(r)/r \quad 1.16$$

where the wavefunction $P_{n\ell}$ obeys a radial equation (Fano and Cooper, 1968),

$$\frac{d^2 P_{n\ell}}{dr^2} + (2m/\hbar^2) [E_{n\ell} - U(r) - \ell(\ell+1)\hbar^2/2mr^2] \\ \times P_{n\ell}(r) = 0. \quad 1.17$$

It is this equation which must be solved in the central field approximation. The functions $\Theta_{\ell m}(\theta)$, $\Phi_m(\phi)$ and σ_s need not be considered since they are of the same form for a many electron atom as for a one electron atom and can be solved exactly (Eisberg, 1967). This is due to the spherical symmetry of the potential.

Consider now the final state wavefunction. If we consider just the single outgoing electron, then its wavefunction can also be given by an equation of the form 1.13 and the solution reduces to one of finding the radial wavefunction,

$$U_{\epsilon\ell}(r) = P_{\epsilon\ell}(r)/r \quad 1.18$$

where $P_{\epsilon\ell}(r)$ obeys a radial equation of the form 1.17.

The radial wavefunctions for both the initial and final states are solutions of the radial wave equation in a central potential and it is the need to know the radial dependence of this field that complicates their solution. For a simple coulombic field, an analytic expression is available but in general the potential field is more complex due to the effect of the field of the other electrons. A technique for finding the potential is the Hartree self consistent field and this will be discussed in the next section.

1.2.3 THE HARTREE SELF CONSISTENT FIELD

The Hartree theory (Hartree, 1928 (a), (b)) considers each of the Z electrons to be moving independently in a central potential of the nuclear charge and the average charge of the other $(Z-1)$ electrons (Eisberg, 1967; Schiff, 1968). The Schrödinger equation is then of the

form of Equation 1.12 and since the electrons are assumed to be independent, a solution is chosen that is the product of the individual wavefunctions of the Z electrons.

$$\psi_T = \psi(r_1, \theta_1, \phi_1)\psi(r_2, \theta_2, \phi_2) \dots \psi(r_Z, \theta_Z, \phi_Z) \quad 1.19$$

It is then possible to divide Equation 1.12 into Z single electron Schrodinger equations. To solve the equations however, the form of the central potential for each electron must be known. This is estimated by the Hartree self consistent method which can be visualised as follows (Eisberg, 1967). First a reasonable guess is made for the form of the potential and the set of equations is solved giving Z eigenfunctions. Using these, the configuration of the atom is constructed satisfying minimum total energy and the Pauli exclusion principle. Then new values of the potentials are each calculated as that potential acting on a particular electron from the combined field of the nucleus and the spherically averaged field of the other electrons. With the new set of potentials, the process is repeated until a set of self consistent potentials is obtained. The eigenfunctions then calculated from these potentials are a set of single particle eigenfunctions describing the motion of the electrons.

Analytically, the Hartree method follows from the variation principle by finding the average of the Hamiltonian for the system and varying the one electron orbitals to minimise the energy.

A disadvantage of the technique is that the constructed wavefunction 1.19 does not satisfy the requirement of antisymmetry, that is the exact wavefunction must be such that the interchange of two electrons changes the sign of the wavefunction. This can be rectified by starting with a determinantal wavefunction,

$$\psi_T = \frac{1}{(N!)}^{\frac{1}{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_Z(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_Z(2) \\ \vdots & & & \\ \psi_1(Z) & & & \psi_Z(Z) \end{vmatrix} \quad 1.20$$

which is an antisymmetric function (Slater, 1963). Application of this wavefunction to the self consistent technique is called the Hartree-Fock method and increases the accuracy of the results. The potential field of the Hartree-Fock treatment differs from the Hartree in that the contribution to the charge density from electrons of the same spin as the one considered is reduced by an amount called the exchange charge density. However, this term adds considerably to the computational effort required to solve the Hartree-Fock equation (Herman and Skillman, 1963) and a simplification has been given by Slater (1951). This replaces the exchange term by a local potential proportional to the cube root of the charge density (Walker and Waber, 1974) and the method is referred to as Hartree-Slater. Its accuracy would be expected to lie between that of the Hartree and Hartree-Fock.

Using the Hartree-Fock technique, it is then possible to find the wavefunctions for the initial and final states needed to evaluate the cross section. For the initial bound state it is a matter of applying the Hartree-Fock method as outlined and the result is an estimate for the radial wavefunctions.

For the final state wavefunction, the method used relies on the fact that the wavefunction of an electron in the continuum does not affect the self consistent determination of the radial wavefunctions of the bound electrons (Fano and Cooper, 1968). Therefore the technique

is to apply the Hartree-Fock method to the atom minus the photoionized electron, that is, the ion. The wavefunctions of the bound electrons are calculated and thence the potentials and exchange functions. The latter represent the electron exchange that arises from the antisymmetry of the wavefunction as mentioned above. Using these, the radial equation for the continuum electron is solved. However, the equation used is not quite the radial equation 1.17, but contains as well the electron exchange. It is derived from an analytic expression of the Hartree-Fock method and is of the form (Manson, 1978).

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + E - U(r) \right] P_{\ell}(r) + X(r) = 0 \quad 1.21$$

where $X(r)$ is an exchange term.

1.2.4 SPIN-ORBIT INTERACTIONS

A final point that needs to be mentioned is interaction between the orbital angular momentum ℓ_i and the spin s_i of the electrons. When this occurs, each can no longer be considered well defined.

The most common form of interaction is Russell-Saunders or (L, S) coupling. In this, it is assumed that the ℓ_i, s_i and s_i, ℓ_i are strongly coupled amongst themselves to give a resultant angular momentum L and spin S . These add together to give a total angular momentum J of the electrons in the atom. Thus the total spin and orbital angular momentum are now considered as well defined quantities rather than the individual values for each electron.

A less common occurrence is (j, j) coupling. In this case each ℓ_i and s_i couple to give a resultant j_i . These then add together to form the resultant angular momentum J .

1.3 ATOMIC PHOTOELECTRON ANGULAR DISTRIBUTIONS

If we assume the electric dipole approximation, then the differential cross section for photoionization of an unpolarized target by polarized radiation is given by (Cooper and Zare, 1969),

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos\theta)] \quad 1.22$$

where $P_2(\cos\theta)$ is the second Legendre polynomial and equals $\frac{1}{2}(3 \cos^2\theta - 1)$. The angle θ is between the electron and the electric vector, while β is known as the asymmetry parameter. For the cross section to remain non-negative, the value of β is between -1 and $+2$. For $\beta=2$, the electron intensity has a maximum predominantly at right angles to the beam, while for $\beta=-1$, it is along the beam. The value $\beta=0$ is for an isotropic distribution. These are shown in Figure 1.2

A corresponding expression can be obtained for unpolarized light by considering unpolarized light as the sum of two incoherent mutually orthogonal polarized beams. The electron direction ϕ is now measured relative to the photon beam giving (Cooper and Manson, 1969)

$$\frac{d\sigma}{d\Omega} \propto (1 - \frac{1}{2} \beta P_2(\cos\phi)) \quad 1.23$$

Yang (1948) has shown that the above expressions depend only on the process being electric dipole and the target unpolarized. However, a number of further approximations must be made in order to find an expression for the asymmetry parameter. One such expression results from the Cooper-Zare model and this will be discussed in the following section.

UNPOLARISED LIGHT

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[1 - \frac{\beta}{4} (3\cos^2\theta - 1) \right]$$

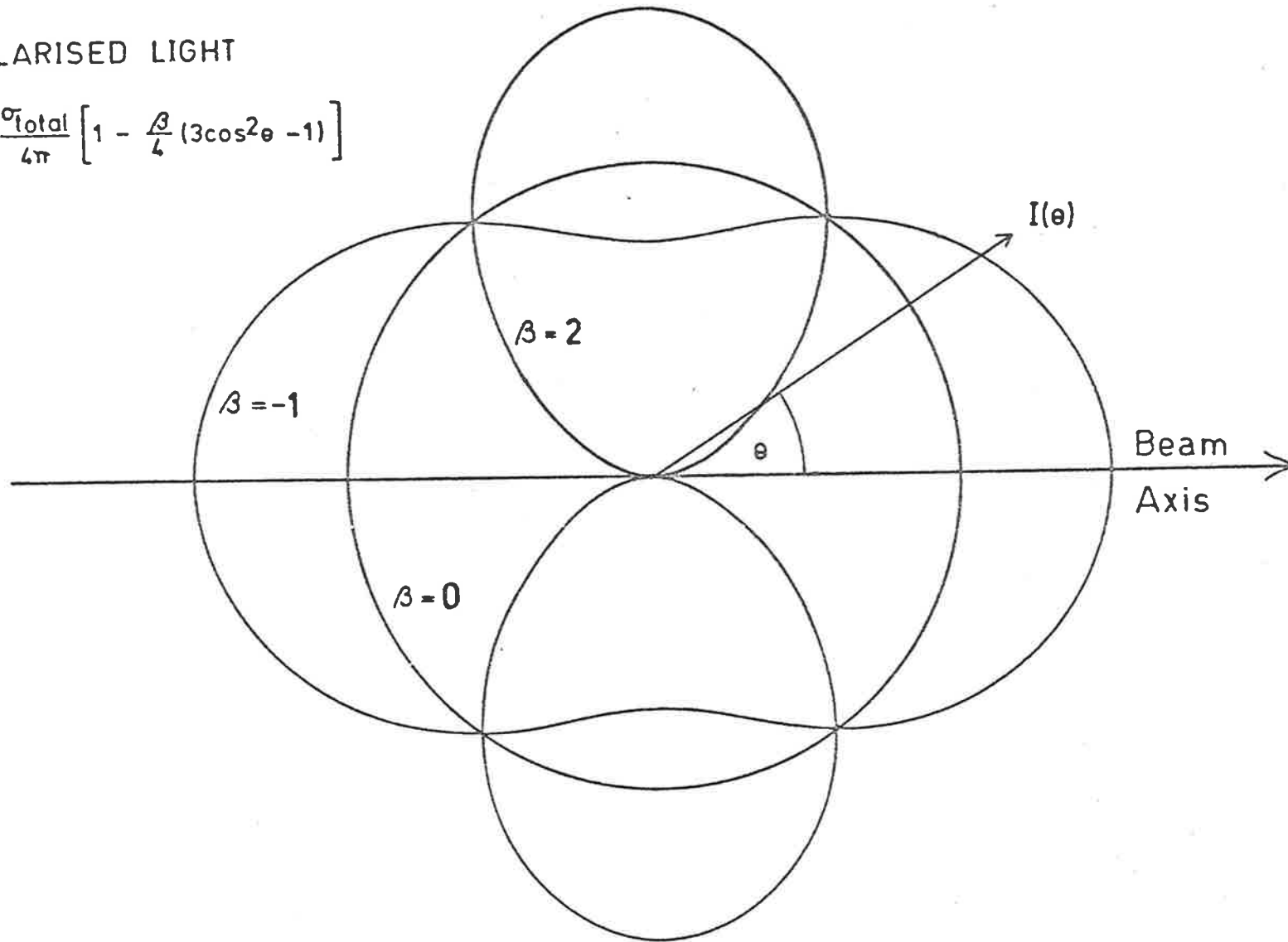


FIG. 1.2 Polar Diagram of the electron intensity for three values of β .

1.3.1 COOPER-ZARE MODEL

Three assumptions that have been discussed in previous sections are necessary for the Cooper-Zare model. These are the electric dipole approximation, the central field model and LS coupling. Two further facts need to be mentioned. Firstly, we are only interested in the photoionization of a single electron. The remaining electrons then have the same initial and final states which means that core relaxation effects are ignored. The result is that all electron orbitals other than that of the photoionized electron integrate out to unity in the dipole matrix element (Manson, 1976; Cooper, 1962).

The second is a restriction on the change in the quantum number ℓ between the bound electron and the outgoing electron. This is that it must change by one, that is $\Delta\ell = \pm 1$ (Herzberg, 1944).

Within this framework, Cooper and Zare (1969) were able to derive the following expression for β ,

$$\beta = \frac{\ell(\ell-1)|R_{E,\ell-1}|^2 + (\ell+1)(\ell+2)|R_{E,\ell+1}|^2 - 6\ell(\ell+1)R_{E,\ell+1}^* R_{E,\ell-1} \cos \delta}{(2\ell+1) [\ell |R_{E,\ell-1}|^2 + (\ell+1)|R_{E,\ell+1}|^2]} \quad 1.24$$

where $R_{E,\ell\pm 1}$ are the radial dipole matrix elements,

$$R_{E,\ell\pm 1} = \int P_{E,\ell\pm 1} r P_{n,\ell} dr \quad 1.25$$

where $P_{E,\ell\pm 1}$ is the radial part of the continuum wavefunction and $P_{n,\ell}$ is the radial part of the initial wavefunction.

The quantity δ in equation 1.24 is the phase difference between the continuum wavefunctions for the two $\ell\pm 1$ outgoing channels. These phase shifts are defined in the asymptotic region of the continuum wavefunction (Manson, 1976),

$$P_{\ell}(r) \xrightarrow{r \rightarrow \infty} \pi^{-1/2} E^{-1/4} \sin(E^{1/2}r - \frac{1}{2}\ell\pi - E^{-1/2} \ln 2E^{1/2}r + \sigma_{\ell}(E) + \delta_{\ell}(E)) \quad 1.26$$

where $\sigma_{\ell}(E) = \text{Arg } \Gamma(\ell+1 - i E^{-1/2})$ is the coulomb phase shift and $\delta_{\ell}(E)$ is the non coulomb phase shift (Manson, 1977).

The expression for β in Equation 1.24 contains the squares of the matrix elements for the $\ell+1$ and $\ell-1$ outgoing waves weighted by functions of ℓ , the orbital angular momentum. However, of interest is the third term in the numerator.

This depends on the matrix elements for both the $\ell+1$ and $\ell-1$ outgoing waves and the cosine of the phase shift difference. Angular distributions can thus be considered as an interference between the two outgoing waves and it is this dependence on phases and the signs of the matrix elements which provides extra information not available from cross sections.

The value of β for individual $\ell \pm 1$ outgoing channels originating from s, p and d orbitals is shown in Table 1.1 The photoionization of an s electron is the only case where there is a single outgoing wave and the value of β is 2 at all energies. For all other orbitals, the photoelectron angular distribution will be proportional to a weighted sum of the intensities of the two channels and the cosine of the phase difference between them. Both the matrix elements and the phases of the continuum waves are energy dependent, and since this is different for each wave, β too will be energy dependent.

1.3.2 ANGULAR DISTRIBUTION CALCULATIONS

The evaluation of Equation 1.24 for finding β requires a knowledge of the radial dipole matrix elements. These in turn require knowledge of the radial wavefunctions for the initial and final states of

ℓ	Transition	β	$\frac{d\sigma}{d\Omega}$
0	ns $\rightarrow$ kp	2	3 $\cos^2 \theta$
1	np $\rightarrow$ ks	0	1
	np $\rightarrow$ kd	1	.5[1+3 $\cos^2 \theta$]
2	nd $\rightarrow$ kp	.2	.3[3+ $\cos^2 \theta$]
	nd $\rightarrow$ kf	.8	.6[1+2 $\cos^2 \theta$]

TABLE 1.1 Angular distribution for the individual channels for photo-ionization of s, p and d orbitals (from Marr, 1976).
[θ is the angle between the ejected electron and the electric vector.]

the photoelectron. A technique for finding these using the Hartree self consistent method has been discussed in Section 1.2.3.

Hartree-Fock and Hartree-Slater derived wavefunctions have been used with the Cooper Zare model for a range of atoms and initial orbitals (Kennedy and Manson, 1972; Manson, 1972/73; Manson, 1973(b); Manson, 1971; Manson and Cooper, 1970; Manson and Kennedy, 1970). Of these, the inert gases provide an ideal basis of study since being gaseous at room temperature, they are well suited to experimental measurements. In particular, the outer p subshell has been extensively studied experimentally both at discrete wavelengths (Berkowitz and Ehrhardt, 1966; Berkowitz *et al*, 1967; Vroom *et al*, 1969; McGowan *et al*, 1969; Leng and Nyberg, 1977; Karlsson *et al*, 1976; Mason *et al*, 1977; Morgenstein *et al*, 1970; Carlson and Jonas, 1971; Niehaus and Ruf, 1972; Hancock and Samson, 1976; Dehmer *et al*, 1975) and as a function of wavelength (Lynch *et al*, 1972; Watson and Stewart, 1974; Mitchel and Codling, 1972; Lynch *et al*, 1973; Houlgate *et al*, 1976; Houlgate *et al*, 1974; Codling *et al*, 1976, Torop *et al*, 1976a). The theoretical calculations together with some of the experimental measurements are shown in Figures 1.3 through 1.6.

Consider firstly the $2p$ electron from neon. There are two main features of the curves shown in Figure 1.3. Near threshold there is a rapid variation in the asymmetry parameter caused by a corresponding rapid change in the coulomb phase shift (Manson, 1972/3). Beyond that, the β value flattens and moves towards the asymptotic value of $\beta = 1.5$ predicted by the Cooper-Zare model (Marr, 1976).

In general, the main features of the curves were found to be relatively insensitive to the details of the calculation, that is whether

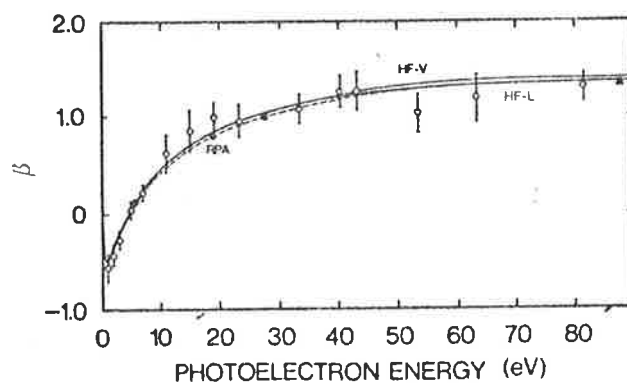


FIG. 1.3 The asymmetry parameter as a function of photoelectron energy for neon 2p (from Manson, 1977).

Theoretical results: HF-L, HF-V, Kennedy and Manson (1972). RPA, Amusia *et al* (1972).

Experimental results: $\blacktriangle$ Wuilleumier and Krause (1974); $\bullet$ Dehmer *et al* (1975); $\circ$ Codling *et al* (1976).

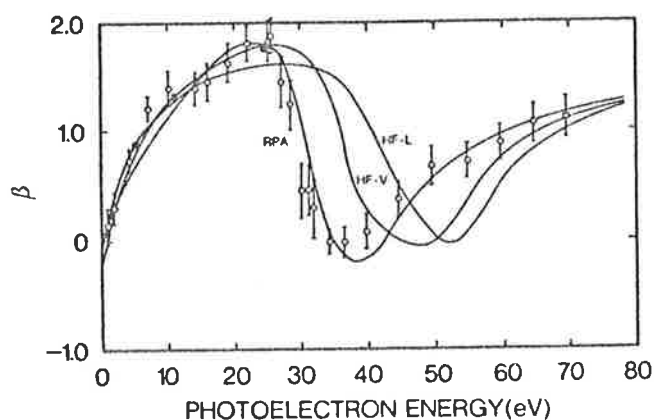


FIG. 1.4 The asymmetry parameter as a function of photoelectron energy for argon 3p (from Manson, 1977).

Theoretical results: HF-L, HF-V, Kennedy and Manson (1972); RPA, Amusia *et al* (1972).

Experimental results: $\bullet$ Dehmer *et al* (1975).
 $\circ$ Houlgate *et al* (1976).

Hartree-Fock or Hartree-Slater wavefunctions were used (Manson, 1972/73). This is due to the matrix elements occurring in both the numerator and denominator of the expression for β (Equation 1.24). Thus changes in the matrix elements tend to cancel out and the β value is then primarily sensitive to the phase shifts.

However, variations in the matrix elements assume more importance when the photoionization matrix element goes through a Cooper minimum (Cooper, 1962). This occurs where the radial matrix element becomes zero as it crosses from negative to positive with increasing energy. This only happens for the $\ell \rightarrow \ell+1$ channel for the outer shells and β is then determined solely by the $\ell \rightarrow \ell-1$ channel. In the case of a p electron, the $\ell-1$ channel is an s wave causing β to be zero in the minimum.

Such a minimum can be seen in argon (Figure 1.4) but neither the Hartree-Fock velocity nor length formulations agree with the data. However, there is reasonable agreement before the minimum whilst beyond it, theory and experiment appear again to be converging.

The fit to the experimental data can be improved by using the random phase approximation which allows for multi-electron correlations (Amusia *et al*, 1971; Amusia *et al*, 1972) which are absent in the Hartree-Fock. In particular this takes into account the strong intra-shell correlations between the p subshell and a nearby d subshell (Dehmer, 1978). This is absent in neon, but present in the heavier atoms. For argon, there is a configuration interaction between the $3p^6$ configuration and states of the type $(3p^4, nd^2)$ (Dehmer, 1978).

Similarly, good agreement is found between the random phase

approximation results and the krypton data. However, this is not the case for xenon. This is because a further effect must now be introduced namely, final state interchannel correlations (Manson, 1977). For xenon, this is between the 5p state and the 4d state which has its threshold about 50 eV above the 5p threshold. Furthermore, the 4d matrix elements are quite large in the region of 50 to 150 eV, particularly the $4d \rightarrow \epsilon f$ channel, while the 5p matrix elements are small due to the Cooper minimum (Manson, 1977; Dehmer, 1978). Figure 1.6 shows the random phase approximation calculation both with the correlation included and without it (Amusia and Ivanov, 1976). As can be seen, it is only when it is included that good agreement is found with the experimental data of Torop *et al.* (1976a).

Apart from the inert gases, Hartree-Slater type calculations have been performed for the p, d and f subshells of a range of elements (Manson, 1972/73; Manson, 1977) but experimental results for comparison are lacking in this area. However, the calculations provide some general properties of the expected angular distribution curves.

The p subshells have the same features as those discussed for the inert gases. That is, a rapid fluctuation near threshold, the possibility of a Cooper minimum, and then a long gradual increase. This is seen in Figure 1.7 for the 5p subshell of elements $Z = 83, 92$ and 100, with only $Z = 83$ displaying a Cooper minimum (Manson, 1973b; Manson 1977).

Similar shapes are found for d states, with the addition that for some atoms, a shape resonance can affect the β value. For example, Figure 1.8 shows β for xenon 4d (Kennedy and Manson, 1972). There is

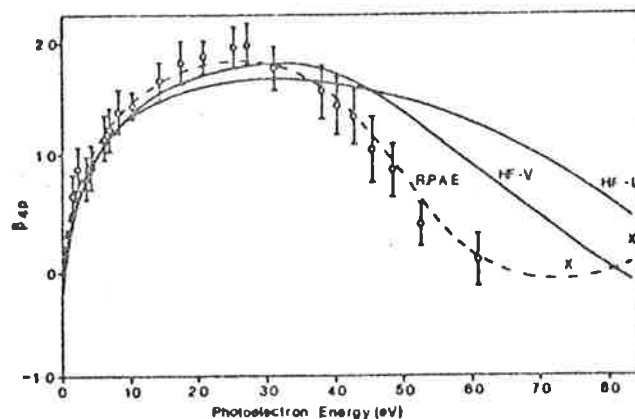


FIG. 1.5 The asymmetry parameter as a function of photoelectron energy for krypton 4p (from Marr, 1976)

Theoretical results: HF-V, HF-L Kennedy and Manson (1972); RPAE, Amusia et al (1972)

Experimental results: o Houlgate (1976);
x Torop *et al* (1976b)

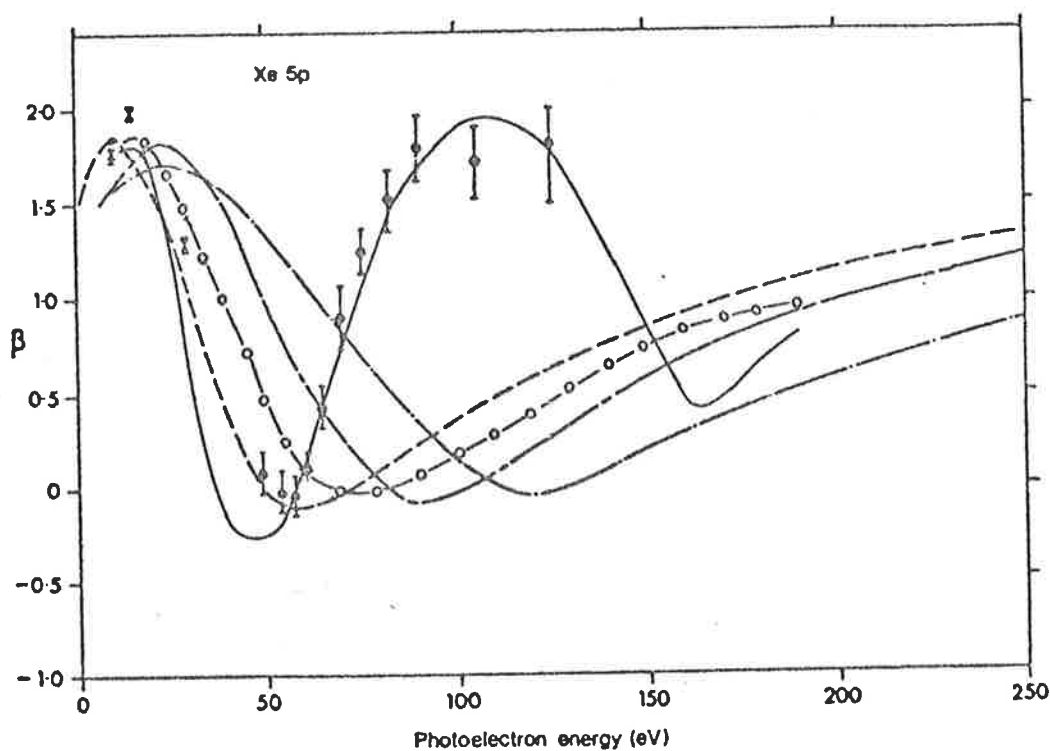


FIG. 1.6 The asymmetry parameter as a function of photoelectron energy for Xenon 5p

Experimental points: x, Dehmer *et al* (1975)

•, Torop *et al* (1976a)

Theoretical results: ---- HS, Manson and Cooper (1970)

— — — HF-V } Kennedy and
— · — HF-L } Manson (1972)

— o — RPA calculation without
the $4d^{10}$ shell included,
and with the $4d^{10}$ (Amusia
and Ivanov, 1976)

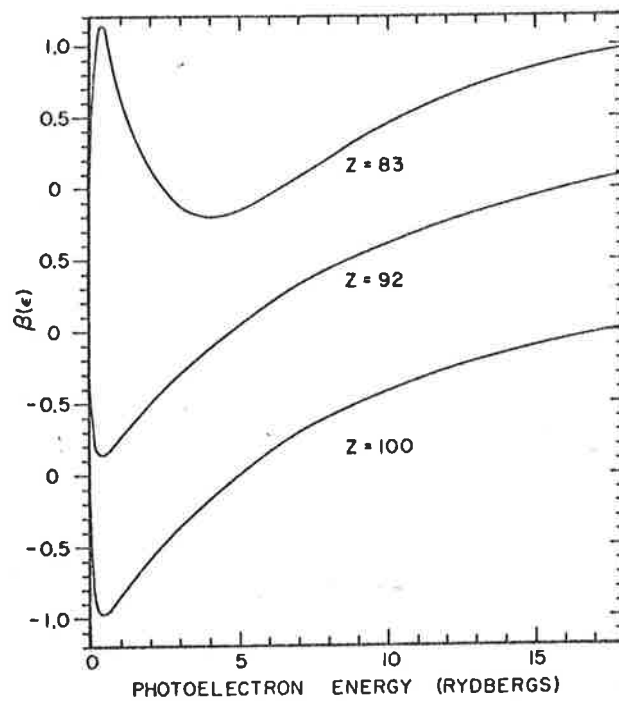


FIG. 1.7 Theoretical calculation using H-S wavefunctions in the C-Z model for 5p subshell of $Z = 83, 92$ and 100 (Manson, 1972/73)

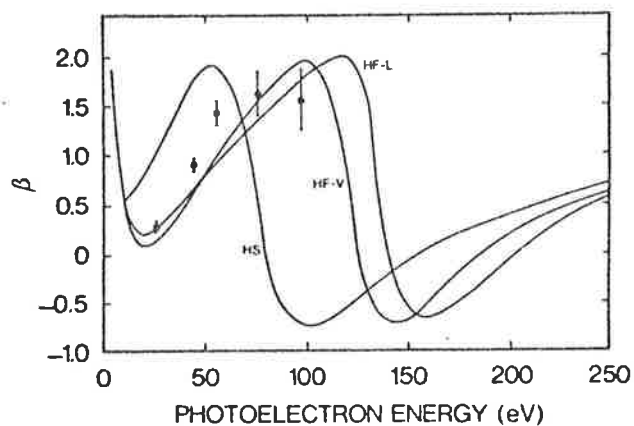


FIG. 1.8 The asymmetry parameter as a function of photoelectron energy for xenon 4d (from Manson, 1977).

Theoretical results : Kennedy and Manson (1972)

Experimental results : Torop *et al* (1976a)

an initial rise in β at threshold from the value .5 (not shown in diagram) followed by a trough due to a shape resonance in the f-wave channel. This is an example of an oscillation caused by the non-Coulomb phase shift (Manson, 1977). The minimum following that is a Cooper minimum.

Examples of 4f subshells are shown in Figure 1.9 and here the rapid oscillation near threshold is absent (Manson, 1977). This is due to the dipole matrix element for the g wave channel being very much less than for the d wave channel. With increasing energy the balance between the channels is restored but only after the normal rapid variation of the Coulomb phase shift near threshold has virtually finished (Manson, 1977).

1.3.3 ANGULAR MOMENTUM TRANSFER

A limitation of the Cooper Zare model is that it treats photoionization as a simple one-step process and thus cannot take into account autoionization or any interaction between the photoelectron and the ion that results in the transfer of angular momentum. A theory that allows for these processes and at the same time provides some insight into the mechanisms involved, is the angular momentum transfer formulation (Fano and Dill, 1972).

Consider a photoionization process (Dill *et al*, 1974),

$$A(J_0, \Pi_0) + h\nu (j_{ph}, \Pi_{ph} = -1) \rightarrow A^+(J_c, \Pi_c) + e^-(\ell, s, j, \Pi_e = (-1)^\ell) \quad 1.27$$

where J_0 and J_c are the angular momentum of the target atom and residual ion respectively and Π_0 and Π_c the parities; j_{ph} and Π_{ph}

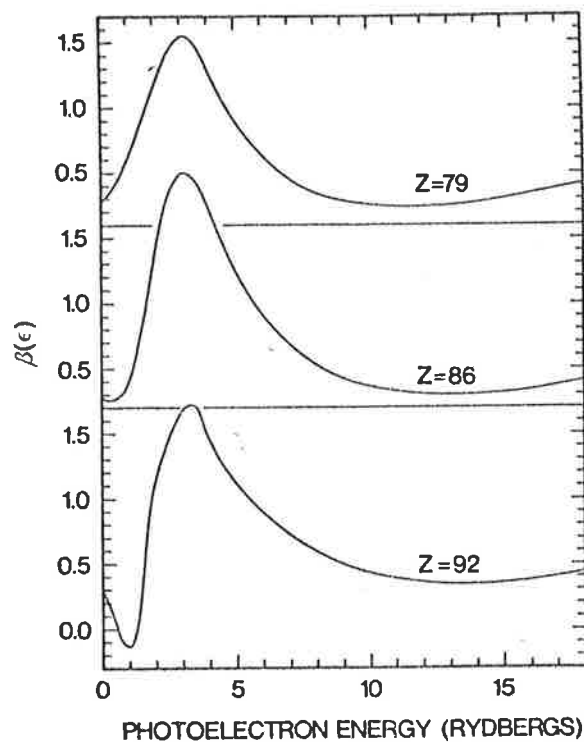


FIG. 1.9 Theoretical calculations using H-S wavefunctions in the C-Z model for 4f subshell of $Z = 79, 86, 92$ (Manson, 1977).

are the angular momentum and parity of the photon and ℓ , s , j , and Π_e are the orbital angular momentum, spin, angular momentum and parity of the outgoing electron. The parity is defined as odd or even depending on whether or not the wavefunction for the state changes sign under reflection through a point at the centre. A necessity of the interaction is conservation of angular momentum and parity,

$$J_0 + j_{ph} = J_c + \ell + s \quad 1.28(a)$$

$$\Pi_0 \Pi_{ph} = \Pi_c \Pi_e \quad 1.28(b)$$

The angular momentum transfer refers to a vector j_t which is the angular momentum transferred between the unobserved initial and final angular momenta in the reaction (Dill *et al*, 1975; Fano and Dill, 1972). This unobserved initial angular momentum is the total angular momentum of the target while the unobserved final angular momentum is the combination of the angular momentum of the residual ion and the photoelectron spin. This assumes that there is no measurement of either the spin of the photoelectron or the orientation of the residual ion.

$$j_t = J_c + s - J_0 \quad 1.29$$

By conservation of angular momentum,

$$j_t = j_{ph} - \ell \quad 1.30$$

That is, the angular momentum transfer is the difference between the angular momentum input to the atom by the photon and the orbital angular momentum removed by the electron (Dill *et al*, 1975). The cross section

can then be resolved into contributions corresponding to allowed values of j_t . These are determined from the conservation of angular momentum and parity (Manson, 1976).

If the scattering matrix in terms of J , the total momentum, is used, the cross section contains a double summation over values of the total angular momentum. However, if instead j_t is used, only a single incoherent sum over j_t is obtained (Fano and Dill, 1972). Furthermore, for each j_t there is a particular value of β and the final value of β for the photoionization is the sum of the β 's for the different channels labelled by j_t , weighted by the cross sections.

$$\beta = \frac{\sum_{j_t} \sigma_{jt} \beta_{jt}}{\sum_{j_t} \sigma_{jt}} \quad 1.31$$

The value of β for a particular channel j_t has one of two alternative forms determined by parity change for that channel. This is given by

$$\Pi_{\text{TARGET}} \Pi_{\text{CORE}} = - \Pi_{\text{CORE}}^2 (-1)^{\ell} = - (-1)^{\ell} \quad 1.32$$

and depending on whether it equals $(-1)^{j_t}$ or $-(-1)^{j_t}$, the values of j_t are called parity favored or unfavored respectively (Dill, 1973).

For a parity favored channel, β is a function of the photoionization amplitude for the given j_t (Dill, 1973), but for a parity unfavored channel, β has the single value of -1 (Dill and Fano, 1972). The value of β for the photoionization transition is then,

$$\beta = \frac{\sum_{j_t, \text{fav}} \sigma_{jt} \beta_{jt} - \sum_{j_t, \text{unfav}} \sigma_{jt}}{\sum_{j_t} \sigma_{jt}} \quad 1.33$$

This expression is dependent only on the conservation of total angular momentum and parity. Any restrictions such as LS coupling, are introduced later in the evaluation of the cross sections and the parity favored angular distribution parameters.

The Cooper-Zare model is a special case of this theory where j_t has the single parity favored value equal to the initial orbital angular momentum (Dill and Fano, 1972).

1.3.4 ANISOTROPIC ELECTRON/ION INTERACTION

The Cooper-Zare model views the ion as a spectator in the photoionization process, ignoring any transfer of angular momentum between the ejected photoelectron and the ion core. A theoretical treatment of this interaction has been carried out within the angular momentum transfer formulation by Dill *et al.*, (1975) which at the same time further elucidates the limitations of the Cooper-Zare model.

Photoionization can be viewed as a two step process (Dill *et al.*, 1975) with the first stage the initial photoabsorption and the second stage the escape of the electron from the ion.

In the first stage, the angular momentum of the photon is transferred to the electron which, in an independent particle model, has initial orbital momentum ℓ_0 . Its final orbital momentum is $\ell = \ell_0 + j_{ph}$ and the angular momentum transferred to the target is just,

$$j_t = j_{ph} - \ell = -\ell_0 \quad 1.34$$

For the second stage, if we assume LS coupling, the interaction of the electron and the ion is an interaction between the orbital momentum

of the electron (ℓ) and the total orbital momentum of the ion core (L_c). Thus there is a coupling between ℓ and L_c with a resulting exchange of angular momentum k between them, changing the photo-electrons orbital momentum from ℓ to ℓ' (Dill *et al*, 1975). The angular momentum transfer is now,

$$j_t' = j_{ph} - \ell' = j_t - k \quad 1.35$$

The coupling results in the phase shifts and dipole matrix elements being dependent on the total angular momentum of the electron plus ion, and it is because of this dependence that the interactions are called anisotropic (Dill *et al*, 1975).

This of course does not apply if the angular momentum of the core is zero, in which case anisotropy is impossible (Dill, 1973).

It is at this point that the overlap between the j_t formulation and the Cooper-Zare model is apparent. The Cooper-Zare model only considers the first stage with the single value of $j_t = \ell_0$, and assumes the residual ion plays no part in the process. This explains the success of the Cooper-Zare model in analyzing closed shell atoms where the electron/ion interaction is isotropic (Dill *et al*, 1975).

However, this is not the case for open shell atoms. Photo-ionization of the 3s electron of chlorine, for example, is expected to have a β of 2 by the Cooper-Zare model. However when analysed to take into account the anisotropy, the value differs greatly from 2 near threshold, and only slowly approaches this value with increasing energy (Starace *et al*, 1977).

Calculations for atomic sulphur also show anisotropic effects

with terms $j \neq l_0$ (Dill *et al.*, 1975), but atomic oxygen does not (Starace *et al.*, 1974). The criterion for determining the possibility of anisotropy and hence the applicability of the Cooper-Zare model, is the phase shift difference between alternate final-state channels (Dill *et al.*, 1975). It seems this needs to be at least .1 radian for appreciable anisotropic effects to be evident (Dehmer, 1978). For atomic sulphur this difference is about .7 radians, whilst for atomic oxygen it is only about .2 radians (Dill *et al.*, 1975).

As regards other elements, the anisotropy appears to be a maximum for a value of n , the principal quantum number, equal to three, and decreases on either side of this (Dehmer, 1978).

Experimentally, angular distributions of open shell atoms pose difficulties and there have been few measurements. An exception is atomic oxygen which has been measured at 30.4 nm (Dehmer and Dehmer, 1977), 58.4 nm and 73.6 nm (Samson and Hancock, 1977) but as has already been mentioned, atomic oxygen lacks anisotropy and the results are adequately explained by the Cooper-Zare theory (Starace *et al.*, 1974).

1.3.5 SPIN-ORBIT EFFECTS

Thus far, the discussion has assumed LS coupling to hold and consequently in the single particle model the angular distribution depended only on the quantum numbers n and l . However, if there is (j, j) coupling, that is the individual l_i 's and s_i 's couple together, each outgoing wave has two components, $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$.

Unlike the anisotropy discussed in Section 1.3.4 which affected the β value for open shell atoms, (j, j) coupling can also

affect closed shell atoms. A good example can be found in the photo-ionization of an s orbital. Here the outgoing p wave has two components $j = \frac{1}{2}, \frac{3}{2}$. If these two components differ then an interference between them is expected which could cause the value of β to deviate from the Cooper-Zare value of 2.

The inclusion of (j, j) coupling is readily attained with the use of relativistic wave functions. Walker and Waber (1973(a), (b)) have derived an expression for β in this case and for an s electron, this reduces to (Ong and Manson, 1979),

$$\beta = 2\rho (\rho + 2 \cos \Delta)/(2\rho^2 + 1) \quad 1.36$$

where ρ is the ratio of the matrix elements for the $j = \frac{3}{2}$ component to the $j = \frac{1}{2}$ component and Δ is the phase shift difference $\delta_{\frac{1}{2}} - \delta_{\frac{3}{2}}$. In the non-relativistic limit in the absence of spin orbit coupling, $\rho=1$ and $\Delta=0$ and β reduces to the value 2. Consequently, if either ρ or Δ deviate from these values, β in turn will differ from 2.

There are two possible reasons that the ratio of the matrix elements may differ from one. Firstly, there is the kinetic energy effect (Walker and Waber, 1974) which arises from the fact that the two components have slightly different energy. Therefore if the partial cross section is rising or falling with energy, the value of ρ would be expected to differ from one accordingly. Secondly, there is the possibility that the matrix elements may actually be different since the radial wavefunctions for the two bound states are slightly different and hence the overlap with the continuum will be different (Walker and Waber, 1974).

The phase shift Δ must also be considered. This is always positive since the interaction is attractive for the $p_{1/2}$ wave and repulsive for the $p_{3/2}$ wave (Ong and Manson, 1979). These phase shifts have been calculated for the outer s subshell of the inert gases neon through xenon using the Dirac-Fock model by Ong and Manson (1979). The largest shift was found for xenon which is in line with the increasing importance of spin-orbit coupling with increasing z (Fano, 1970). However the phase shift difference was found to be quite small even though the calculated value of β , especially for xenon, deviated significantly from 2 as shown in Figure 1.10. Thus, in this case, the main cause of the variation in β appears to be the ratio of the matrix elements (Ong and Manson, 1979).

The variation of the matrix element ratio is most extreme where either channel goes through a Cooper minimum (Cooper, 1962). Thus if $R_{3/2} = 0$, then $\beta = 0$ while if $R_{1/2} = 0$, then $\beta = 1$. Due to the differences in the matrix elements, it is possible that the minima will be at different energies. In fact this is known to occur and is used to explain the existence of a non-zero Cooper minimum in the photo-ionization of alkali metals (Walker and Waber, 1973(b), Fano and Cooper, 1968). Figure 1.11 shows an example of the variation in β that can occur when these minima are at different energies. It is for the $6s$ state of cesium (Ong and Manson, 1978) and in the energy range considered, β varies from 1.6 to -1 and the two arrows indicate the positions at which $R_{1/2} = 0$ and $R_{3/2} = 0$. Here again the phase shift difference is very small in this region and the variation of β with energy predominantly due to a difference in the matrix elements (Huang and Starace, 1979).

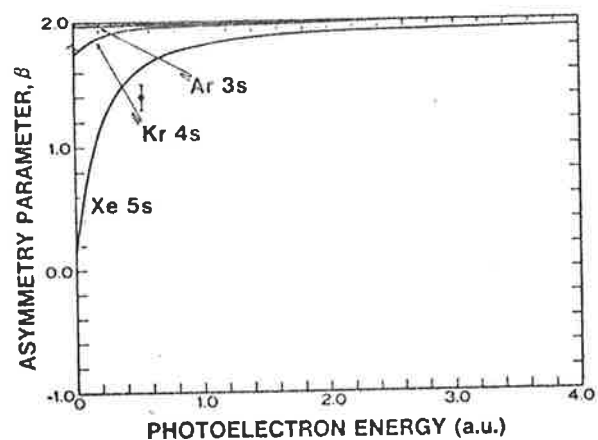


FIG. 1.10 Asymmetry parameter for the outer s electrons of argon, krypton and xenon calculated using Dirac-Fock formulation (Ong and Manson, 1979). Data point for xenon 5s from Dehmer and Dill (1976b).

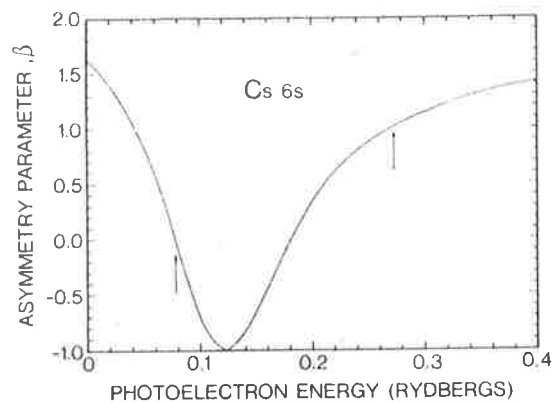


FIG 1.11 A symmetry parameter for Cesium 6s (Ong and Manson, 1978). The left hand arrow indicates the position where $R_{1/2} = 0$ and the right hand arrow $R_{3/2} = 0$.

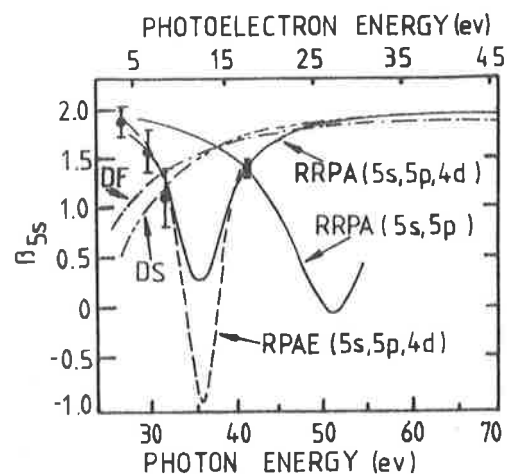


FIG 1.12 Theoretical and experimental asymmetry parameters for Xe $5s \rightarrow \epsilon p$ (from White *et al*, 1979).

Experiment: circles, White *et al* (1979); squares, Dehmer and Dill (1976b)

Theory: long-and-short dashed line, Walker and Waber, 1974; dash-dotted line, Ong and Manson (1978); long-dashed line, Cherepkov (1978); solid line, Johnson and Cheng (1978).

Returning to the Dirac-Fock calculation for xenon shown in Figure 1.10, the low value of β near threshold is due to a Cooper minimum in the $j = \frac{3}{2}$ channel just below threshold (Ong and Manson, 1979). However, experimentally the minimum in the 5s cross section occurs above threshold (Samson and Gardner, 1974; Gustafsson, 1977). This discrepancy is not surprising since it has already been shown in Section 1.3.2 that the correct location of the minimum requires the inclusion of electron correlations. Thus the relativistic random phase approximation used by Johnson and Cheng (1978) gives a good fit to the experimental data of Dehmer and Dill (1976b) and White *et al* (1979) as shown in Figure 1.12. Calculations with both two shell (5s + 5p) correlation and three shell (5s + 5p + 4d) have been done and as expected the three shell correlation provides a better fit to the theory. Also shown is a non-relativistic RPAE (5s + 5p + 4d) calculation of Cherepkov (1978). It also fits the experimental data, however it disagrees with the RRPA calculation as to the depth of the minimum in β .

Thus far the discussion has centred around the angular distribution of s electrons and in particular for xenon since this dramatically shows the result of spin-orbit coupling. Other experimental examples include the splitting of the outer p subshell of the inert gases with xenon again showing the largest effect. However a discussion of this will be postponed to Chapter Three.

A further example is the angular distribution of photoelectrons from mercury which has yielded different values of β depending on whether the ion is left in the $^2D_{5/2}$ or $^2D_{3/2}$ state (Niehaus and Ruf, 1971; Harrison, 1970). From a comparison with a non-relativistic

Hartree-Slater type calculation, Manson (1973a) suggested that the difference was predominantly due to the kinetic energy effect, although a relativistic Dirac-Slater calculation by Walker and Waber (1974) has shown a small difference in β for the $5d_{5/2}$ and $5d_{3/2}$ electrons separate from the kinetic energy effect. However, further work, both experimental and theoretical is required in this example.

One further anomaly is for photoelectrons from cadmium ionized by 58.4 nm radiation. Harrison (1970) measured a β value of $1.5 \pm .13$ for the ion in the $^2D_{5/2}$ state and $-.12 \pm .03$ for the $^2D_{3/2}$ state. This is larger than the difference found with mercury and is somewhat difficult to understand since both cadmium and mercury have the same outer subshell structure d^1s^2 but cadmium has a lower Z for which relativistic effects should be less. Theoretical calculations that have been performed are a Dirac-Slater calculation by Walker and Waber (1974) and a non-relativistic many-body perturbation theory calculation by Carter and Kelly (1978). However, there is a discrepancy between theory and experiment which indicates the need for more detailed calculations (Theodosiou, 1979).

1.3.6 AUTOIONIZATION

The emission of an electron through autoionization is a two step process. Firstly, there is a resonant absorption of a photon which raises one or more electrons to an upper level producing an excited state. The energy required for this transition may be greater than the ionization potential of a more loosely bound electron. In this case, the system may be viewed as the overlap of an excited state with the continuum. This results in a mixing of the two states and the possibility of a

radiationless transition between the two. However, once into the continuous state, the photoelectron is emitted, leaving the ion.

Each autoionization resonance appears as a peak in the cross section as can be seen in Figure 1.13 for the photoabsorption by xenon between the $^2P_{1/2}$ and $^2P_{3/2}$ thresholds. It is then to be expected that a similar plot of β through a resonance will show pronounced structure. In fact, possibly even more so than the cross section since whereas the cross section depends on the squares of the photoionization amplitudes, β depends on the moduli and phases of the amplitudes (Dill, 1973).

The extended nature of the interaction between the electron and the core generally results in the interaction being anisotropic (Dill, 1973) and the Cooper-Zare model is thus insufficient to analyse the phenomenon. Continuing with the angular momentum transfer formulation discussed in Section 1.3.3, this means there are values of j_t other than $j_t = \ell_0$. An examination of autoionization in xenon and mercury by Dill (1973) has shown that these alternate values of j_t are due to anisotropic interaction between the outgoing electron and the ion core and the occurrence of spin orbit coupling.

Samson and Gardner (1973) have measured β through part of the autoionizing structure of xenon between the $^2P_{3/2}$ and $^2P_{1/2}$ thresholds. The measured variation shows β oscillating over a large range through the resonance. This is in good agreement with the calculations of Dill (1973) where the β value was found to have contributions from two channels, one of which is parity favored ($j_t = 1$), the other parity unfavored ($j_t = 2$). The parity unfavored value is due to spin orbit

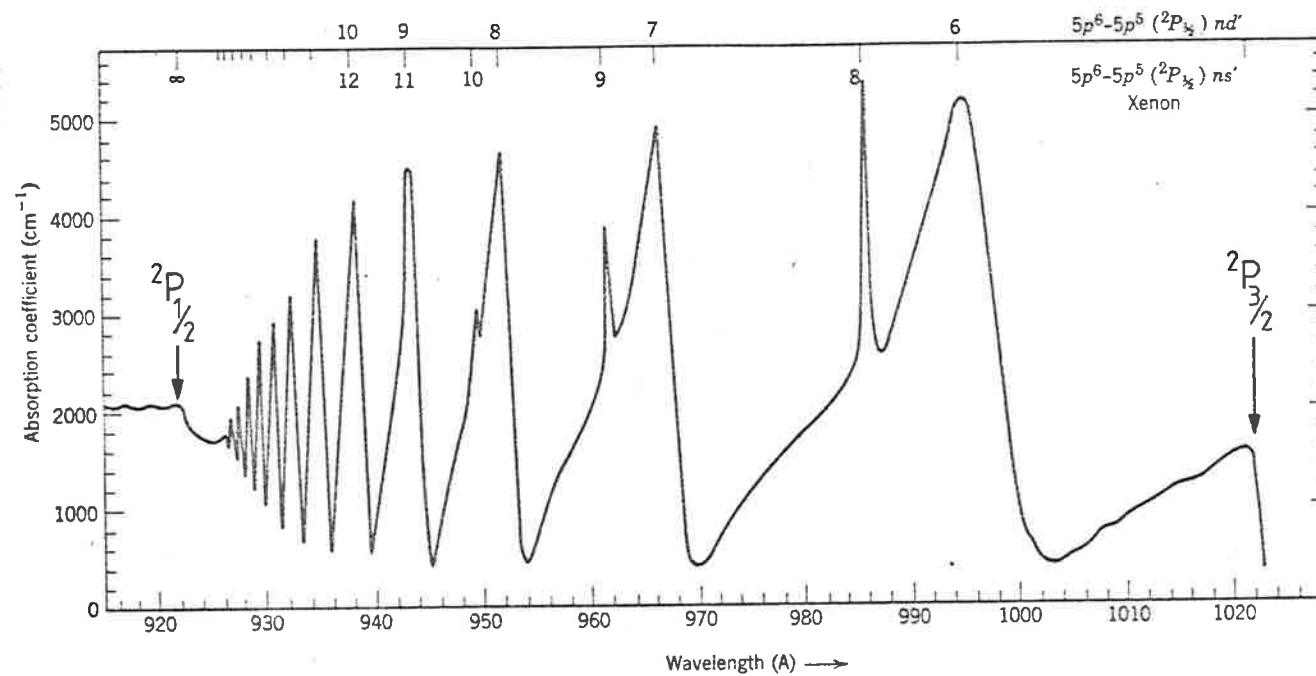


FIG 1.13 Photoabsorption coefficient through a series of autoionizing resonances between the $^2P_{1/2}$ and $^2P_{3/2}$ thresholds for xenon (from Samson, 1967).

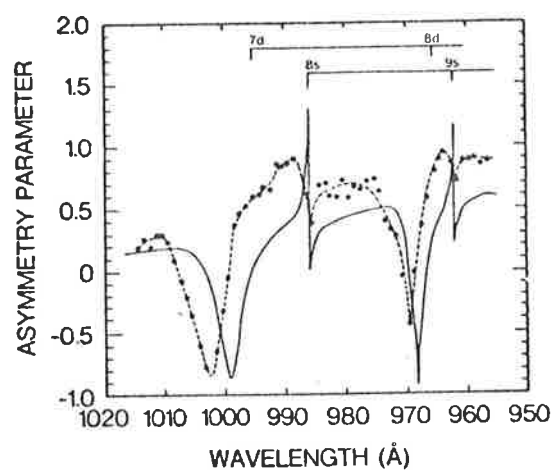


FIG. 1.14 The asymmetry parameter for xenon 5p as a function of wavelength through an autoionizing resonance between the $^2P_{3/2}$ and $^2P_{1/2}$ thresholds. Theoretical calculation (solid line), Dill (1973). Experimental data, Samson and Gardner, (1973).

interaction and the resultant breakdown in LS coupling (Dill, 1973).

A measurement of the photoelectrons from mercury leaving the ion in the $^2S_{1/2}$ state by Niehaus and Ruf (1972) at 104.8 nm and 106.6 nm yielded angular distribution parameters of $2.13 \pm .1$ and $1.25 \pm .1$ respectively. The 106.6 nm line falls on the high energy shoulder of an autoionizing level, and the large difference in the β 's indicates the presence of parity unfavored ionization (Dill, 1973).

Calculations have also been carried out for neon and argon ($n s n p^6 m p$ state) by Kabachnik and Sazhina (1976). However, both theoretically and experimentally, information on the variation of β through a resonance is scarce and it represents an, as yet, relatively untapped source of information on resonance photoionization. It is expected that wherever there is autoionization, resonances in β will also occur (Dill, 1973).

1.4 MOLECULAR PHOTOIONIZATION

In molecular photoionization, part of the photon energy can contribute to rotation and vibration of the molecule. For the simplest case of a diatomic molecule, the vibration is a variation in the inter-nuclear distance, that is a stretching and contraction of the bond, while rotation is a motion about the centre of mass of the molecule. A further possibility is the dissociation of the molecule, but that will not be considered here.

The Einstein equation now becomes,

$$\text{Photoelectron energy} = hc/\lambda - \text{I.P.} - E_{\text{ROT}} - E_{\text{VIB}} \quad 1.37$$

This results in a series of photoelectron energies determined not only by the electronic ionization potential, but also by the vibrational and rotational state of the ion. However, the spacing of vibrational levels is about an order of magnitude smaller than that for the electronic states and the spacing for the rotational levels is smaller again. Thus within each ionic state there are a series of vibrational states, and within those a series of rotational states. Photoelectron spectrometers are generally able to resolve vibrational structure, but rotational structure is difficult to fully resolve (Gardner and Samson, 1976).

A photoelectron spectrum showing vibrational structure for the different ionic states of carbon monoxide is shown in Figure 1.15. The spectrum is shown on a vertical energy axis on the left side, while on the right are the corresponding potential wells and wavefunctions. Being diatomic it has only one vibrational mode, namely the stretching and contraction of the carbon-oxygen bond. It can therefore be

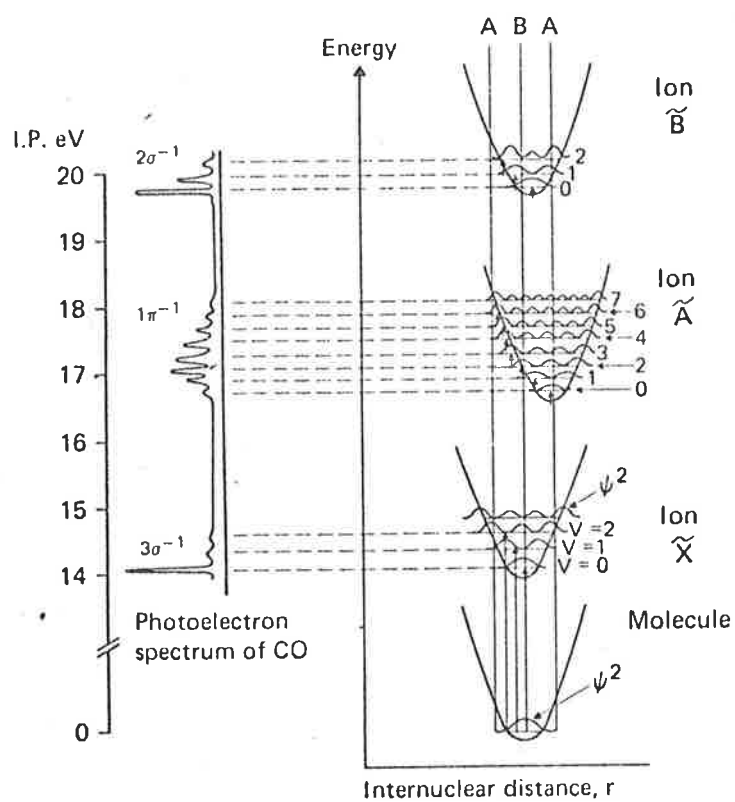


FIG. 1.15 Potential energy wells for CO for the ground state of the molecule and the first three states of the ion. Also shown are the vibrational levels and the photoelectron spectrum produced from 58.4 nm photons. (from Brundle and Baker 1977)).

represented by a two-dimensional diagram with energy on the y-axis and internuclear spacing on the x-axis.

The transitions are shown from the lowest vibrational level of the molecule since it is assumed in room temperature single photon EUV photoelectron spectroscopy that all molecules are in this state. Transitions to the lowest vibrational level of the ion are termed adiabatic transitions, whilst the transition to the vibrational level which gives the maximum photoelectron intensity is the vertical transition. Referring to Figure 1.15 and observing the photoelectron spectrum on the left, it can be seen that for the X state of the ion the vertical and adiabatic transitions coincide, while for the A state, the vertical transition is a transition to the $v=2$ level. In most cases there are separate ionization potentials associated with the two transition types.

Molecules introduce two major complications over atoms. Firstly the existence of rotational and vibrational structure increases the complexity of the spectrum and secondly, the multicentred nature of the nuclear potential makes the calculations more difficult. The first simplifying step is to separate the electronic and nuclear motions and consider the relative effects of each. This results in the adiabatic approximation, which is discussed in Section 1.4.1, and also the Franck-Condon factorization (Section 1.4.2) which gives a measure of the cross-section for photoionization to different vibrational states of the ion.

Section 1.5 is concerned with the theoretical calculations of the cross section. The difficulty that arises here is in the handling of the multi-centred nuclear potential intrinsic to molecules, and some

of the techniques that are employed are discussed. Section 1.5.2 draws on experimental measurements to provide some intercomparison between theory and experiment. However, the complexity of molecular calculations means that this comparison is less satisfying than was the case for atoms.

Finally, in Sections 1.5.3 and 1.5.4, the angular distribution for transitions between different vibrational and rotational states is discussed. This is a relatively new area that is slowly being expanded, especially for the vibrational states. However, the difficulty in resolving rotational structure has led to a paucity of results in this area.

1.4.1 ADIABATIC APPROXIMATION

The complete description of a molecule is a composite of the motion of the electrons and the oscillation and rotation of the nuclei. However, the mass of the electron is considerably less than that of the nuclei, and hence the electrons travel much faster. The adiabatic approximation states that as a first approximation for the electronic wavefunction, we can assume the nuclei are at rest.

A sufficient condition for its application is that the frequency of nuclear vibrations is small compared with the frequencies of the electronic transitions (Davydov, 1976). Thus,

$$h\omega \ll | \epsilon_m(R) - \epsilon_n(R) | \quad 1.38$$

where ω is the frequency of the nuclear vibrations and $| \epsilon_m(R) - \epsilon_n(R) |$ is the energy difference between the two levels of the electron motion. The applicability therefore rests on the proportion of energy

contributed by the rotation and vibration to the mean energy (Fano and Fano, 1972). Born and Oppenheimer (1927) expanded the energy of the molecule in a power series in $(Me/M)^{1/4}$. From this, the ratio of vibrational energy to electronic energy is of the order of $(Me/M)^{1/2}$, while for rotational it is of the order of (Me/M) . Since the ratio (Me/M) is much less than one, the use of the adiabatic approximation as a first approximation seems reasonable.

1.4.2 FRANCK-CONDON PRINCIPLE

An indication of the relative strengths of transitions to various vibrational levels can be gained from the Franck-Condon principle (Franck, 1925; Condon, 1928). This states that the time taken for the transition is short compared with the vibrational period and hence the internuclear separation and velocity are constant for the duration of the photoionization.

Again referring to the diatomic molecule in Figure 1.15, this means that the most probable transition is a vertical transition whereas the adiabatic transition when it involves a change in the internuclear spacing, is less likely. Furthermore, since classically the molecule spends most of its time close to the edge of the well, the most probable transition is to the vibrational state closest to the point where the vertical line from the initial state crosses the ionic potential curve.

Quantum mechanically, the intensity is given by (Herzberg, 1950),

$$I \propto \bar{R}_e^2 \left[\int \psi_v' \psi_v'' dr \right]^2 \quad 1.39$$

where $\bar{R}_e$ is the mean or equilibrium value of the electronic transition

moment. The mean value is used since the electronic wave function has only a weak dependence on the internuclear separation for small displacements from its mean position (Davydov , 1976). The squared integral is the Franck-Condon factor for the transition between the v' and v'' vibrational states and is the square of the overlap between the two vibrational wavefunctions. The variation of this term with vibration number is a theoretical estimate of the variation of the photoelectron intensity.

1.4.3 PRE-IONIZATION

Pre-ionization in molecules is essentially the same phenomenon as autoionization in atoms; the existence of an excited molecular state which overlaps with the continuum of an ionic state and which then decays by a radiationless transition ejecting a photoelectron. However, a molecule differs from an atom in that there are three ways it can absorb energy to reach an excited state, that is by electronic, vibrational or rotational transitions (Herzberg, 1950). Thus apart from electronic autoionization, molecules can also undergo vibrational and rotational autoionization.

Strongly linked to pre-ionization is pre-dissociation. This is a process in which the excited state overlaps a continuum corresponding to the dissociation of the molecule. Again this can eventuate from electronic, vibrational or rotational excitation.

1.5

MOLECULAR PHOTOELECTRON ANGULAR DISTRIBUTIONS

Theoretical calculations of β for molecular photoelectrons are more difficult than for the atomic case due to the multicentred form of the ionic potential, the increased degrees of freedom and the inherent lack of symmetry. As well there is the increased detail in the photoelectron spectrum from vibrational and rotational structure which needs to be considered in a complete analysis.

However, to a first approximation this structure can be ignored by assuming the vibrational and rotational periods are long compared with the time for the photoionization process. Thus for the vibrational envelope, only the ionic state need be considered and not the individual vibrational level. This is a consequence of the Franck-Condon factorization (Section 1.4.2) where the intensity is factored into a product of an average electronic transition moment and the overlap integral of the vibrational wavefunctions. Since it is the electronic transition moment that contains the "angle information", the angular distribution depends only on the ionic state and not the vibrational level. Conditions under which this breaks down will be discussed in Section 1.5.3.

Any rotational effect is normally averaged out unless it is being specifically investigated, since it is rarely resolved in experimental measurements. This is done by assuming the molecule to be stationary during the process of photoionization and then averaging over all orientations (Tully *et al*, 1968). Such an assumption would not hold near threshold, but it will be presumed to be the case for the moment and will be considered in more detail in Section 1.5.4.

1.5.1 THEORETICAL MODELS

The first problem is to formulate wavefunctions for the initial bound state of the electron and final state of a free electron. For the outgoing electron, a natural starting point is to refer it to a single centre, however, the molecular orbitals are more commonly constructed as a linear combination of atomic orbitals (LCAO) which is multi-centred. Nevertheless, there is an advantage in evaluating both the molecular orbital and the outgoing electron at a common single centre (Chapman, 1975; Buckingham *et al.*, 1970). The problem then reduces to one of radial integrals (Marr, 1975) and in principle there is no limit on the complexity of the molecules (Chapman, 1975). Furthermore, analogies can be drawn with the atomic case where a central expansion has a more natural application (Chapman and Hayes, 1977).

The single centre chosen is the centre of gravity of the molecule. However, Buckingham *et al.* (1970) have indicated that the continuum wavefunction is "determined by the potential of the ion and therefore is most closely approximated by an energy eigenfunction for a central potential where the origin is the centre of charge of the ion". Therefore the use of the technique would appear most accurate when the centre of mass and the centre of charge are close (Buckingham *et al.*, 1970).

The molecular orbital can be constructed in a single centre form by a partial wave expansion (Ritchie, 1974a),

$$\psi_i = \sum_{\ell} (\phi_{\ell m}/r) Y_{\ell m}(\theta_r, \phi_r) \quad 1.40$$

The function $Y_{\ell m}$ contains the angular dependence with θ_r, ϕ_r and r the coordinates of the electron with respect to the centre. The

functions $\phi_{\ell m}/r$ are partial waves with the notation of s wave for $\ell=0$, p wave for $\ell=1$ and so on (Marr, 1975). The summation is over ℓ , but this assumes there is only one value of m associated with each partial wave. If there is more than one value, the summation must be over quantum numbers ℓ, m .

The necessity to perform a summation of partial waves of different orbital angular momentum ℓ reflects the fact that in general for a molecule, ℓ is not a good quantum number. For an atom, within the central field approximation each orbital has a single ℓ value. But for a molecule, the more complex orbital does not have a well defined value of ℓ about the arbitrarily chosen centre. Thus the partial wave expansion can be considered as a construction of the correct "shape" from orbitals of different ℓ . Although the summation is infinite, the partial waves used will depend on the type of molecular orbital and its symmetry; for example, for gerade symmetry, the summation is limited to even values of ℓ (Marr, 1975).

Substitution of Equation 1.40 into the Schrödinger equation yields an infinite coupled set of differential equations. To achieve a solution, the series is normally severely truncated (Temkin, 1963; Cohen and Coulson, 1961). The rationale for this is the presence in the equation of the centrifugal term which guarantees that as one goes to higher and higher ℓ values, the amplitude of the corresponding radial terms gets more and more depressed in the region of interaction" (Temkin, 1963).

Alternately, the molecular orbital can be constructed in the LCAO form and converted into single centre by the transformation given by Faisal (1970).

The wavefunction for the outgoing electron can similarly be written as a sum of partial waves,

$$\psi_f = \sum_{\ell_1} (\phi_{\ell_1 m_1} / r) Y_{\ell_1 m_1}(\theta_r, \phi_r) \quad 1.41$$

where the quantum numbers (ℓ_1, m_1) refer to the outgoing electron and $\phi_{\ell_1 m_1}$ is the radial wavefunction.

The simplest single centre form for the ejected electron is a plane wave, that is the wavefunction used is that of a free electron. This however, ignores both the close-in electron/ion interaction and the coulomb field of the ion. The result is that when used in the velocity formulation, the photoelectron angular distribution peaks along the electric vector of the radiation resulting in a β of 2 for all energies (Thiel and Schweig, 1972; Schweig and Thiel, 1974; Rabalais *et al*, 1974).

Some influence of the molecular potential can be injected into the problem by orthogonalising the plane wave to all occupied molecular orbitals (Rabalais and Debies, 1974; Rabalais *et al*, 1974; Debies and Rabalais, 1975) but this still ignores the coulomb field of the ion.

Iwata and Nagakura (1974) have used orthogonalised hydrogen-like continuum functions which thus include both the coulomb field and the orthogonalisation to occupied orbitals. However, this is only likely to apply for the photoionization of orbitals far from the nucleus or at high energies where the effect of the anisotropic molecular field on the electron is small. As well, it is known from atomic photoelectron angular distribution studies that both the coulomb and non-coulomb parts of the

field need to be considered to obtain the correct phase shift information.

If the general partial wave expansion given in Equation 1.41 is used for the outgoing electron, the solution for the radial wavefunction is made complicated by coupling between the partial waves. This arises as follows. Consider the sum of partial waves required to result in an outgoing wave which asymptotically has the orbital angular momentum quantum number ℓ_1' and magnetic quantum number m_1' . This is given by,

$$\psi_{\ell_1' m_1'} = \sum_{\ell_1, m_1} (\phi_{\ell_1 \ell_1' m_1 m_1} / r) Y_{\ell_1 m_1}(\theta_r, \phi_r') \quad 1.42$$

This can then be substituted into the Schrödinger equation. Multiplying throughout by $Y_{\ell_1 m_1}^*(\theta_r, \phi_r')$ and invoking orthogonality yields,

$$\begin{aligned} \left(\frac{d^2}{dr^2} - \frac{\ell_1(\ell_1+1)}{r^2} - U_{\ell_1 \ell_1 m_1 m_1} + k^2 \right) \phi_{\ell_1 \ell_1 m_1 m_1} \\ = \sum_{\substack{\ell_1' \neq \ell_1 \\ m_1' \neq m_1}} U_{\ell_1 \ell_1' m_1 m_1'} \phi_{\ell_1 \ell_1' m_1 m_1'} \end{aligned} \quad 1.43$$

This equation assumes fixed nuclei and the electron initially in the ground state (Ritchie, 1974a); also the use of incoming boundary conditions (Ritchie, 1974a). The function $U_{\ell_1 \ell_1' m_1 m_1'}$ is defined (Ritchie, 1974a, 1974b),

$$U_{\ell_1 \ell_1' m_1 m_1'} = \frac{2m}{\hbar^2} \int d\Omega Y_{\ell_1 m_1}^* V_{e^-, A^+} Y_{\ell_1' m_1'}$$

where V_{e^-, A^+} is the effective electron-molecular ion potential. In general, this is a complicated function with an exact form only possible

for simple systems such as H_2^+ (Ritchie, 1974a) while for larger molecules, functional forms need to be constructed, phenomenologically (Ritchie, 1974b).

It is the right hand side of Equation 1.43 that arises from the anisotropic interaction. The equation represents a set of coupled differential equations with the order of the coupling determined by the number of terms retained in the coupling term on the right hand side (Chapman, 1975). There is no general analytic method for decoupling the equations and approximate techniques must be used (Ritchie, 1974a; Chapman, 1975). A necessary condition on the use of the single centre technique, is that the series expansions converge, preferably within a few terms. Thus for the initial orbital, it relates to the number of terms necessary for the series to converge to the point where it has well approximated the singularities in the potential due to the nuclei. Ritchie (1974b) has found this to be a function of internuclear spacing with the result that the single centre expansion may not be useful for very long bond lengths. However, it can be said that provided the series for the bound orbital is sufficiently convergent, then the single centre form of the continuum wavefunction will also be accurate, provided the electron velocity is comparable to the orbital velocity (Ritchie, 1974b).

The form of the differential cross section, when a partial wave expansion is used, can be considered as composed of two types of terms. Firstly, there is the incoherent sum of components from each partial wave and secondly, a set of interference terms between the partial waves (Chapman and Hayes, 1977).

The alternative to the single-centred approach is the multi-centred technique. An example is the use of an ellipsoidal coordinate

system (Shaw and Berry, 1972) but this is only appropriate for diatomic molecules.

A more general multi-centred technique is the multiple scattering method used by Dill and Dehmer (1974) where the molecular potential is represented by a cluster of non-overlapping spherical potentials about each atomic site and one surrounding the molecule (Dehmer and Dill, 1976a). Being a multi-centred approach, it intrinsically includes the anisotropy of the molecular field due to the nuclei and hence could be expected to give a good indication of the anisotropic electron/ion interaction (Wallace *et al*, 1979).

Initial calculations dealt with inner shell electrons, namely the k shell of nitrogen and carbon monoxide (Dehmer and Dill, 1976). Here the initial state of the electron is closely associated with one particular atom and can be considered localised within that atomic sphere. This localisation also means that the outgoing electron should be a p wave ($\ell=1$) with a resultant β of 2. However, the anisotropic electron/ion interaction scatters the electron into alternate ℓ values, resulting in β deviating significantly from 2 (Dehmer, 1978) for both nitrogen and carbon monoxide. The technique has also been applied to the valence electrons of nitrogen and carbon monoxide (Wallace *et al*, 1979).

1.5.2 THEORETICAL CALCULATIONS

The difficulty in calculating the angular distribution parameter for molecular photoionization has limited the range of molecules studied. However, the simplest molecule, hydrogen, has been extensively analyzed (Dill, 1972; Shaw and Berry, 1972; Tully *et al*,

1968; Ritchie, 1975; Hirota, 1976; Huang and Ellison, 1974; Dutta *et al*, 1977) and there are a range of experimental results for comparison (Niehaus and Ruf, 1971; Carlson and Jonas, 1971; McGowan *et al*, 1969; Marr *et al*, 1979b). Figure 1.16 shows some of the experimental and theoretical results. Although there is poor agreement among the experimental results, they in general show a lower value of β than predicted by theory. It has been suggested that this is due to a difference in the β 's for the $\Delta N=0$ and $\Delta N= \pm 2$ rotational structure (Marr *et al*, 1979b). The experimental results include both branches but the calculations, by averaging over molecular orientations, apply to the $\Delta N=0$ branch. The difference in β 's for the alternate branches will be discussed further in Section 1.5.4, but it illustrates that even for hydrogen, the calculations must include many details of the molecular structure.

Calculations for other diatomic molecules include the orthogonalised plane wave calculation for nitrogen (Rabalais *et al*, 1974), the pseudopotential approximation calculation of Duzy and Berry (1976) also for nitrogen and the deformed coulomb potential calculation of Hirota (1976) for nitrogen, carbon monoxide and oxygen. Multiple scattering calculations have been done for nitrogen and carbon monoxide for both the K shell photoionization (Dehmer and Dill, 1976a; Dill *et al*, 1978, 1979; Dehmer and Dill, 1975) and the valence shell electrons (Wallace *et al*, 1979). The majority of experimental measurements for these gases have been done at the few fixed wavelengths available from the resonance radiation of inert gases (McGowan *et al*, 1969; Carlson

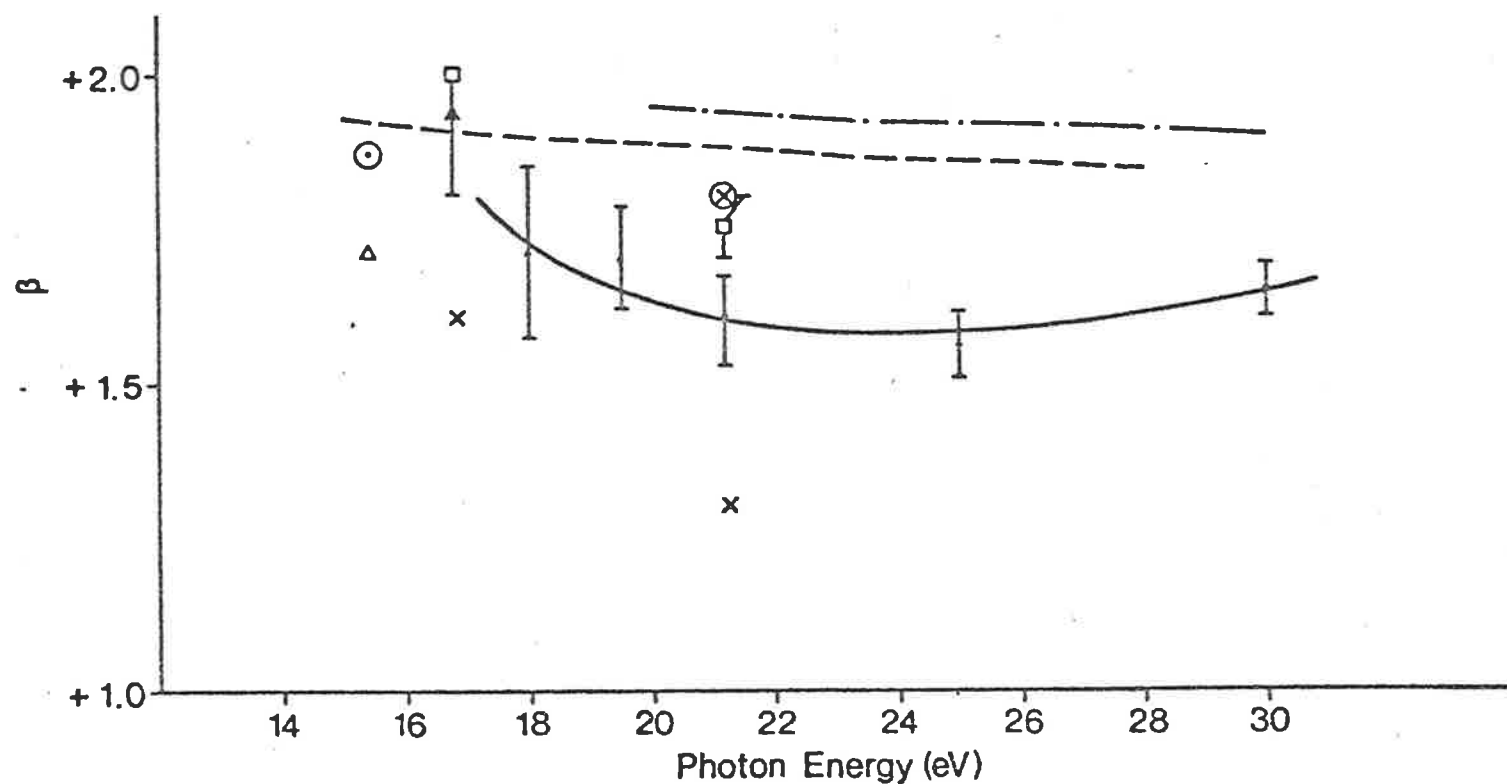


FIG. 1.16 Asymmetry parameter for ground state H_2 as a function of photon energy (Marr, 1979b).

Theoretical results : - . - . - Dutta *et al* (1977); --- Hirota (1976);
 Δ Dill (1972); $\odot$ Chang, 1978.

Experimental results : $\bullet$, and solid line, Marr (1979b)
 $\times$, McGowen *et al* (1969); $\otimes$, Mintz and Kupperman (1978);
 $\square$ Carlson *et al* (1972); $\blacktriangle$ Niehaus and Ruf (1971).

and Jonas, 1971; Hancock and Samson, 1976; Carlson *et al*, 1972). However, recently the use of synchrotron radiation has permitted wavelength dependent studies of the angular distributions for photoelectrons from nitrogen and carbon monoxide where the ion is left in the X, A or B state (Marr *et al*, 1979a) and oxygen for the X state (McCoy *et al*, 1978). This allows a comparison between theory and experiment and examples are given in Chapter Three, but to date, no one theory is able to adequately reproduce all the results, although in a number of cases, the theory is able to reproduce the trend in the data (Marr *et al*, 1979a; Wallace *et al*, 1979).

There is a need for further measurements as well as increased sophistication in the models. For example more advanced theories could include the effect of nuclear motion. This is generally avoided by invoking the adiabatic approximation, however some indication of its importance can be seen in the work of Dehmer *et al* (1979). Here a strong dependence of the dipole amplitude on the internuclear distance has been found for nitrogen in the vicinity of the shape resonance in the σ_u channel. Also generally ignored is the correlation between the outgoing electron and the other ionic electrons (Wallace *et al*, 1979).

Calculations have also been carried out for polyatomic molecules such as CH_3 , CH_4 (Ritchie, 1974b), H_2O , H_2S and NH_3 (Iwata and Nagakura, 1974). Asymmetry parameters for some of these have been measured (Carlson and McGuire, 1972/73; Hancock and Samson, 1976) but at present, no correlation between theory and experiment has been attempted. Indeed the situation is true of polyatomic molecules in

general, where further theoretical calculations are required especially if angular distributions are to fulfil their chemical role as orbital identifiers (Sell *et al*, 1978).

Apart from using experimental angular distributions as a check for theoretical calculations, it may be possible to have a hybrid situation where experimental data is used to extract information from the theoretical model. This has been the main theme in a series of publications by Ritchie (1974(a), 1974(b), 1974(c), 1975). - to use the measurement of β to extract the parameters used in the expansion of the molecular orbital.

This still requires an accurate expression for the continuum wavefunction, but he argues that, in general, this is more easily obtained than the wavefunction for the initial orbital. It is based on the argument that the "size" of the continuum wavefunction is large compared with the size of the molecule, and hence is largely influenced by long range forces. Thus the continuum wavefunction is more easily calculated than the orbital wavefunction which is affected by forces close to the nuclei (Ritchie, 1975).

Sichel (1970) has also suggested the use of angular distribution measurements to determine molecular orbital parameters, but the technique relies on the resolution of rotational structure.

1.5.3 VIBRATIONAL STRUCTURE

Provided autoionization is not present, it is expected that the angular distribution of the photoelectron should be independent of the final vibrational state of the ion. As explained in Section 1.5, this follows from the Franck-Condon factorization where the photoelectron

intensity is factored into an average electronic matrix element and the overlap integral of the vibrational part of the wavefunctions. It is the electronic matrix element that contains the angular information and this is independent of the vibrational state of the ion. At most there could be a small difference in β across a vibrational envelope due to different ionic vibrational states resulting in slightly different free electron energies and β is known to be energy dependent.

For a large number of cases, this approximation appears sufficient (Carlson and Jonas, 1971), however, there have been a significant number of measurements where the angular distribution has been found to depend on the vibrational state of the ion (Carlson and Jonas, 1971; Carlson, 1971; Sell *et al*, 1979; Mintz and Kupperman, 1978; Hancock and Samson, 1976; Mattsson *et al*, 1977). These cases suggest either the presence of alternate paths to the same state as occurs with autoionization versus direct ionization, or a breakdown in the Franck-Condon factorization. This would happen if the electronic matrix element were not independent of the internuclear distance (Kalman, 1977).

An example where autoionization is the cause has been shown clearly in the case of oxygen ionized by 16.85 eV photons (Carlson, 1971). For the ground state of the ion, some fourteen vibrational levels were detected which fell into two distinct groups; a large envelope of ten lines with average β of about zero, and a smaller envelope of four lines with a β of about $-.6$. It has been suggested (Carlson, 1971) that the two groups are formed by different paths, the zero β vibrational envelope by autoionization and the $\beta = -.6$ envelope by direct ionization. Evidence for this can be found in spectrum obtained when 21.2 eV photons are used. At this energy, which is away from the resonance, only the smaller envelope of lines occurs.

Carbon monoxide is another molecule that displays anomalies in the angular distribution for different ionic vibrational states (Carlson and Jonas, 1971; Hancock and Samson, 1976; Sell *et al*, 1979). This is most apparent in the data of Sell *et al*, (1979) who have measured 24 vibrational transitions belonging to the first three ionic states at the wavelength 58.4 nm. Here again the anomaly has been attributed to autoionization (Sell *et al*, 1979) and this emphasises the sensitivity of angular distribution measurements to resonance phenomena.

However, autoionization does not seem to be the answer for the anomaly in nitrogen ionized by 58.4 nm photons. A large difference exists between the values of β for the first two vibrational levels of the ionic ground state (Carlson, 1971; Hancock and Samson, 1976). There is no evidence of autoionization at this energy (Carlson and Jonas, 1971) and an hypothesis proposed is that the transition dipole moments vary with internuclear separation (Duzy and Berry, 1976).

A detailed analysis of this anomaly together with others in the angular distributions for nitrogen by Mintz and Kupperman (1978) failed to completely explain the phenomenon. However, more recently it has been reasoned by Dehmer *et al*, (1979) that the anomaly is due a shape resonance in the σ_u ionization channel. This causes a strong coupling between the vibrational and electronic motions and a dependence then of the dipole amplitude on the internuclear spacing. The anomalous difference in the β values for the two vibrational states arises because "transitions to alternative final vibrational states preferentially sample different regions of R [the internuclear distance]" (Dehmer *et al*, 1979).

1.5.4 ROTATIONAL STRUCTURE

The fineness of rotational structure (Gardner and Samson, 1976) has precluded its resolution in most experiments. Consequently, the majority of theoretical calculations have avoided its inclusion by assuming the molecule to be fixed in space during the photoionization period. The differential cross section is then averaged over all spatial orientations (Tully *et al*, 1968).

However, if rotation is explicitly included, the form of β contains functions involving the dependence of the coupling between the molecular rotation and the electronic orbital angular momentum (Marr, 1975). An expression for β in this case has been derived by Buckingham *et al* (1970) for the two coupling conditions, Hunds cases (a) and (b) (Marr, 1968; Herzberg, 1950) using the single centre expansion. If a temperature average over the initial and a sum over the final rotational levels is performed, their formulas reduce to the non-rotational forms derived by spatial averaging (Sichel, 1970).

The effects of rotational autoionization on the angular distribution of molecular hydrogen have been examined by Dill (1972) within the angular momentum transfer formulation. In addition, this work affords a comparison with the only experimental measurement of rotationally resolved angular distribution that has been done (Niehaus and Ruf, 1971). Both reveal different values of β depending on whether the rotational quantum number N remains the same or changes during the photoionization. For $\Delta N=0$, the primary value of j_t is 0 and hence $\beta=2$ (Dill, 1972). This agrees well with the experimental value of $1.95 \pm .03$ (Niehaus and Ruf, 1971). For $\Delta N= \pm 2$, the value of j_t is 2 with $\beta= .2$, but experimentally the value was $.85 \pm .14$. Thus whilst

the trend from $\Delta N=0$ to $\Delta N= \pm 2$ agrees with theory, the absolute value for $\Delta N= \pm 2$ does not. A possible explanation advanced by Dill (1972) is that the calculation assumed the outgoing photoelectron to be a p ($\ell=1$) wave whereas it may have a small mixture of f wave.

Alternatively, Chang (1978) has re-analysed the data of Niehaus and Ruf (1971) in a different manner and obtained the value of $.45 \pm .87$. Whilst this now overlaps the theoretical value, the very large error prevents it being able to verify the theory.

1.6 MULTIPOLE TERMS

The differential cross section can be written in a general form as the sum of Legendre polynomials (Tseng *et al*, 1978).

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \sum_{n=0}^{\infty} B_n P_n(\cos \theta) \quad 1.44$$

In the discussion thus far, the electric dipole approximation has been assumed. That is, the exponential term in the differential cross section (equations 1.2 and 1.3) is expanded into a Taylor series,

$$e^{i \underline{k} \cdot \underline{r}} = 1 + i \underline{k} \cdot \underline{r} + \frac{1}{2} (i \underline{k} \cdot \underline{r})^2 + \dots \quad 1.45$$

and the series approximated by the first term. In this case only the B_0 and B_2 terms are non zero, and for polarized light the expression is,

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} (1 + \beta P_2(\cos \theta)) \quad 1.46$$

The introduction of higher terms in the expansion would include $\underline{k}$, the photon direction, and the back/forward symmetry of the angular distribution would be lost. Considering the second term in the expansion of the exponential (i.e. $i \underline{k} \cdot \underline{r}$), its inclusion introduces electric quadrupole and magnetic dipole terms (Bethe and Salpeter, 1957). These cause further orders of the Legendre polynomial other than $P_2(\cos \theta)$ to appear in the differential cross section. Also there are interference terms between the multipoles (Cooper and Zare, 1969) and the cross section now has the form

$$\sigma = \sigma^{E_1 \cdot E_1} + \sigma^{E_1 \cdot E_2} + \sigma^{E_1 \cdot M_1} + \sigma^{E_2 \cdot M_1} + \sigma^{E_2 \cdot E_2} + \sigma^{M_1 \cdot M_1}$$

where $\mathbf{E}_1, \mathbf{E}_2$ and $\mathbf{M}_1$ are the electric dipole, electric quadrupole and magnetic dipole terms respectively (Tully *et al*, 1968). The matrix elements for the electric quadrupole and magnetic dipole are of the order v/c smaller than that of the electric dipole, where v is the velocity of the ejected electron. Since the cross sections $\sigma^{\mathbf{E}_1 \cdot \mathbf{E}_2}$ and $\sigma^{\mathbf{E}_1 \cdot \mathbf{M}_1}$ are linear in these matrix elements, they too are smaller than the electric dipole cross section $\sigma^{\mathbf{E}_1 \cdot \mathbf{E}_1}$ by v/c . The remaining terms $\sigma^{\mathbf{E}_2 \cdot \mathbf{E}_2}$, $\sigma^{\mathbf{E}_2 \cdot \mathbf{M}_1}$ and $\sigma^{\mathbf{M}_1 \cdot \mathbf{M}_1}$ are of the order v^2/c^2 smaller than the electric dipole (Tully *et al*, 1968).

Expressions for the $\sigma^{\mathbf{E}_1 \cdot \mathbf{E}_1}$, $\sigma^{\mathbf{E}_1 \cdot \mathbf{E}_2}$ and $\sigma^{\mathbf{E}_1 \cdot \mathbf{M}_1}$ terms have been given by Tully *et al*, (1968). The $\mathbf{E}_1 \cdot \mathbf{E}_2$ interference term contains $P_1(\cos \theta)$ and $P_3(\cos \theta)$ polynomials, while $\mathbf{E}_1 \cdot \mathbf{M}_1$ contains just the $P_2(\cos \theta)$ term (Peshkin, 1970). In addition both terms have a ϕ dependence, that is they depend on the direction of the light propagation (Tully *et al*, 1968).

However, in most instances in extreme ultraviolet photo-electron spectroscopy, the photon energy is such that the velocity of the outgoing electron is very much less than the speed of light. Thus in cases where these multipole terms are needed, they will be closely linked with relativistic corrections and thus applicable to high energy photons or targets of large Z .

The effects of multipole and relativistic corrections on the coefficients B_n in the expression for the differential cross section, have been examined by Tseng *et al*, (1978). It is interesting to note that for the total cross section, integration over all angles leads to cancellation of the multipole and relativistic effects of the order

(v/c) which is not the case for the differential cross section. Thus the non-relativistic dipole approximation is expected to hold to higher energies for the total cross section than for the differential cross section (Ron *et al*, 1977).

CHAPTER 2 : THE MEASUREMENT OF PHOTOELECTRON ANGULAR DISTRIBUTIONS

2.1 INTRODUCTION

This chapter has two aspects. Firstly, to give a general overview of the techniques for measuring gaseous photoelectron angular distributions, and secondly, to give a detailed account of the experimental techniques used to obtain the results presented in Chapter 3 of this thesis.

It commences in Section 2.2 with a general discussion of the experimental methods. These basically involve the application of the equation given previously for the differential cross section in terms of β , the asymmetry parameter. Recalling Chapter 1, if we assume linearly polarized radiation, an unpolarized target and an electric dipole interaction, then the differential cross section given by,

$$\frac{d\sigma}{d\Omega} \propto 1 + \beta \left(\frac{3}{2} \cos^2(\theta) - \frac{1}{2} \right)$$

where θ is the angle between the ejected electron and the electric vector of the radiation. It was also shown in Chapter 1 that the form of the above equation is different if the incident radiation is unpolarized. Thus the experimental technique depends on the form of the radiation and the methods for unpolarized and polarized radiation are discussed separately in Sections 2.2.1 and 2.2.2 respectively. This is followed in Section 2.2.3 with a brief mention of the pseudo-photon method of obtaining angular distributions using electron-electron coincidence measurements.

Based on the discussion in Section 2.2, Section 2.3 commences with an outline of the research program objectives of which this thesis

forms the first stage. It continues in Section 2.3.1 with a discussion of the method employed to measure the angular distributions and then in Section 2.3.2 through to 2.3.4 gives a detailed description of the electron energy analyser, the vacuum equipment and mechanism to rotate the analyser.

The extreme ultraviolet source that was used is described in Section 2.4. It is a somewhat rarely used form of lamp called a charged particle oscillator. It was chosen as offering a useful source of 30.4 nm radiation. This was required to make use of the one known value of β , namely that of $\beta=2$ for helium photoelectrons, as a test of the system. As well it allowed the measurement of the angular distributions of photoelectrons produced by 30.4 nm radiation which have been less extensively measured than those from 58.4 nm.

Section 2.5 is concerned with the elimination of the earth's field in the vicinity of the analyser. This was done to improve the resolution of the analyser and also to lessen any effects the magnetic field might have on the measured angular distribution.

Section 2.6 discusses the alignment of the analyser. In the measurement of photoelectron angular distributions, the analyser must rotate about some invisible point in space. This section is concerned with the method that was used to achieve this aim with the least error.

Section 2.7 is entitled angle correction. This is concerned with a problem that occurs when the angular distribution is measured by rotating the analyser in a plane containing the light beam. It has to do with the fact that as the analyser moves away from the position at 90° to the beam, the source geometry changes and this must be corrected for before the data can be analysed. Generally this is approximated by a

simple function of the angle, but in the present work, due to the large 10° entrance aperture of the analyser, the relationship between the observed signal and the geometry was studied in some detail.

The basic system operation is described in Section 2.8. This is concerned with the intricacies of the electronics to both rotate the analyser and collect the data.

Section 2.9 deals with the actual analysis of the data. Firstly, the raw data must be converted to a set of electron counts at particular angles and then secondly, these must be analysed to find β . The assumptions made and the possible errors involved are discussed.

Finally, Section 2.10 entitled "Quality of Data" is a brief discussion on the tests that were undertaken to try and place some confidence on the measured values of β .

2.2 EXPERIMENTAL TECHNIQUES

In Chapter One, the expression for the differential cross section for an electric dipole interaction between linearly polarized light and an unpolarized target was given by,

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{POL}} = \frac{\sigma_{\text{TOT}}}{4\pi} (1 + \beta P_2(\cos \theta)) \quad 2.1$$

where β is asymmetry parameter, $P_2(\cos \theta) = \frac{3}{2} \cos^2 \theta - \frac{1}{2}$ and θ is the angle between the direction of the photoelectron and the electric vector of the radiation.

Experimentally then, it is obvious that if linearly polarized radiation is used, one need only measure the count rate as a function of θ and apply Equation 2.1 to find β . However, when polarized radiation

is used, it is more likely to be partially polarized. This would be the case if a monochromator was used (Samson and Gardner, 1973). An extension of Equation 2.1 for this case has been given by Samson (1969, 1970). Partially polarized radiation can be considered as the sum of two linearly polarized mutually perpendicular beams with random phases. If the light is incident along the z -axis and I_x, I_y the radiation components along the x and y axes, then the differential cross section is the weighted sum of the differential cross sections due to the two contributions.

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{TOT}}{4\pi(I_x + I_y)} [I_x (1 + \beta P_2 (\cos \theta_x)) + I_y (1 + \beta P_2 (\cos \theta_y))] \quad 2.2$$

where θ_x and θ_y are the angles of the photoelectron with respect to the x and y axes respectively as shown in Figure 2.1. Defining a degree of polarization $g = I_x/I_y$, the equation can be re-written (Samson, 1970),

$$\left. \frac{d\sigma}{d\Omega} \right|_{\substack{\text{PARTIALLY} \\ \text{POLARIZED}}} = \frac{\sigma_{TOT}}{4\pi} \left(1 - \frac{\beta}{2} + \frac{3\beta}{2(g+1)} (g \cos^2 \theta_x + \cos^2 \theta_y) \right) \quad 2.3$$

Thus Equation 2.3 gives the differential cross section for partially polarized light. There is the increased complication that now there are two angles to be measured, but this can be reduced to manageable form by choosing the proper plane in which to make the measurements. This will be shown in Section 2.2.2. However, it is necessary to know the degree of polarization and the methods for measuring this will also

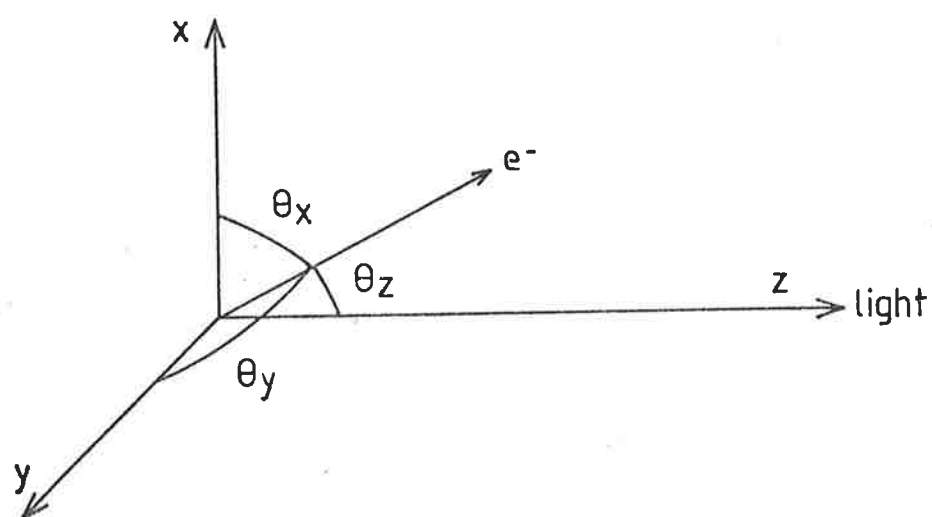


FIG 2.1. Diagram illustrating the notation used in the text.

be discussed in Section 2.2.2.

A further possibility is that the radiation is elliptically polarized. An expression for this case has been derived by Schmidt (1973). However, Samson and Starace (1975) have shown that provided the x and y coordinates of Equation 2.3 align with the major and minor axes of the ellipse, then the expression given by Schmidt (1973) reduces to Equation 2.3 above.

Lastly, there is the possibility of unpolarized light. The expression for the differential cross section in this case has already been given in Chapter One, but it can also easily be found from Equation 2.3 by setting $g = 1$.

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{UNPOL}} = \frac{\sigma_{\text{TOT}}}{4\pi} \left(1 + \frac{\beta}{2} \left(\frac{3}{2} \sin^2(\theta_z) - 1 \right) \right) \quad 2.4$$

Thus the most general expression for the experimental measurement of β is Equation 2.3. For polarized radiation there are a large number of different combinations of angles θ_x, θ_y that can be used to measure β , while for unpolarized light the cylindrical symmetry about the light beam reduces these considerably. This results in a difference in the techniques applied for polarized and unpolarized radiation and the following discussion is divided into two sections based on this division.

Also included is a discussion of the measurement of photo-electron angular distributions by electron-electron coincidence. This is given in Section 2.2.3 and although it is somewhat outside the scope of this thesis in that it does not involve extreme ultraviolet radiation, it needs to be mentioned since in theory the method is equivalent to the

measurement of angular distributions with a variable wavelength source.

2.2.1 UNPOLARIZED RADIATION

The majority of the experimental measurements of β have been made using unpolarized radiation. This is due to the widespread use of undispersed light sources which have the advantage of being simple to construct and having high intensity. The limitation though, is that only a few wavelengths are available in the EUV.

For unpolarized radiation, it is necessary to measure the photoelectron intensity as a function of the angle between the photon beam and the emerging electron. This is described by Equation 2.4.

A simple technique was used by McGowan *et al* (1969). The photoelectrons were produced at the centre of a sphere which was divided into 11 segments, each of which subtended an angle of 15 degrees at the centre. Between the photoelectron source and the collector were two grids. One was at earth potential so that the electrons were formed in a field free region, and the other was a retarding grid to select particular energy electrons. By measuring the current at each segment, the angular distribution could be investigated. Values of β were obtained for a number of gases (McGowan *et al*, 1969), but anomalous distributions that did not fit Equation 2.4 were also found (Vroom *et al*, 1969).

More sensitive measurements have since shown these anomalies to be instrumental effects (Morgenstern *et al*, 1970). One problem with this type of apparatus is the necessity to assume the collecting efficiency of each segment to be the same. Succeeding measurements have

used a small electron energy analyser that could be rotated in the plane of the beam. In that way measurements at each angle are made with the same analyser. In addition, the electrons are detected using a channel electron multiplier allowing the detection of single electrons. This will be explained in Section 2.3.3.

In most cases, electrons of more than one energy are formed and some form of energy analysis is necessary. There are a variety of techniques to do this (Steckelmacher, 1973) but only a few types have been used as rotatable analysers. Of these, the simplest is the retarding grid (Leng and Nyberg, 1977; Berkowitz *et al*, 1967). This measures the energy of the electrons by applying a voltage ramp to a grid through which the electrons must pass. Only those with an energy greater than the voltage on the grid can pass through to be detected. The resulting photoelectron spectrum consists of a series of steps where the voltage at which the step occurs indicates the energy of the photoelectron, and the height of the step the number of electrons of that energy. This is illustrated in Figure 2.2.

Such analysers are high pass energy filters and are called integral analysers. They have the advantage of simplicity and compact size but the disadvantage that determination of the step heights can be subject to poor signal to noise ratios. This arises simply because the height of the step will often involve the difference of two large numbers. Also the energy measured is the energy of the electron normal to the grid and off-axis electrons reduce the resolution.

Different from these are the dispersive analysers which behave as a band pass energy filter. Electrons from an entrance aperture are deflected electrostatically to a focus at the exit aperture. At a

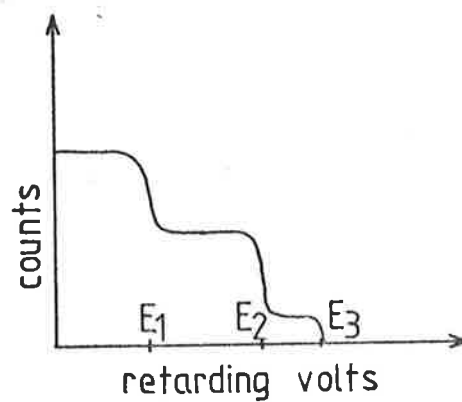
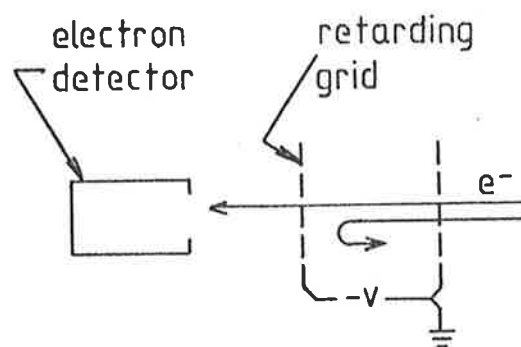


FIG 2.2 Showing the principle of the retarding grid energy analyser. The spectrum shows the result for electrons of three different energies.

particular focussing voltage, only those electrons of a certain energy will pass through. An example is the 127° analyser used by Niehaus and Ruf (1972). A pair of curved parallel plates focus the electrons after travelling 127° (Hughes and Rojansky, 1929). This is illustrated in Figure 2.3. The relationship between the voltage difference on the plates and the energy E of the electrons that pass through the analyser is,

$$V_2 - V_1 = 2 ER \log(R_1/R_2) \quad 2.5$$

where the terms are as defined in Figure 2.3.

However, the focussing is only in one dimension. Two dimensional point to point focussing can be achieved with a spherical deflector in which the electrons are injected into the field between two hemispheres and travel 180 degrees (Purcell, 1938). Such an analyser has been used by Dehmer *et al* (1975), Mason *et al* (1977) and Kobayashi and Nagakura (1975).

The necessity to rotate the analyser requires it to be small and lightweight. An alternative approach has been used by Carlson and Jonas (1971) where a fixed analyser is used, but the light beam is rotated.

A problem encountered with rotatable analysers is the variation of the source geometry with the angle. If the gas is uniform throughout the vacuum chamber, the electron source is the length of the photon beam while the source seen by the analyser is then the intersection of photon beam and the field of view of the analyser. This increases as the analyser moves to either side away from the direction normal to the beam. It is normally corrected by multiplying

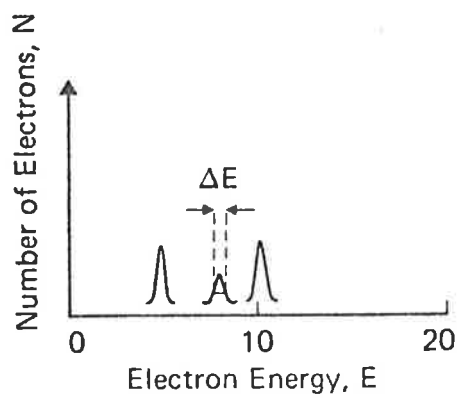
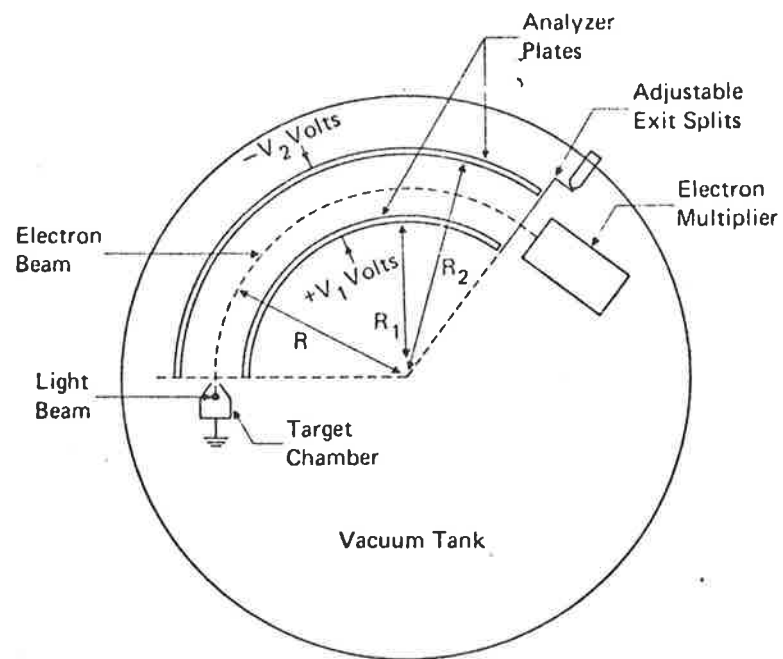


FIG 2.3 An example of a 127° analyser and the form of the resulting spectrum (from Brundle and Baker, 1977).

the electron count by the sine of the angle, but this will be discussed more fully in Section 2.7.

2.2.2 POLARIZED RADIATION

Multiple wavelength sources such as from a continuum or multilane lamp (Samson, 1967) or from synchrotron radiation (Codling, 1973) allow the measurement of the angular distribution as a function of wavelength. However, the wavelengths must be separated with a monochromator and the resultant emerging radiation is generally polarized.

If the moving analyser technique is used with polarized radiation then by reference to Equation 2.3 it is obvious that there are many alternate planes of rotation available. However, the usual one chosen is the plane normal to the beam. The formula for this configuration can easily be obtained from Equation 2.3 by setting $\theta_z = \pi/2$ and $\theta_x + \theta_y = \pi/2$ to give,

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \frac{3\beta}{2(g+1)} \left((g-1)\cos^2\theta_x + 1 \right) - \frac{\beta}{2} \right] \quad 2.6$$

This relies on the value of g , the polarization, being known and that its value is significantly different from one. An advantage of this configuration is that there is no change in the source geometry with angle unlike the case where the analyser moves in the plane of the beam.

The difficulty with using polarized radiation is the necessity to measure g , the ratio of the intensities of the x and y components. If the wavelengths being used are less than the ionization threshold of helium, that is less than 50.4 nm, then g can be

measured by recording the angular distribution of photoelectrons from helium and assuming $\beta=2$ (Torop *et al.*, 1976a). An alternative is to measure the polarization directly (Samson and Gardner, 1973; Samson, 1976) using the reflection method of Rabinovich *et al.* (1965). Either method also allows the locating of the axes of symmetry of the polarization which defines the x and y axes and hence θ_x .

A different technique for measuring β uses a polarizer to deliberately polarize radiation from an undispersed source. The electrons are then viewed at a fixed angle to the beam and the plane of polarization rotated. This technique has been used by Hancock and Samson (1976) and a diagram of the instrument is shown in Figure 2.4. Radiation passes through the polarizer where it undergoes three reflections with the entrant and emergent beams co-axial. The polarizer can be rotated to rotate the plane of polarization and the value of g was measured at about 11.5. The radiation passes to the reaction chamber where it interacts with the gas and the photoelectrons are collected in a 6-degree cone at right angles to the beam.

The main disadvantage is the 90% reduction in the lamp intensity due to the polarizer. Also, the amount of polarization varies with time due to contamination of the mirrors and g must be continually re-measured. An advantage though is the lack of moving parts within the reaction chamber. Thus the problem of varying electric fields as an analyser rotates does not exist in this case and the technique is particularly attractive for measuring the angular distribution of low energy electrons.

A similar polarizer has been used by Karlsson *et al.* (1976) using a four-fold reflection. The resultant beam is almost linearly polarized but the transmission is only 1%.

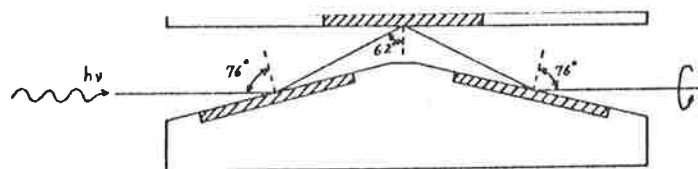


FIG. 2.4 Diagram of rotatable reflection type polarizer of Hancock and Samson (1976).

2.2.3 PSEUDO-PHOTON MEASUREMENTS

The measurement of angular distributions with pseudo-photons is a special case of electron-electron coincidence measurements. These measurements involve the firing of a beam of electrons through a gas target. This may result in the scattering of an electron from a gas atom or molecule resulting in the ejection of an electron from the target. There will then be a decrease in the energy of the scattered electron since energy is used to both ionize the target atom and provide kinetic energy for the ejected electron.

By considering the incident electrons to be fast enough for the first Born approximation (Schiff, 1968) to be used, the differential cross section for the ionization of an atom in state i to a final state j , can be shown to be given by (Manson, 1976)

$$\frac{d\sigma_{ij}(e)}{d\Omega} = \frac{4\pi a_0^2 Z^2}{T/R} \left[\frac{1}{4\pi} |M_{if}|^2 \left\{ 1 - \frac{\beta}{2} P_2(\cos \theta) \right\} \ln \frac{4T}{R} \right. \\ \left. + \gamma(\theta) + O(E/T) \right] \quad 2.7$$

where a_0 is the Bohr radius, T the kinetic energy of the incident electron, R the Rydberg energy, E the energy lost by the scattered electron, θ the angle between the ejected electron and the incident electron, β the asymmetry parameter, M_{if} the matrix element and γ is a function which is independent of T . Pseudo-photon spectroscopy considers a special case of the above where the initial energy of the incident electron is large and the momentum transferred to the ejected electron is small, that is $T/R \gg 1$ and $E/T \ll 1$. In that case, only the first term of Equation 2.7 above is significant (Manson, 1976) and as can be seen, the equation then is simply the expression for the

differential cross section for photoionization in the electric dipole approximation. Thus under the two conditions of high initial energy and small momentum transfer, the scattering process is equivalent to photoionization.

A pictorial argument as to why this is the case, is given as follows. We are considering only glancing collisions of high energy electrons where the momentum transferred to the ejected electron is small and thus this momentum will be almost perpendicular to the direction of the incident projectile. The situation then is nearly equivalent to photoionization with radiation in same direction as the incident electron and the polarization direction in the direction of the momentum transferred (Kim, 1972; Van der Wiel and Brion, 1972/73(a)).

The technique has been used by Van der Wiel and Brion (1972/73(a); 1972/73(b)) using a pair of fixed analysers, one to measure the forward scattered electrons, and the other to detect electrons ejected at right angles to the incident electron beam. In line with the criteria discussed above the incident energy is 3.5 KeV and the maximum value of the momentum transferred is .2 au which occurs for a scattering angle of 1.2×10^{-2} radians at an energy loss of 50 eV.

The scattered electron analyser is set to detect electrons that have undergone an energy loss of E electron volts. This is equivalent to the photon energy in photoionization. Then electrons detected by the 90° detector in coincidence with these are energy analysed. The energy of these ejected electrons will be equal to the difference between the energy lost by the scattered beam and the ionization potential of the ejected electron.

Thus the scattered electron analyser measures the number of scattering events with a particular energy difference while the ninety degree analyser measures the number of those events which result in an electron being ejected in that particular direction. The relative value of β is then given by (Van der Wiel and Brion, 1972/73(b))

$$\beta(e) \propto \frac{1}{C(E)} \left[\frac{N_c(E,e)}{N(E)} T(e) - 1 \right] \quad 2.8$$

where E is the energy loss, e the energy of the ejected electron, $N(E)$ the number of forward scattered electrons and $N_c(E,e)$ the number of coincidence counts. The function $C(E)$ is a function of the energy loss and is obtained from an integration over all momentum transfers that contribute to the forward scattered signal (Van der Wiel and Brion, 1972/73(a); Branton and Brion, 1974). The function $T(e)$ is the correction function for the transmission of the ejected energy analyser and its relative shape can be found by applying Equation 2.8 to a measurement of the ionization of helium and assuming $\beta=2$.

Thus the variation of β with energy loss or "photon energy" can be found. However, since the data is only relative, at least one absolute value obtained from photoionization theory or measurements is needed to convert the variation to absolute.

A qualification on Equation 2.8 is that it assumes there is only one process contributing to the measurement of the forward scattered signal. If the energy loss being measured is such that it coincides with more than one ionization potential, then the resulting β value will be in error by an amount dependent on their relative cross sections.

The technique has been used to measure the angular distributions of the outer p subshell electrons from neon, argon and krypton (Van der Wiel and Brion 1972/73(b); Branton and Brion, 1974). The angular

distribution for the neon electrons was measured up to 30 eV ejected electron energy and the results agree with both the photoionization measurements and Hartree-Fock calculations. For krypton the maximum energy for the ejected electron was 40 eV and for argon 55 eV. In both these cases, the results agreed with the photoionization measurements up to about 20 eV but above that the pseudo photon measurements gave β values lower than the photoionization measurements.

Despite the fact that the technique seems to offer a cheap alternative to synchrotron radiation, it does seem to possess a number of disadvantages. These include the need to normalise the results and the error that occurs in the forward scattered signal if it is due to electrons from more than one photoelectron transition. However, more importantly, there is the unsettling aspect of the disagreement between the pseudo photon experiments and the photoionization data as outlined above. Whether this can be improved upon by refined instrumentation or instead points to a breakdown in the assumptions involved in the method is not known. But it does seem to indicate that the pseudophoton measurements are not a viable alternative to photoionization with a variable wavelength source.

2.3 SYSTEM DESCRIPTION

For a number of years, this laboratory has been concerned with the measurement of partial cross sections of gaseous photoelectrons as a function of wavelength (Gardner, 1970; Blake, 1966). The light source generally used for this work was the Hopfield continuum in helium (Samson, 1967) dispersed by either a 1m normal incidence monochromator or a $\frac{1}{2}$ m. Seya-Namioka style instrument. The ultimate aim now is to extend these wavelength dependent measurements to the measurement of photoelectron

angular distributions.

However, it became obvious early in the program that a significant stage of learning and testing was required in order to achieve reliable angular distribution results. It was realised that this testing could most easily be carried out using the high intensity available from an undispersed light source. As well, it was decided that a source of 30.4 nm radiation would be of use since then photoelectrons from helium would be accessible and their known value of $\beta=2$ would provide a very useful test of the system. The low intensity of 30.4 nm generally obtained also demanded an undispersed light source.

It is this work with an undispersed light source that is the subject of this thesis. However, the instrument design was influenced by the fact that at some later stage, it would be necessary to be able to measure photoelectron angular distributions from both dispersed and undispersed sources, that is from both polarized and unpolarized radiation. The design analysis that was undertaken and the conclusions reached are discussed in Section 2.3.1.

Another decision based on the need for testing was to initially use a very simple analyser. This is described in Sections 2.3.2 and 2.3.3. Finally, Section 2.3.4. describes the type of vacuum chamber and rotating mechanism used.

2.3.1 SYSTEM ANALYSIS

To measure the angular distribution for unpolarized radiation simply requires the rotation of the analyser in the plane of the beam. Such a technique can also be used for polarized light, but it requires the measurement of g , the degree of polarization. However, it is possible to orientate the plane of rotation of the analyser with respect

to the plane of polarization such that the polarization factor is removed.

Recalling Equation 2.3, if the plane of rotation of the analyser is orientated midway between the x and y axes of symmetry of the polarization, that is $\theta_x = \theta_y$, the equation reduces to,

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{TOT}}{4\pi} \left(1 - \frac{\beta}{2} + \frac{3}{2} \beta \cos^2 \theta_x \right) \quad 2.10$$

which is independent of the degree of polarization. The expression can easily be converted to θ_y , the angle between the analyser and the beam since,

$$\cos^2 \theta_x + \cos^2 \theta_y + \cos^2 \theta_z = 1 \quad 2.11$$

and thus,

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{TOT}}{4\pi} \left(1 + \frac{\beta}{2} \left(\frac{3}{2} \cos^2(\theta_z) - 1 \right) \right) \quad 2.12$$

which is simply Equation 2.4, the equation for unpolarized light.

However, the difficulty with this method is determining the x and y axes. This can be avoided by extending the technique to the measurement in two planes, both of which contain the beam axis but which are 90° apart, although arbitrarily orientated with respect to the polarization direction. The expressions for the angular distribution in each plane are,

$$\frac{d\sigma}{d\Omega} \Big|_1 = \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{(g+1)} \left(g P_2(\cos \theta_y) + P_2(\cos \theta_x) \right) \right] \quad 2.13(a)$$

$$\frac{d\sigma}{d\Omega} \Big|_2 = \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{(g+1)} \left(g P_2(\cos \theta_x) + P_2(\cos \theta_y) \right) \right] \quad 2.13(b)$$

If we take the mean of these two distributions, we obtain,

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{MEAN}} = \frac{\sigma}{4\pi} \left[1 - \frac{\beta}{2} P_2 (\cos \theta_z) \right] \quad 2.14$$

which again is the expression for unpolarized light. However, in practise, it is obvious that given the two sets of data taken under the conditions described above, some form of normalisation between them is necessary before they can be added. The method to use can be seen by noting that at $\theta_x = \theta_y = 90^\circ$, that is along the direction of the radiation, the two distributions are equal. Therefore the data from the two distributions, are normalised such that they are equal at that angle. The distribution cannot of course be measured along the beam direction but the value can be found by extrapolation of the data.

Since the work described in this thesis used an undispersed and hence unpolarized source, this technique for finding β when using polarized radiation was not used. However, it was anticipated that it might be needed in later work and as such the system was designed to allow motorized rotation of an analyser in the plane of the beam, and manual rotation of this rotation plane about the beam axis. This latter rotation was not motorized since it would not be done continuously. In this way the equipment would be used for unpolarized radiation and later for polarized radiation using either the two distribution method or the simple technique at 45° .

2.3.2 ELECTRON ANALYSER

The first requirement for an electron energy analyser is that it is small enough to comfortably fit in the vacuum chamber and light enough not to put an unnecessary strain on the rotating mechanism.

Electron energy analysis can be achieved by either magnetic or

electrostatic fields. However, the latter is more often used for the low energies encountered in EUV photoelectron measurements due to the difficulty in using low magnetic fields and problems of shielding the interaction region from their fields. Electrostatic fields, on the other hand are very easily produced and can be easily shielded.

It was decided that the research program requirements would best be suited by initially using a very simple analyser. In this way, as much of the development time as possible could be spent on investigating and understanding the special problems associated with angular distribution measurements. Thus a simple retarding grid analyser was chosen. Furthermore, plane grids were decided upon for their simplicity and ease of construction, although they generally result in lower resolution than can be obtained with spherical grids (Lindemans *et al* 1979).

The design is shown in Figure 2.5. It is to be noted that a large acceptance angle of 10 degrees has been used. This is much larger than the three degrees or less used by many other investigators (e.g. Morgenstern *et al*, 1970; Leng and Nyberg, 1977) and was chosen to provide a large electron count rate at the expense of energy resolution. The effect of the large angle on the measured angular distribution was investigated by a computer analysis to be described in Section 2.7. It is sufficient to say at this point that it had little effect on the measured value of β .

The field of view of the analyser is defined by a series of concentric thin discs. The straight through line is a cylinder of diameter .9 cms. This will be referred to as the umbra. The penumbra is then the rest of the field of view making up a cone of 10 degrees half

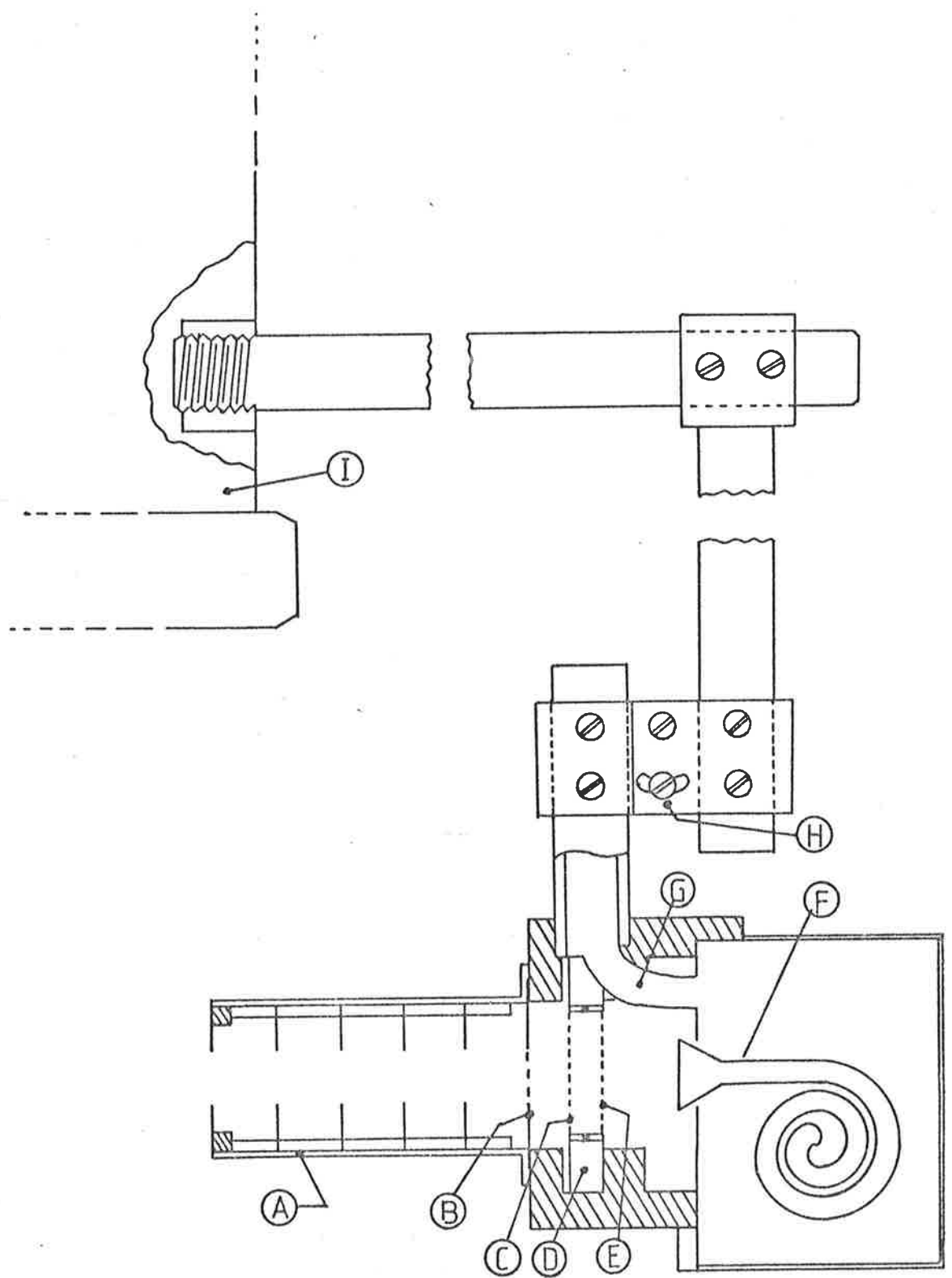


FIG. 2.5 The electron energy analyser drawn full size. Shown are: (A) collimator, (B) earth grid, (C) first retarding grid, (D) perspex grid support, (E) second retarding grid, (F) channel electron multiplier, (G) wiring channel, (H) adjustable coupling, (I) rotatable tube.

angle. The collimator discs are very thin to discourage scattering of electrons from their edges. This is further assisted by coating the interior with aquadag, a colloidal graphite solution. This also provides a uniform potential surface which might not otherwise be the case with the dissimilar metals used in the construction of the collimator.

Electrons that come through the collimator pass through a grid at earth potential and then if energetic enough, through two retarding grids to be detected by a channel electron multiplier (CEM). This electron detector will be described in Section 2.3.3.

The purpose of the earth grid is to isolate the voltage on the retarding grid from the interaction region. It is constructed from a fine electroform mesh with approximately .02 mm diameter wires spaced .1 mm apart. The transmission is about 70%. The first retarding grid is also constructed of electroform mesh, but the second is a coarse grid with wires about 1 mm apart and a transmission of over 90%. The reason for this second grid was to minimise penetration of the field from the +200 volts on the front of the channel electron multiplier through into the deceleration region between the earth grid and the first retarding grid.

The first retarding grid is of closely spaced wires to present as closely as possible a uniform potential across its surface. In general, the potential between the wires will be different from that on them. The variation in potential across the grid will depend on the voltage on the grid and the field on either side of it. However, in the present situation, it can be seen that if the second retarding grid is at earth, then the potential between the grid wires of the first retarding grid will be less than the voltage on the wires themselves. Thus as the scanned retarding grid becomes more negative than the electron energy, the

detected electron signal will not stop abruptly but will slowly decrease as the slightly lower potential between the wires approaches the electron energy. The greater the deviation in the field across the grid, the worse the resolution. This then was the intended purpose of the second retarding grid. It is operated at the same voltage as the first grid which in itself helps to minimise the dips, but more importantly provides some shielding from the +200 volts on the channel electron multiplier. For a quantitative view of the effects of retarding grids, the reader is referred to Huchital and Rigden (1972) and Staile (1972).

A further limitation on the resolution is due to electrons that enter the retarding region at an angle other than 90 degrees to the earth grid. If this angle is say θ , then for an electron of energy E only the component of energy normal to the grid, namely $E \sin^2 \theta$ is measured. In the analyser, the minimum value of θ is 80 degrees and therefore the energy measured will be $.97E$.

Both of these limitations on the resolution of the analyser are illustrated in the spectrum shown in Figure 2.6. It has been divided into three regions A, B and C although the divisions are somewhat arbitrary and allocated simply to ease the explanation.

Region B is the major part of the curve showing the decrease in electron counts as the voltage on the retarding grid becomes more negative. Ideally this would be a step function but both the limitations discussed above act here to produce the slope. Region C, on the other hand, is due entirely to the difference in potential between the point between the grid wires and the grid wires themselves. This results in the spectrum having a high energy tail for reasons discussed previously. Finally, region A is due primarily to off-axis electrons and results in

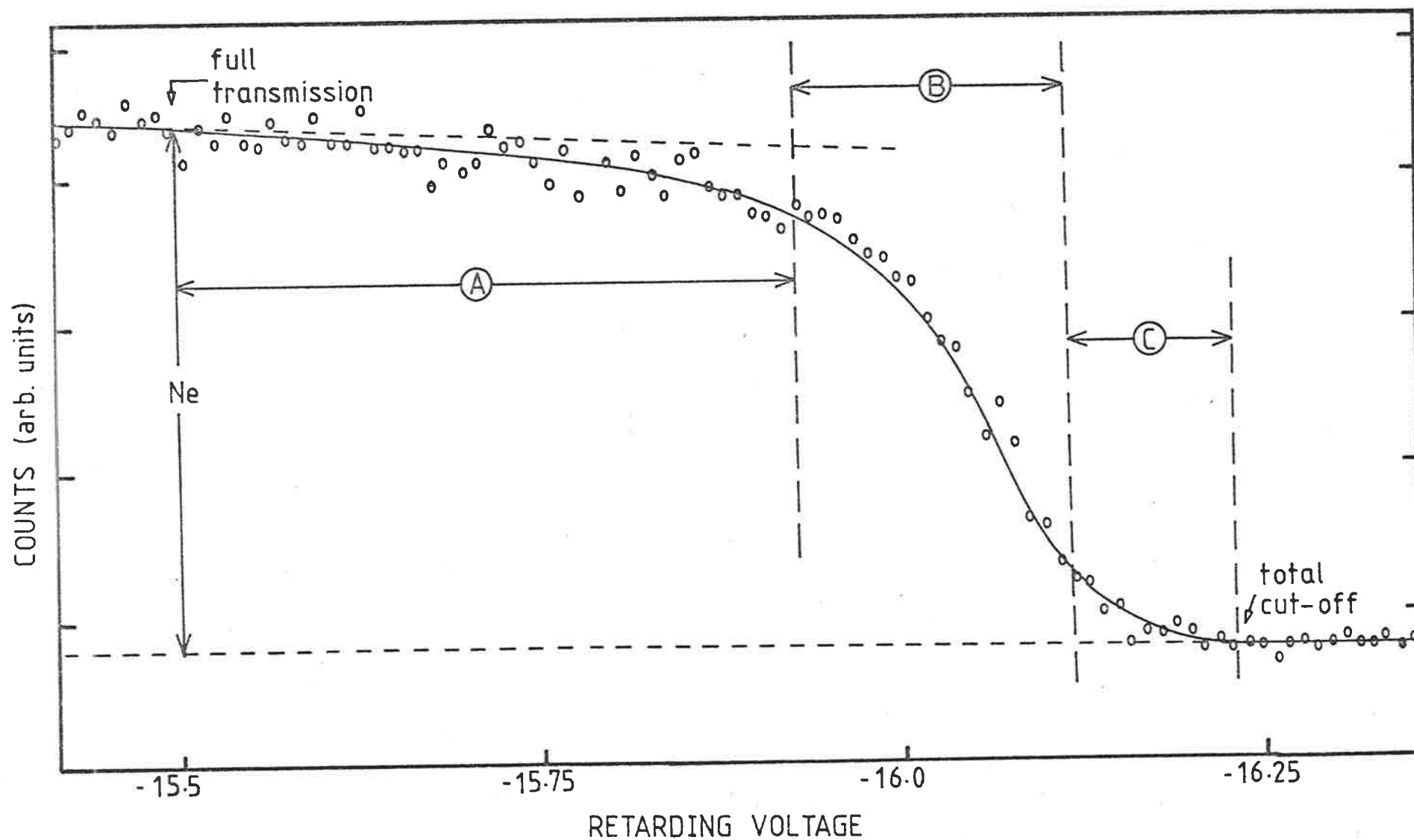


FIG 2.6 Example of a spectrum for electrons from the photoionization of helium by 30.4 nm radiation.

the electron count only very slowly approaching the point of full transmission. It is obvious that it is the off axis electrons which predominantly affect the resolution. However, this was considered a reasonable sacrifice for the benefit in signal to be gained by using a large field of view.

The asymmetry of the retarding curve complicates any numerical discussion of the resolution. If we define the resolution as $\Delta V/V$ where ΔV is the voltage range to completely cut off the electrons and V the voltage at 50% transmission, then this equals about 4%.

There is one other aspect of the retarding curve in Figure 2.6. The part of the curve beyond the cut off is not a level line, but slightly sloped. This is the same at the opposite end above full transmission. This indicates that there is a small but constant background component. To measure the electron count that the curve corresponds to, the background beyond the cut off must be extrapolated and the vertical distance from this line to point at which there is just full transmission, measured. This can be a complicated procedure where poor statistics or overlapping curves occur and the techniques that were used will be discussed in Section 2.9.

The analyser is constructed entirely from copper and brass with the one exception being the perspex annulus that supports the retarding grids. The presence of insulators within the analyser can lead to problems due to surface charging and the retarding grid has been constructed much larger than the collimator opening so that the insulator is as far away as possible from the electron paths. It is also apparent, from an inspection of Figure 2.5 that the insulator is almost completely surrounded by the combination of the earthed body of the analyser and the retarding grids. Thus it is considered that the penetration of any fields from the insulator into the retarding region is slight.

Figure 2.7(a) shows the equipotentials in both the retarding region and the area in front of the channel electron multiplier. These were calculated using a program written by the author that iteratively solves Laplace's equation at an array of points in a two dimensional plane. A condition is that this plane must be part of a cylindrically symmetric bounded region where one of the boundaries of the plane is the axis of the cylinder. In the illustration, the two retarding grids and the boundary marked (x) are at -4 volts, while the front of the CEM is +200 volts. The remaining boundaries are at zero volts. Since the program is designed to apply to cylindrically symmetric systems, only half the analyser is used. It should be pointed out that in these computer generated plots the horizontal axis is slightly compressed relative to the vertical axis. This is due simply to the method of computer output and does not affect the results nor the conclusions.

The equipotentials in the retarding region are approximately .364 volts apart while those in front of the CEM are 7.54 volts apart. The program is not equipped to handle insulators directly and they have been assumed to be equipotential surfaces. It can be seen that by having a large retarding grid, the field is reasonably uniform over the important region, namely up to the size of the collimator opening.

The second effect to be investigated by the computer program was the fate of off axis electrons. Part of the computer program allows the calculation of electron trajectories. Three such trajectories are shown in Figure 2.7(b). The initial angle of all three is the maximum allowed by the collimator for electrons at their respective starting points. The electron energy is 5 eV with -4 volts applied to the retarding grids. It has already been pointed out that the program

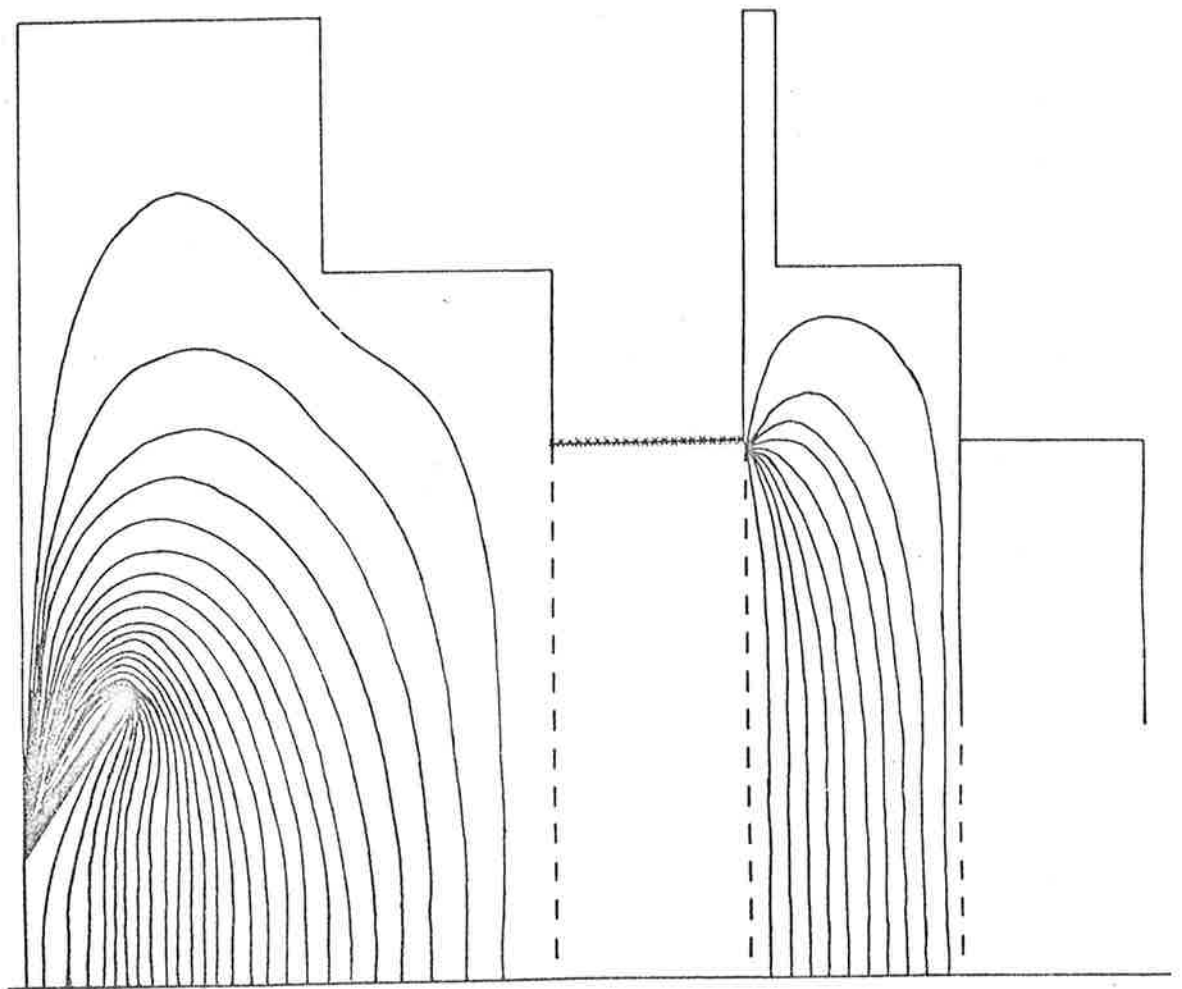
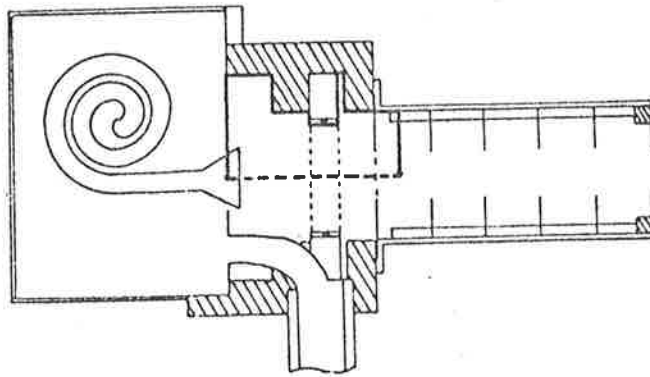


FIG 2.7(a) Calculated equi-potentials in the electron analyser. Those in front of the CEM are 7.54 volts apart and those between the retarding grid and the earth grid are .364 volts apart. In the diagram at the top, the heavy solid and dashed lines indicate the region modelled.

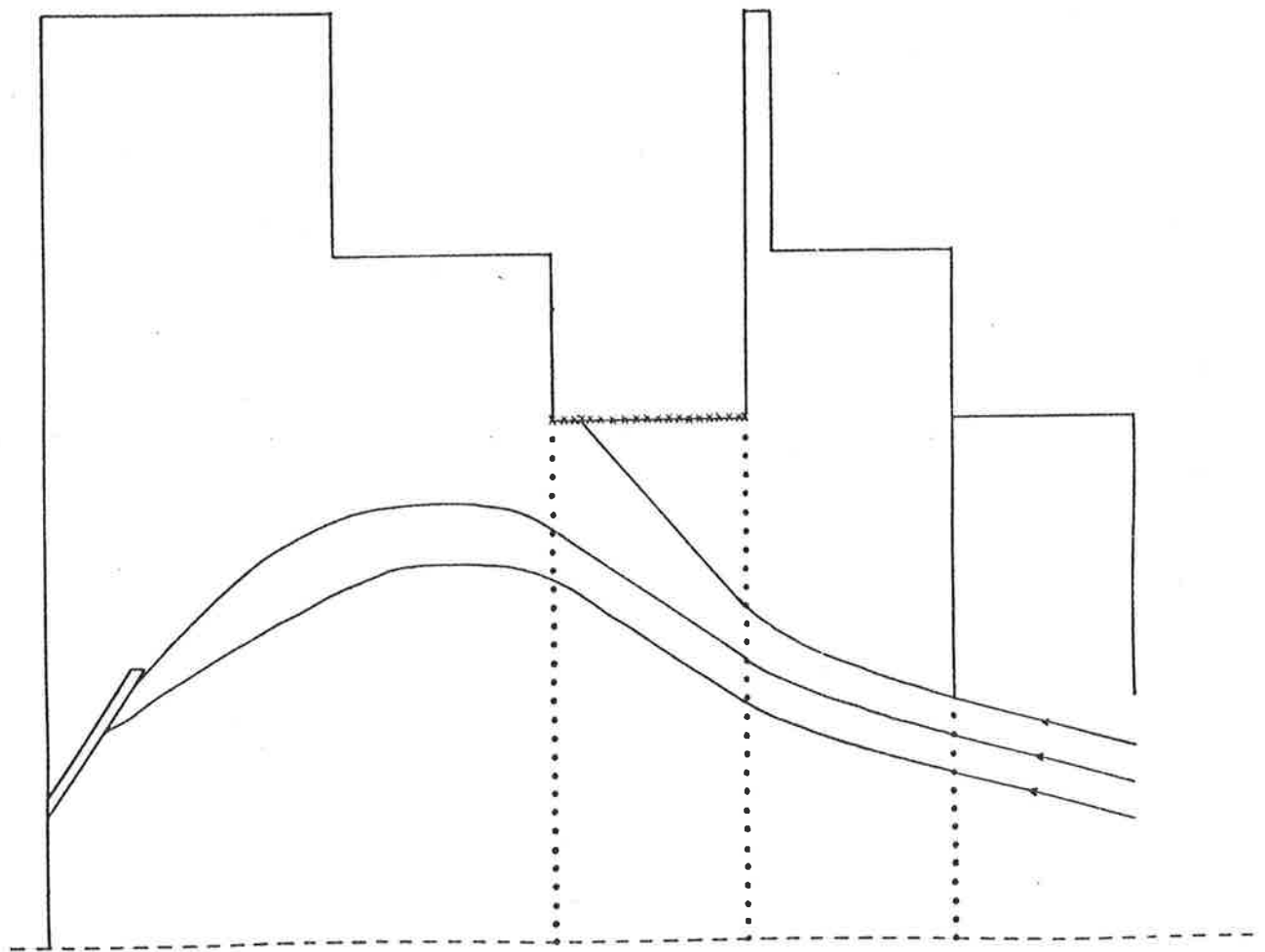
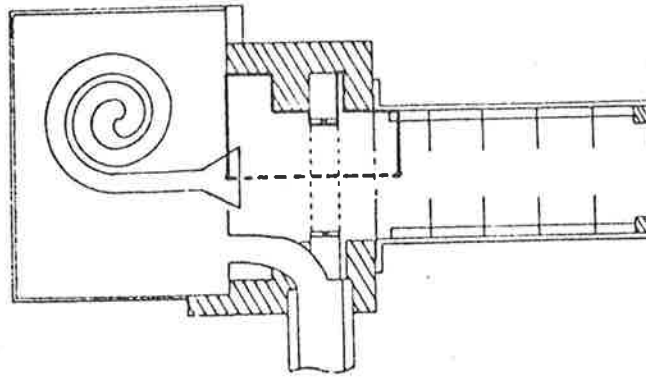


FIG 2.7(b) Calculated electron trajectories for three electrons with 5 eV initial energy and -4 volts on both regarding grids. In the diagram at the top, the heavy solid and dashed lines indicate the region modelled.

calculates the field at an array of discrete points. Each of the dots representing the grid is a point in the field and therefore there is no allowance for field penetration between the grid wires.

A further consequence of the discrete nature of the calculated potential field is that the field very near the CEM is too coarse to properly show the fine detail of the final collision between the CEM and the electron. It has been assumed that if the calculated electron trajectory brings the electron into the cone of the CEM, then it is detected.

It is interesting that the upper electron in Figure 2.7(b) does not even get through the two grids. This is due to its trajectory being curved so much at the retarding grid that when it enters the region between the grids it drifts in a straight line to strike part of the analyzer and hence is not detected. The occurrence of this depends on the amount of curvature suffered by the electron which in turn depends on the difference between the electron energy and the retarding voltage. The smaller the difference, the greater the curvature. Thus the effect of this is to discriminate against some off axis electrons and worsen the low energy tail or region A in Figure 2.6.

This was undesirable and an experimental investigation was undertaken whereby the two retarding grids were electrically isolated and a positive potential voltage applied to the second grid to pull these electrons through. However, it was found to have little effect on the shape of the spectrum which implied that if any electrons were being lost, it was too small a number to be statistically significant. The reason the computer program is in error is thought to be due to the simplification of not allowing field leakage between the grid wires,

especially for the second retarding grid which is some ten times coarser than the first. Therefore it is possible that leakage of the +200 volts through this grid was sufficient to pull the electrons through. Thus, although the second grid was added to inhibit the field of the CEM from influencing the retarding field, nevertheless the use of a coarse grid was somewhat fortuitous in that allowing a small amount of field leakage definitely assisted electron detection.

Two analysers of the type described above were constructed. One was used as the rotatable analyser, the other was fixed. They were mounted such that each was outside the field of view of the other.

The reason for the fixed analyser was to provide a monitor of the gas pressure and lamp intensity. In the pressure region used, the count rate is proportional to the product of the gas pressure and the lamp intensity and the fixed analyser could therefore be used to compensate for variations in these parameters. It was used extensively in the early part of the investigation when there was difficulty maintaining a stable light output. However, in later work improvements to the lamp rendered the fixed analyser unnecessary for this task and since the pressure also was reasonably stable, it was no longer used.

2.3.3. ELECTRON DETECTOR

The prime requirements for an electron detector of high gain and low background are satisfied by secondary electron multipliers (Baumgartner and Huber, 1976). Of these, the channel electron multiplier (CEM) has been used extensively due to its simplicity and small size.

The CEM is a glass tube typically less than 5 mm in diameter with a ratio of length to inside diameter of between 50 and 100. The

shape of the tube may be straight, bent in an arc or in a spiral.

The inner surface of the glass is made semi-conductive by using lead or vanadium doped glass and baking in a reduced atmosphere. This results in an end to end resistance of about 10^{10} to 10^{11} ohms. A potential difference is applied between the ends producing a field along the tube. For detecting electrons, the entrance of the tube is at a positive voltage and the direction of the field is towards this end.

Provided the voltage at the entrance is greater than about 50 volts, electrons are accelerated into the tube with sufficient energy to emit secondary electrons on colliding with the wall. These secondaries are accelerated down the tube and provided the field is strong enough, will have accelerated sufficiently to produce further secondaries on the next collision. This multiplication process continues along the wall which behaves as a continuous dynode.

However, the gain is limited to about 10^8 . This saturation can be due to space charge effects (Baumgartner and Schmid, 1972; Bryant and Johnstone, 1965) or the depletion of wall current (Harris, 1971; Andresen and Page, 1971). The former is caused by the build-up of charge as the electron cloud travels down the tube. This charge tends to limit the time of flight of any new secondaries by repelling them back towards the wall thus limiting their energy and hence their ability to produce further secondary electrons. An equilibrium situation is reached where an electron is lost to the wall for every one emitted. The depletion of the wall current occurs if there is insufficient wall current available for the number of secondary electrons removed. The field is reduced, thereby reducing the energy involved in wall collisions and hence reducing the number of secondaries.

For electron counting, this saturation is desirable as it produces a nearly uniform pulse height. The conditions for saturation depend on the dimensions of the tube and the potential difference. Commercial CEM's are constructed to sufficient length for saturation to occur with between 2.5 and 3.5 KV potential across them.

A further process that can take place is ion feedback (Evans, 1965). A travelling electron may collide with a gas molecule in the tube and the resulting ion travel back along the tube. If it collides with the wall, it will start another avalanche producing an after pulse. Such a process depends on the gas pressure inside the tube, but it is easily prevented by having the tube curved. In this way, the ions, which are normally produced at the high voltage end cannot travel far without striking the wall. The size of the resultant pulse is then much smaller than the main pulse and easily discriminated against.

An important attribute of CEM's in their low noise of typically .1 Hertz or less due to the work function of the surface being too high for thermal noise. The background that does exist has been shown by Andresen and Page (1972) to mostly occur within the tube itself with only about 5% due to cosmic rays.

There is no dead time associated with a channeltron (Wolber *et al*, 1969), the distance between detectable pulses being determined by the pulse width itself. As a consequence, the maximum count rate is often determined by the associated amplifier-discriminator combination (Bowyer *et al*, 1970).

The channel electron multiplier used in this work was a Mullard type B419 BL. The electrical connections and preamplifier-

discriminator circuitry is shown in Figure 2.8. The rear of the CEM is maintained at +3 KV through a series resistance comprising a one megohm and ten kilohm resistor combination for current limiting. The mid point between these is capacitively coupled to ground to isolate any power supply noise from the CEM.

A capacitor couples the rear of the CEM to a pre-amplifier from which the pulses then pass to a discriminator. This has an adjustable threshold allowing noise rejection. At the same time the discriminator converts the pulses to a constant height suitable for further processing.

2.3.4. VACUUM CHAMBER AND ROTATING MECHANISM

A cylindrical vacuum chamber 47 cms in diameter and 45 cms high was constructed of aluminium. This size was chosen so as to have the distance from the interaction region to the chamber wall as large as possible to minimise any effects on the electrons from contact potentials on the walls.

Around the circumference of the chamber are five ports. Three of these accommodate the vacuum gauge, air inlet valve and electrical feed throughs. The remaining two ports have been accurately aligned to be 180 degrees apart and their respective flanges normal to the centre line that passes through them. It is along this line that the light beam is aligned. The lamp is attached to one port, the other continues to a "T" shaped section attached to a five inch diffusion pump that pumps the chamber. This is shown in Figure 2.9.

A pair of rotatable vacuum seals have been constructed to fit between the lamp and the chamber and between the chamber and the "T"

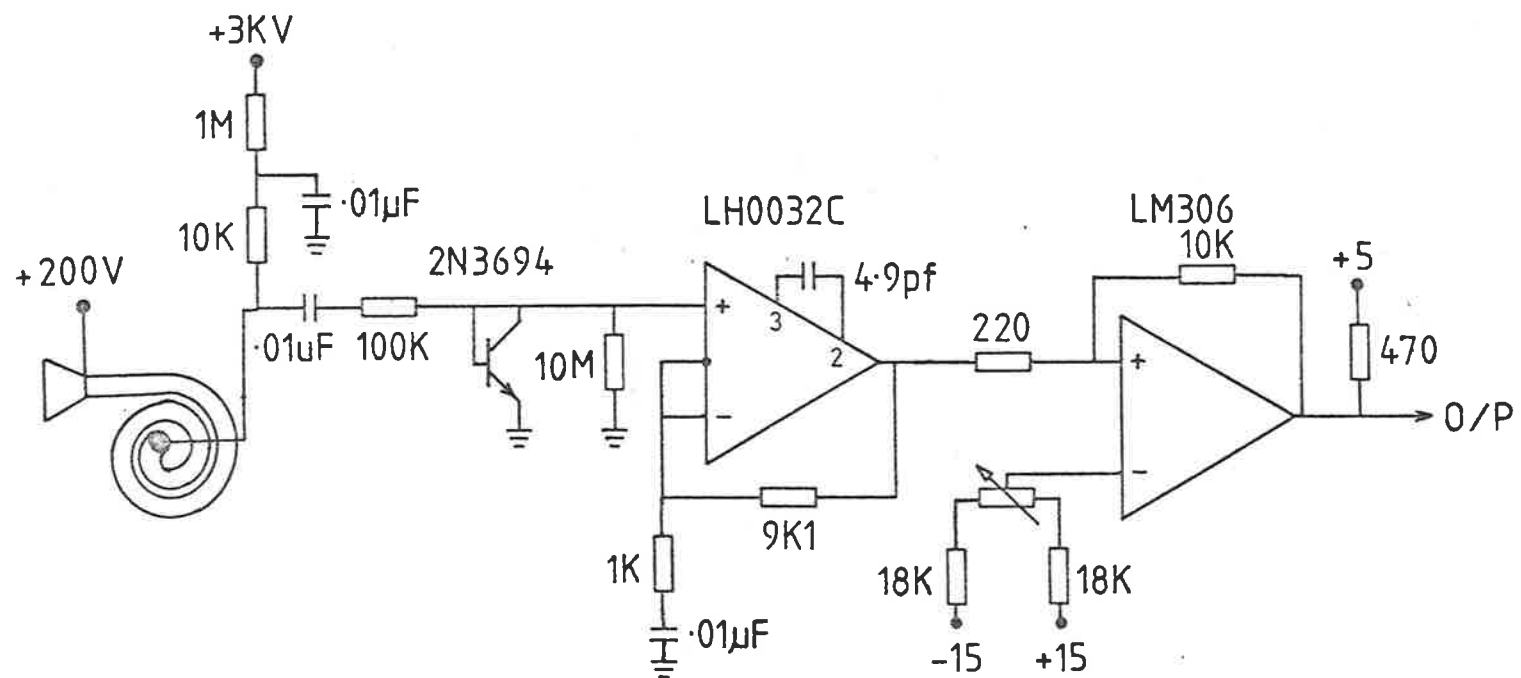


FIG 2.8 Amplifier and discriminator used with the channel electron multiplier.

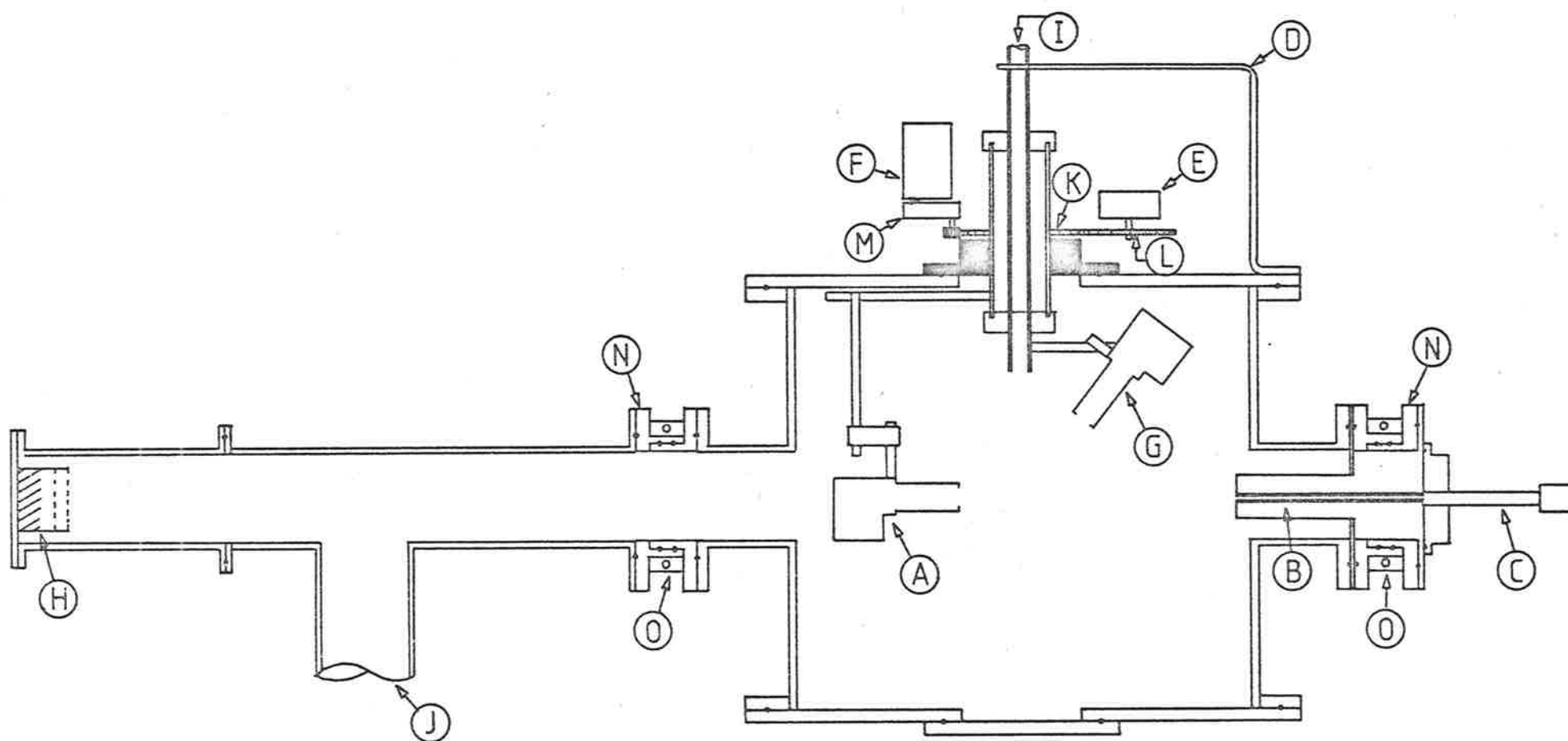


Fig. 2.9 General plan of the system drawn to approximately one sixth scale , showing:
 (A) rotatable analyser, (B) pyrex capillary, (C) lamp, (D) centre tube clamp,
 (E) potentiometer, (F) motor, (G) fixed analyser, (H) beam monitor, (I) gas
 inlet, (J) pumping port, (K) gear to rotate shaft, (L) gear on potentiometer,
 (M) gearbox, (N) rotatable vacuum seals, (O) ball race.

Photograph of the vacuum chamber lid which supports the rotating mechanism. Visible are the rotatable analyser (at the bottom of photo), the fixed analyser, the rotatable head, the motor drive and the potentiometer. Further details can be gained by referring to Fig 2.9.



section. This allows rotation of the chamber and hence the plane of the analyser about the beam axis. The rotatable seals can be seen in Figure 2.9. The 'O' rings provide the vacuum seal while the ball race allows rotation to be achieved under vacuum despite the large forces clamping the seal together.

In the centre of the chamber lid is the rotating head to turn the analyser. This is shown in Figure 2.10. Two concentric shafts, capable of independent movement, each have a clamped PTFE block to both centre them and provide a bearing. An 'O' ring provides the vacuum seal. The inner shaft is normally clamped to the chamber and thus kept fixed in one position. This tube provides the gas inlet to the chamber allowing the gas to diffuse in through a large bore opening to eliminate any abnormal gas concentrations.

The outer shaft is used to rotate the analyser and must be capable of continuous rotation under vacuum. It is driven by a motor external to the vacuum chamber which acts on a gear attached to the shaft. A potentiometer is in turn driven by this gear to provide information about the angular position.

The wiring from the rotatable analyser passes between the two shafts to a set of vacuum electrical feed-throughs attached to the rotatable shaft. The channel electron multiplier preamplifier is also located at that position to situate it as closely as possible to the CEM and thereby reduce the possibility of noise pick-up. All connecting wires from the rotatable analyser to the electronics rack are tied to the shaft to alleviate any strain on the solder joints in the connectors due to the continual back and forth rotation.

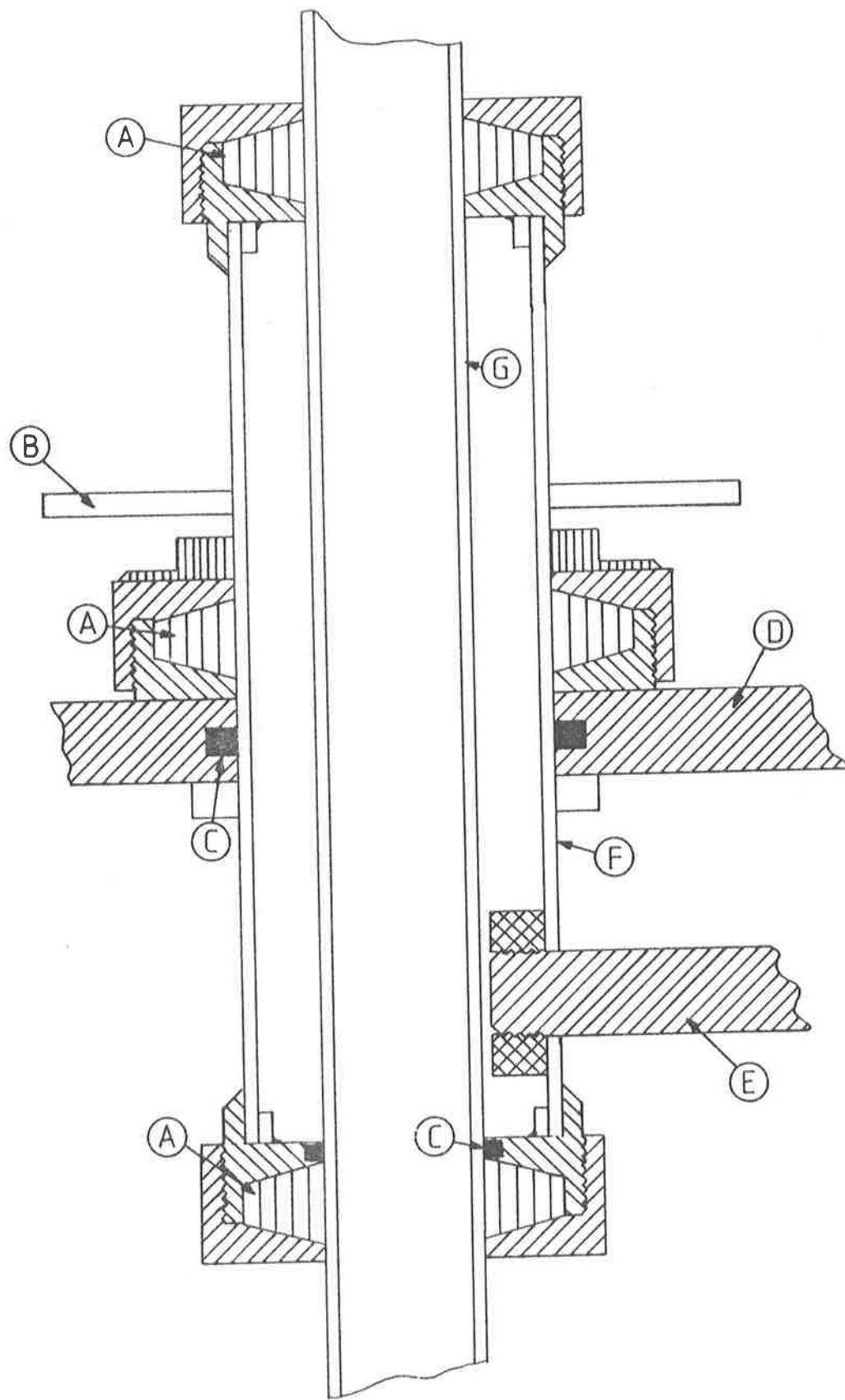


FIG 2.10 Rotating head showing :

- (A) PTFE bearings, (B) gear to drive shaft, (C) 'o' ring seal,
- (D) vacuum chamber top, (E) shaft to support analyser, (F) rotatable shaft,
- (G) fixed shaft.

An inclusion to the vacuum chamber was a scattering shield. Errors encountered in the measurement of angular distributions were thought due to scattering off the wall of the chamber facing the analyser. This was lined with aluminium honeycomb to attenuate the scattered signal. However, its effect was only marginal.

2.4 EUV LIGHT SOURCE

There are a large variety of EUV lamps (Samson, 1967) to satisfy a variety of uses, but with the exception of the synchrotron (Codling, 1973) there is no one source that covers the entire EUV spectrum.

In the present application an undispersed line source was required which would produce the two wavelengths 58.4 nm and 30.4 nm. For some of the initial work, a high voltage AC discharge through a water cooled capillary was used. This lamp proved excellent for producing 58.4 nm and will be described in detail in Chapter 5 in conjunction with the EUV spectrometer where it was extensively used. However, difficulties were encountered in attempting to use it to produce 30.4 nm.

The 30.4 nm radiation is produced by the decay of an excited state of the helium ion and its intensity is inversely proportional to the pressure of helium in the lamp (Brundle *et al*, 1970, 1974). However, as the pressure was decreased, any detectable amount of 30.4 nm radiation was marred by an increase in electrical noise. This might not have been the case if a DC rather than an AC supply had been used, as Poole *et al*, (1974) have obtained useful amounts of 30.4 nm radiation from a capillary style lamp especially when viewing the cathode end of the glow.

There are a number of alternate sources for producing 30.4 nm radiation. These include modified microwave sources (Omura and Hiroshi, 1967(a), (b); Pellach and Sar-El, 1978), hollow cathode lamps (Paresce *et al*, 1971) and the charged particle oscillator (Burger and Meier, 1974, 1975). Of these, the charged particle oscillator was chosen since it appeared to offer a stable output of 30.4 nm radiation. Stability is an important criterion in angular distribution measurements where the light must be constant for the time it takes the analyser to view a range of angles. A secondary consideration was the lamp's ability to run at low current and low pressure. This allowed the use of a readily available power supply and pumping system.

The lamp that was constructed (Figure 2.11) closely follows that of Burger and Meier (1974, 1975). A stainless steel cylinder 1.25 cm in diameter has two .4 mm tungsten wires 3 mm apart running its length. The wires are the anode and are insulated from the cylinder with boron nitride spacers. The cylinder, which is earthed, forms the cathode and is terminated in conducting end caps. The wires are kept under tension with individual springs to compensate for any bowing that occurs during operation from heating by electron bombardment.

The lamp operates on the charged particle oscillator principle of McIlraith (1966, 1972). Electrons from the walls of the cylinder are attracted to the positively charged wires. Of these electrons, some have trajectories which, instead of immediately terminating on one of the wires, pass between them. Figure 2.12(b) shows an example of such a trajectory. The electron, starting at point "a" is accelerated towards the wires but passes between them. It then decelerates, turns round and

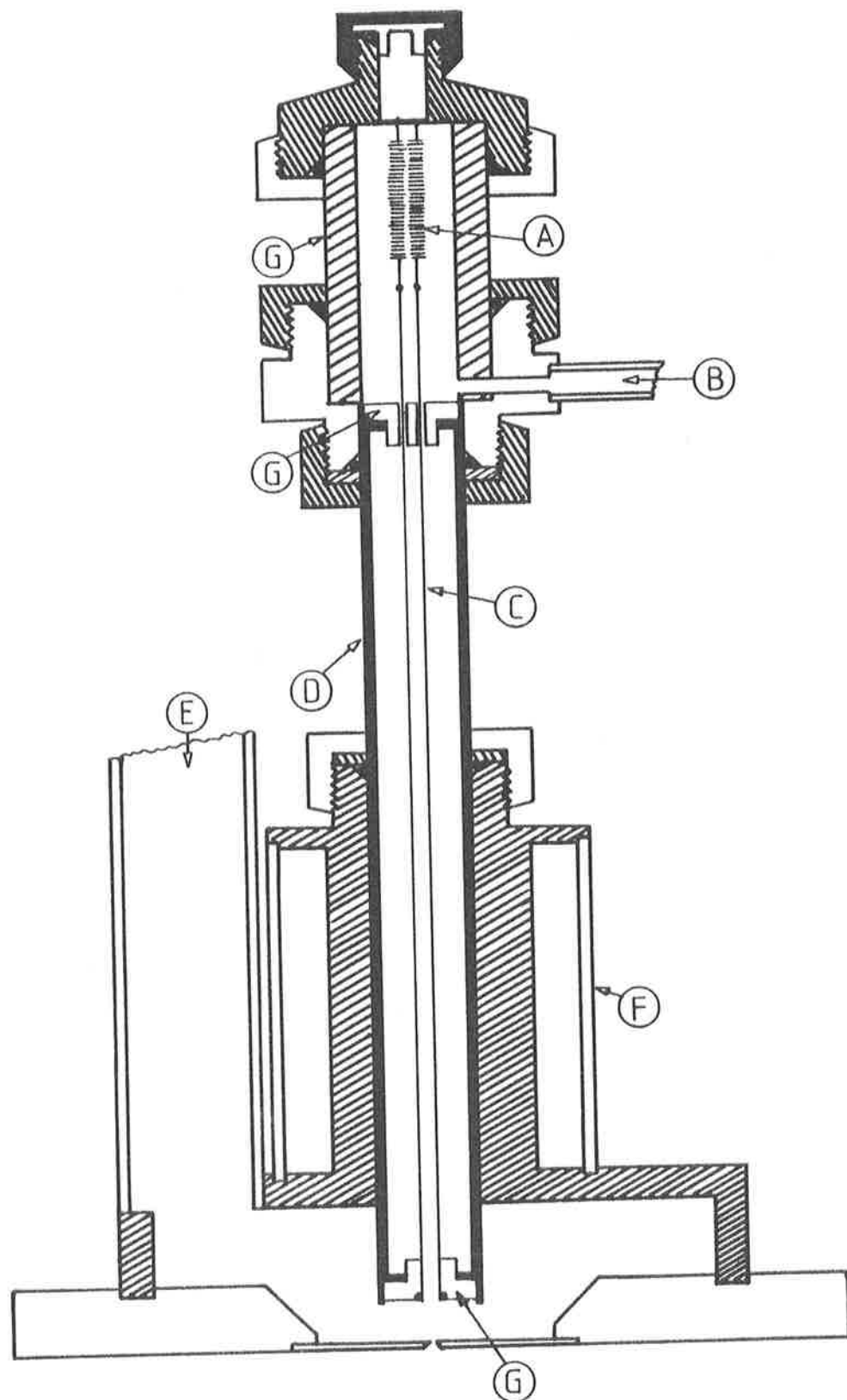
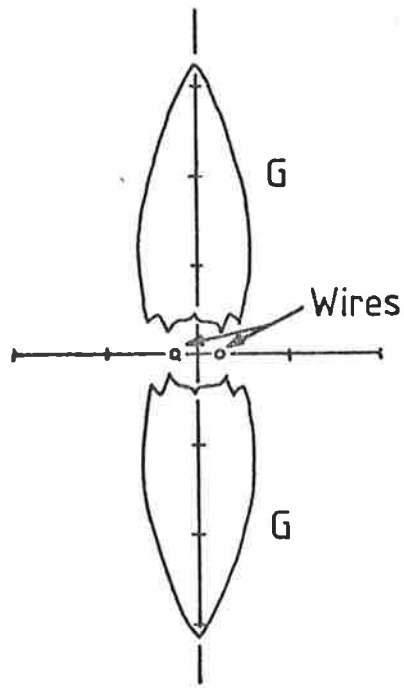
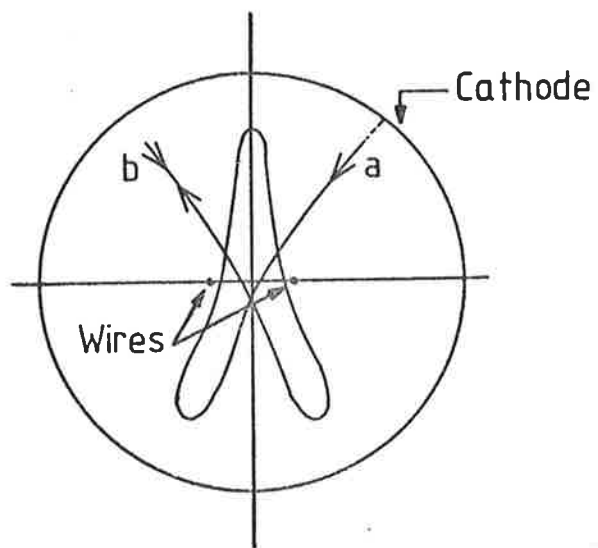


FIG 2.11 Charged Particle Oscillator Lamp, showing: (A) tension springs, (B) gas inlet, (C) tungsten wires, (D) stainless steel tube, (E) pumping port, (F) water jacket, (G) boron nitride insulator.



(a)



(b)

FIG. 2.12 (a) Region for stable oscillations (see text) (from McIlraith, 1972).

(b) Oscillatory electron trajectory (McIlraith, 1966).

again passes between the wires. It continues until it reaches point "b", where it turns and retraces its path. There are many possible trajectories that can lead to an oscillatory path and in fact, all electrons starting from rest in the region G in Figure 2.12(a) will have such trajectories (McIlraith, 1972). This defines an important design parameter for the instrument. Since the source of electrons is the cylinder wall, the inside of the cylinder must intersect this region. From the dimensions of this region, if the ratio of the cathode diameter to anode wire spacing is greater than about twelve, the oscillatory mode will not occur (Fitch and Rushton, 1972).

The advantage of the oscillatory mode is that it can operate at lower lamp pressures than a conventional glow discharge. McIlraith (1966) maintained a discharge down to 8×10^{-5} torr, whilst with only a single anode, 3×10^{-3} torr was the lowest pressure attained.

Since the electron will only oscillate until it strikes a gas atom, as the pressure is increased, a point is reached where the mean free path is so short that the oscillations cease. Rushton *et al* (1973) have investigated the action of the oscillator as a function of pressure and have been able to label three modes of operation. The oscillatory mode occurs for pressures below 2×10^{-4} torr while above 3×10^{-3} torr it is a glow discharge. Between these two there is an intermediate mode. It is difficult to know the actual pressure inside the present lamp, however from a comparison of the ion etching inside the cathode with diagrams given by Rushton *et al* (1973), it is considered that the present lamp is operating in the intermediate mode region. This was not through choice but due to the low power of the power supply used and a difficulty in maintaining stability at lower pressures. However, according

to Lancaster *et al* (1978), it is this region that gives the highest absolute intensity of 58.4 nm and 30.4 nm radiation.

Power for the lamp was provided by a 5KV power supply through a 200 K Ω ballast resistor. This limited the current to less than 20 ma. Although this value was dictated by limitations of the power supply used, higher currents raise the problem of dissipating the heat from the wires. A current of similar magnitude has been used by Burger and Meier (1975) but Coatsworth *et al* (1978) have used 250 ma. However the lower current used in the present lamp ensured a longer lifetime to the wires than the two or three days encountered by Coatsworth *et al* (1978). The lamp would run typically for between 200-300 hours before needing to be taken apart, cleaned and the wires replaced.

Recently, versions of the charged particle oscillator lamp suitable to high current operation have been published. Lancaster *et al* (1978) have replaced the wires with 3/16 inch tungsten rods, while Burger and Meier (1979) have used water cooled tubes. Both of these modifications would also alleviate what was found to be the most critical stage in the assembly of the lamp, namely keeping the wires straight and parallel.

The main advantage of the lamp is its ability to operate for hours with only a small monotonic variation in output which was typically less than a few per cent. This was improved further in later work by forced air cooling the lamp.

The lamp produced approximately equal amounts of 58.4 nm and 30.4 nm radiation. This radiation passed from the lamp through a 2 mm

aperture, then along a 2 mm pyrex capillary to a second aperture to provide a collimated beam. The inclusion of the capillary was found to increase the flux by an order of magnitude. Beyond the chamber, the light was monitored with a photocathode. The current was recorded on a chart recorder during data collection as a check on the constancy of the lamp.

There was however, one point of concern in using this particular lamp. Whilst it is an undispersed light source and hence one which would normally be considered unpolarized, nevertheless, in the oscillatory mode there is a preferred direction for the electrons, namely to pass between the wires. This then defines an axis of symmetry normal to the light beam and the possibility of polarization had to be investigated.

This was done by taking two angular distribution measurements with this electron axis in two orientations, namely perpendicular to the plane of rotation of the analyser and also parallel to it. No appreciable difference was found in the β 's and the beam was considered unpolarized. This is possibly due to the lamp operating in the intermediate mode where the oscillations form only part of the electron current.

Argon photoelectrons had to be used for the above test. If helium had been used, the same β would have eventuated regardless of the polarization of the beam. This can be seen by writing Equation 2.3 in terms of θ_z and ϕ' , the angle between the plane of rotation and the x axis,

$$\frac{d\sigma}{d\Omega} \propto \left(1 - \frac{\beta}{2}\right) + \frac{3\beta}{2(g+1)} [g \cos^2 \phi' + \sin^2 \phi'] \sin^2 \theta_z$$

which for $\beta = 2$, gives a $\sin^2 \theta_z$ distribution independent of g or ϕ' .

A further problem encountered with the lamp was that it seemed responsible for a background signal. This background was in addition to

the general scattered photoelectron background and was not stopped with over sixty volts on the retarding grid. As well, it seemed unaffected by the earth's magnetic field, a fact that was established by switching off the Helmholtz coils used to annul the earth's field and noting that it had no effect. These facts eliminated the possibility of the background being due to photoelectrons produced from light striking parts of the chamber and further tests showed that it was not due to electrons "leaking" into the rear of the analyser. Also eliminated was the possibility of electrical noise.

However, it is known that it was at least partly due to ions. This was discovered by placing a pair of electrostatic deflector plates parallel to the beam and with a voltage applied, the background could be considerably reduced. However these could not be kept in the system as they occupied the space used by the pyrex capillary. This in itself considerably improved the signal to noise ratio but the background remaining had to be tolerated.

This background can be seen in the spectrum for helium photoelectrons in Figure 2.6 beyond the cut-off. Part of it comprises photoelectrons from helium ionized by a small amount of 25.6 nm radiation produced by the lamp. However, the majority belongs to the background discussed above.

2.5 MAGNETIC FIELDS

Magnetic fields can arise from a number of sources. The most widespread is the DC field of the earth which is about .4 gauss. Stronger fields can arise from iron structures and electric motors.

The effect of the magnetic field on the motion of the electron is to deflect it at right angles to its direction of motion with a force

proportional to its velocity and the strength of the field. This will affect the measured angular distribution, although the exact effect is difficult to estimate even for an homogeneous field since it depends on the angle between the electron's direction and the field. In addition, if the field is due to some large scale metal structure, an inhomogeneous field would result rendering a quantitative estimate even more difficult.

A residual magnetic field also affects the energy resolution of a retarding grid analyser even though it does not alter the energy of the electrons. This is due to the analyser only measuring the component of energy normal to the grid. Electrons reaching the retarding grid may be curved by the magnetic field to a more acute angle, increasing the spread in the measured energy distribution. Also, the curved trajectories mean that electrons are more likely to collide with the collimator thereby decreasing the measured electron intensity.

A simple technique to attenuate magnetic fields is to use a magnetic shielding material which has a high magnetic permeability. Such a material is Conetic AA produced by the Perfection Mica Company. However, it saturates at .3 gauss (Wessemeyer) and also suffers a reduction in effective permeability as the magnetic field increases (Shafer). This can be overcome by having an outer shield of Netic, a material produced by the same company. Although this has a lower permeability, its value is less affected by the field and it serves to attenuate the field sufficiently for the Conetic. A general rule in the use of magnetic shielding materials is that if possible, it is more effective to use a series of separated thin layers than one thick layer (Wadey, 1956).

An alternative to static shielding is the use of Helmholtz coils which are a pair of identical coils separated by a distance equal to their radius. Such a combination has the second derivative of the field vanishing on the axis midway between the coils (Rudd and Craig, 1968) and is capable of producing a uniform field. To cancel the earth's field, the coils can be used to produce a field of equal intensity but opposite direction. For example, three sets of mutually orthogonal coils can be adjusted to annul the components of the earth's field. If extremely low residual fields are required, multiple sets of coils can be used (Scott, 1957).

In the present experiment, attention was first paid to removing any unnecessary sources of magnetic fields. For example, it was found that the high tensile strength bolts used to clamp the lid on to the tank were effectively bar magnets and were replaced with brass bolts.

A Conetic/Netic shield was constructed, but it was impossible to make it continuous and at the same time provide access to the centre region. As such it only attenuated the field by a factor of two and was abandoned.

Helmholtz coils were then considered, and a simple arrangement consisting of a single coil pair physically aligned parallel to the earth's field was used. The coils are 94 cm in diameter with the wire size and number of turns determined by available materials, although more precise preliminary determination of these parameters is possible (Ruark and Peters, 1926). The current in the coils was adjusted to give a zero magnetic field at the centre as measured with a hall effect probe.

Some estimate of the useful volume within the coils can be gained from the work of Cacak and Craig (1969). They calculated the

effect of varying the spacing between the coils and the results for a single coil pair are shown in Figure 2.13. The three graphs are for the maximum usable volume in which the field differs from the centre by the percentage shown. The volume is expressed in cubic coil radii as a function of coil spacing.

The volume occupied by the interaction region and the collimator of the analyser is a sphere 20 cms in diameter which is 4×10^{-2} cubic radii. Referring to Figure 2.13, it can be seen that this easily intersects the one percent curve for which the accuracy of spacing of the coils need only be $\pm 10\%$.

The disadvantage of Helmholtz coils is that the residual field is not uniformly attenuated as with static shielding, but will be in the form of a gradient. As such, it proved difficult to estimate the effect of the residual field, but nevertheless it is estimated that the remaining field is at least an order of magnitude less than the earth's field.

The effect of the Helmholtz coils on the 58.4 nm photoelectron spectrum of argon is shown in Figure 2.14. The effects mentioned earlier of reduced resolution and electron count that are caused by the earth's magnetic field are clearly shown.

2.6 ALIGNMENT

It was found that correct operation of the equipment depended very closely on the alignment of the analyser. A definition of alignment can be easily stated as follows. There are three axes present in the equipment, namely, the axis of the light beam, the axis of rotation of the analyser and the axis of symmetry of the field of view of the analyser. For correct alignment, all three must meet at one point and

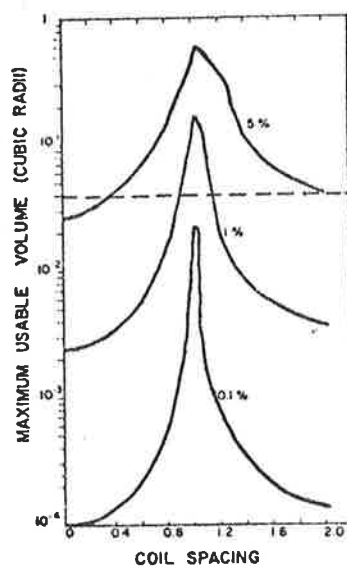


FIG 2.13 Maximum usable volume as a function of coil spacing for a single pair of round Helmholtz coils (Cacak and Craig, 1969). The dashed line indicates the volume in the present experiment where a low field is desired.

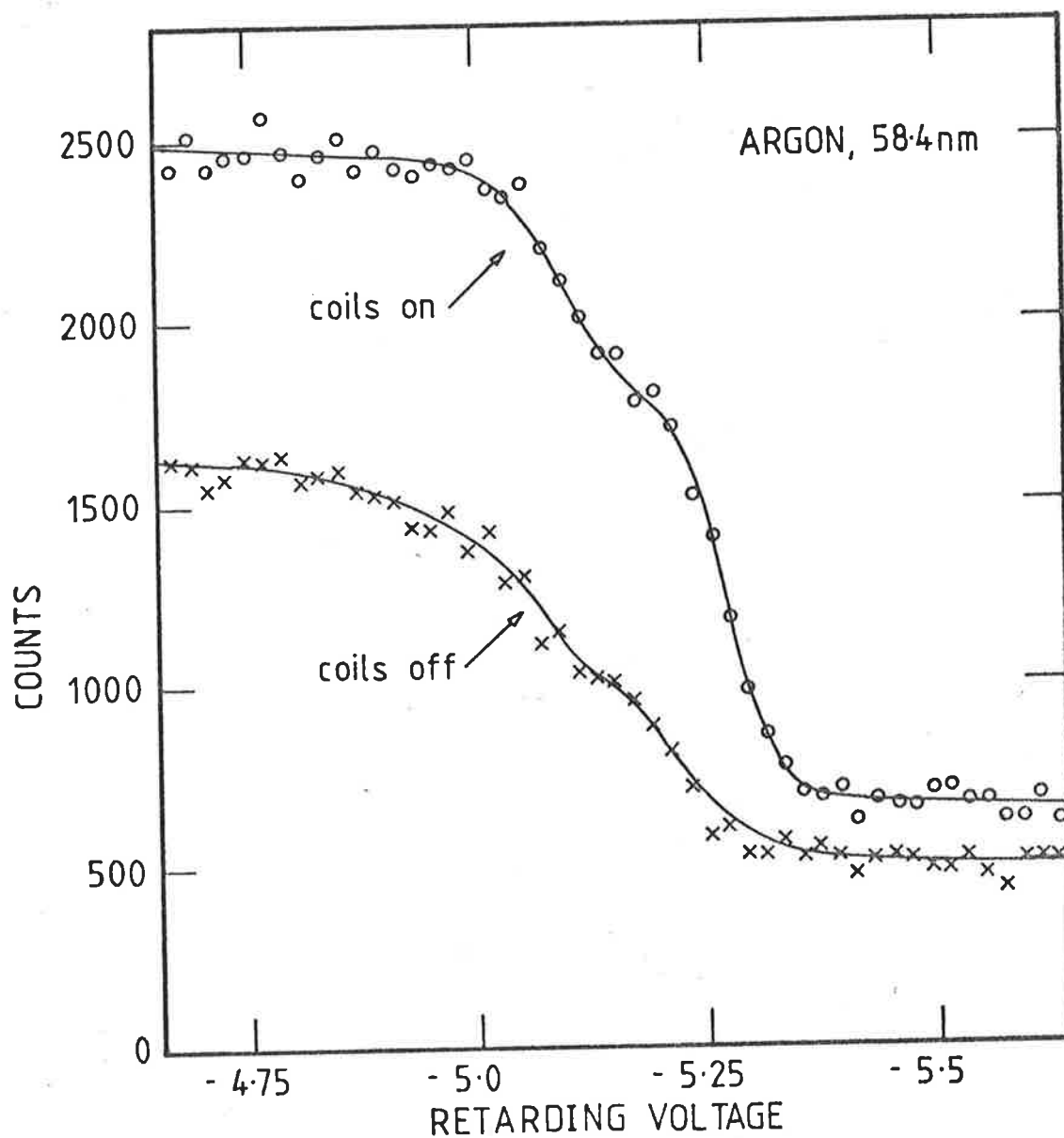


FIG 2.14 Effect on the photoelectron spectrum of argon at 58.4 nm of using Helmholtz coils to attenuate the earth's magnetic field.

furthermore that point must remain fixed relative to the analyser as it is rotated.

The analyser mounting allows three degrees of freedom for alignment, however, the axis of rotation and the location of the light beam were fixed by the mechanical mountings. These could not be altered and any mis-alignment here was due to machining tolerances. The technique to be described allowed the alignment of the analyser together with a measurement of these fixed mis-alignments.

The first step was to use a laser to define the axis of the light beam. A tube of the same diameter as the stainless steel tube of the lamp was constructed. The ends were sealed and .5 mm holes drilled accurately at the centre at each end to form a collimator. The tube was then clamped in the same position as the lamp and used to align a laser.

A second laser was used in the opposite direction with its beam accurately aligned with the first as shown in Figure 2.15. The setting of these lasers was the most important part of the procedure and even slight mis-alignment was sufficient to cause errors because of four metre path length.

Two caps were constructed to fit over the collimator of the analyser. One had a mirror on the face, the other a target. The procedure was to place the mirrored cap on the analyser and rotate the analyser until it reflected one of the laser beams. The analyser was then adjusted to reflect the beam back along itself. The mirrored cap was carefully removed, the target cap slid on and the position of the laser beam relative to the centre of the target noted. The reflective cap was then replaced, the analyser rotated to reflect the other beam

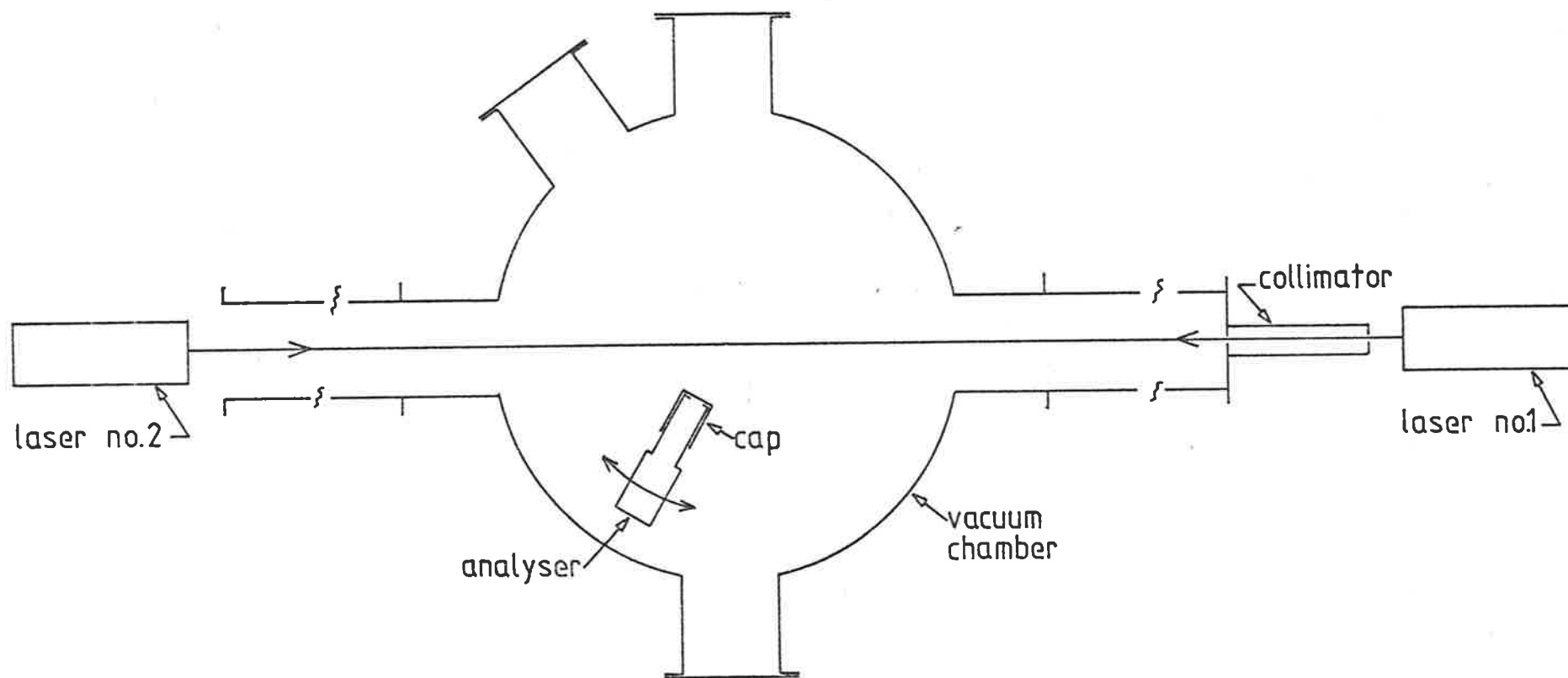


FIG. 2.15 SET UP FOR THE ALIGNMENT PROCESS.

and a second measurement made. The aim of the alignment procedure was to have both beams reflected back on themselves when the spot is in the centre of the target. The measurements made indicated the adjustments necessary to the analyser mounting to attain this goal. This could not be achieved in a single adjustment, but an iterative sequence of adjustments and measurements had to be carried out until alignment was attained.

In the present equipment it was found impossible to satisfy the alignment condition because of a slight mis-alignment of the light beam axis and the axis of rotation. Thus the condition of alignment was changed to one of minimising the distance of the spot from the centre of the target and ensuring this was the same at each end. This error was found to be 1 mm and the final result was equivalent to aligning the analyser on a beam parallel to the light beam but 1 mm away from it. The effect of this on the results will be discussed in Section 2.7.

One problem that was considered was that the alignment procedure was performed at atmospheric pressure and that when evacuated some of the mechanical alignments might change. This was checked by fitting perspex covers on the ports and the measurements repeated with the system evacuated. The only movement that was found was a 2 mm vertical shift in the analyser. This could be easily allowed for in the alignment procedure.

The final use of the lasers was to calibrate the angle measurement since they accurately defined zero and 180 degrees.

2.7 ANGLE CORRECTION

The most common geometry used with unpolarized light and the one used in this work is the rotation of the analyser in the plane of the beam. If the gas is diffused into the vacuum chamber, the

interaction region is defined by the intersection of the beam and the field of view of the analyser. However, this source volume changes as the analyser is rotated and this variation must be removed before the data can be analysed to extract β .

An alternative arrangement that avoids the need for a correction factor has been used by Dehmer *et al* (1975). The gas was squirted into the interaction region from a nozzle co-axial with the axis of rotation of the analyser and situated just below the beam. Provided the gas jet was cylindrically symmetric, no correction was necessary.

However, in general a correction is required, and as a first approximation it can be considered to be a function of the angle between the analyser and the beam. The electron count is then given by,

$$C(\theta) = F(\theta) \left[1 - \frac{\beta}{2} P_2(\cos \theta) \right] \quad 2.15$$

where θ is the angle between the analyser and the beam, $P_2(\cos \theta) = \frac{1}{2}(3 \cos^2 \theta - 1)$ and $F(\theta)$ allows for the change in the source volume with angle. Its inverse will be referred to as the correction factor. If the beam and the analyser field of view are both cylindrical, then $F(\theta) = \sin^{-1} \theta$ and in most instances where the angles of divergence of the beam and the field of view of the analyser are small, say less than about 3° , then this correction factor is sufficiently accurate to within 1% (Carlson and Jonas, 1971; Morgenstern *et al*, 1970). This method of correction has widespread use and will be referred to in this work as the $\sin(\theta)$ correction.

A more accurate expression has been derived by Leng and Nyberg (1977) for a cylindrical beam and a diverging analyser field of

view of half angle α degrees and this is,

$$F(\theta) = 2 \sin\theta / (\cos 2\alpha - \cos 2\theta) \quad 2.16$$

For small α , this is just the $\sin(\theta)$ correction.

A further possibility is to actually measure the correction factor. This is possible if radiation of wavelength less than the photoionization threshold of helium is available. The angular distribution for the helium s electron is measured and the β value taken to be 2. The data can then be used to correct other measurements (Dehmer and Dill, 1976b).

In the present arrangement, neither technique seemed viable. The large field of view of the analyser seemed to preclude the use of a simple $\sin(\theta)$ correction for two reasons. Firstly, the use of a "volume" correction function, which the $\sin(\theta)$ essentially is, assumes that every point in the interaction region subtends the same solid angle at the analyser. This is unlikely to be the case in this analyser due to the large penumbra. Secondly, the $\sin(\theta)$ correction is symmetric about 90 degrees, but again due to the large penumbra and the divergent light beam, it was expected there would be some asymmetry.

The alternate technique of using helium photoelectrons could not be used since the angular distribution of helium photoelectrons was required as a test of the performance of the instrument and thus inelligible as a correction factor.

The alternative that was chosen was to numerically calculate the correction factor by performing a computer simulation of the system. This analysis was also used to investigate whether the large field of view of the analyser would tend to smear out the angular distribution

that was being measured. Section 2.7.1 discusses the numerical method used in the simulation and the results of that analysis are presented in Section 2.7.2.

2.7.1 NUMERICAL ANALYSIS

The calculation was performed by taking the interaction region at a particular angle θ between the analyser and the beam and dividing this region into a set of volume elements. The contribution of each of these to the signal was calculated and the sum of these gave the expected electron intensity at that angle. This can be written,

$$C(\theta) = \sum_{\text{all volume elements}} \left[1 - \frac{\beta}{2} P_2(\cos \gamma_i) \right] \Omega_i \Delta V_i \quad 2.17$$

where $P_2(\cos \gamma_i) = \frac{3}{2} \cos^2 \gamma_i - \frac{1}{2}$, ΔV_i is the volume element which subtends a solid angle Ω_i at the analyser, and γ_i is the angle between the photon beam and the line from the volume element to the analyser.

The summation can be divided into two terms.

$$C(\theta) = \sum_{\text{all volume elements}} \Omega_i \Delta V_i - \frac{\beta}{2} \sum_{\text{all volume elements}} \Omega_i \Delta V_i P_2(\cos \gamma_i) \quad 2.18$$

If the $P_2(\cos \gamma_i)$ term could be moved outside of the second summation, then the correction factor would be $F(\theta) = \sum \Omega_i \Delta V_i$. However since the angle γ_i is not the same for each volume element, this cannot be done. It is now no longer possible to consider a single function that multiplies the angular distribution but rather it is necessary to have two functions $A(\theta)$ and $B(\theta)$ such that

$$C(\theta) = A(\theta) + \beta B(\theta) \quad 2.19$$

The method then is to perform the summation of Equation 2.18 and evaluate these functions.

The geometry is shown in Figure 2.16. The field of view of the analyser is defined by the first and last collimator apertures. The opening through the analyser seen by the volume element was calculated by projecting the front collimator opening on to the plane of the rear opening. From the area of overlap A and the distance R from the backplane to the element, the solid angle subtended by the analyser at the volume element was calculated by,

$$d\Omega_i = A \cos(90 - \gamma_i)/R^2 \quad 2.20$$

where $A \cos(90 - \gamma_i)$ is the projection of the overlap area on to a plane normal to the line from the centre of the volume element to the centre of the overlap area.

However, by definition, this formula assumes the projected area is circular and that it is on the surface of a sphere of radius R . A more accurate expression that can be used is

$$d\Omega = 2\pi(1 - (1 - [A \cos(90 - \gamma_i)/\pi R^2])^{1/2}) \quad 2.21$$

which is the solid angle subtended by a plane circular area $A \cos \gamma_i$. This still of course assumes the area to be circular which in general will not be the case.

A second fault is that the angle γ_i is defined by the photon beam axis and the line from the centre of the volume increment to the centre of the overlap area. However, this angle will vary across the

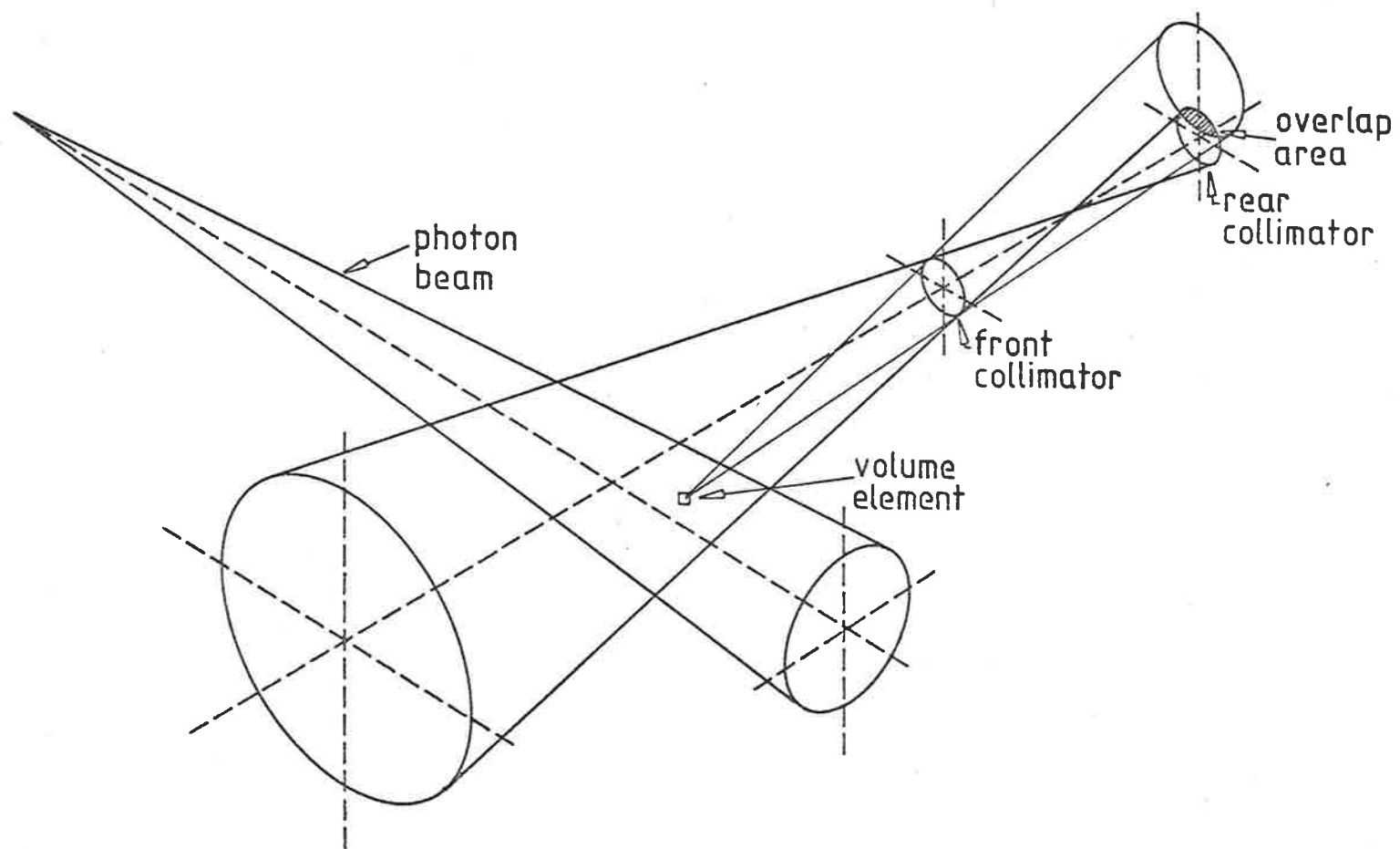


FIG. 2.16 Geometry for calculating the field of view through the analyser from a point in the interaction volume.

overlap area. If the field of view of the volume element through the analyser is a cone of half angle ϕ , then this variation can be allowed for by replacing the $P_2(\cos \gamma_i)$ term by $\frac{1}{2} P_2(\cos \gamma_i) \times \cos \phi (1 + \cos \phi)$ (Lindemans, private communication). In one respect this is a reasonable assumption since the volume increment is some ten times smaller than the overlap area and hence can reasonably be taken as the apex of a cone. However, as was the case previously, the field of view of the volume increment through the analyser will not in general be a cone due to the irregular shape of the overlap area. The correction was included though by using the angle ϕ of a cone with a base area the same as the overlap area. However, it was found that that correction had barely any effect on the results.

The overlap area that has been mentioned throughout was calculated analytically and hence was exact.

In dividing the interaction region into volume increments, use was made of the cylindrical symmetry of the analyser field of view. Slices of fixed width were made through the analyser cone and then divided into annular segments. This is illustrated in Figure 2.17. The reason for doing it this way is that for any slice, all elements an equal distance from the centre subtend the same solid angle at the analyser. This reduces the size of the computation. However, each element has a slightly different γ_i which had to be calculated.

The number of segments chosen was such that each of the $\Delta\alpha$, ΔR and Δx defined in Figure 2.17, was less than some initially fixed value. For most of the work, this was chosen to be 1 mm for ΔR and Δx while for $\Delta\alpha$ it was the angle subtended by an arc of length 1 mm at the radius R . Reducing these by a factor of two had little effect

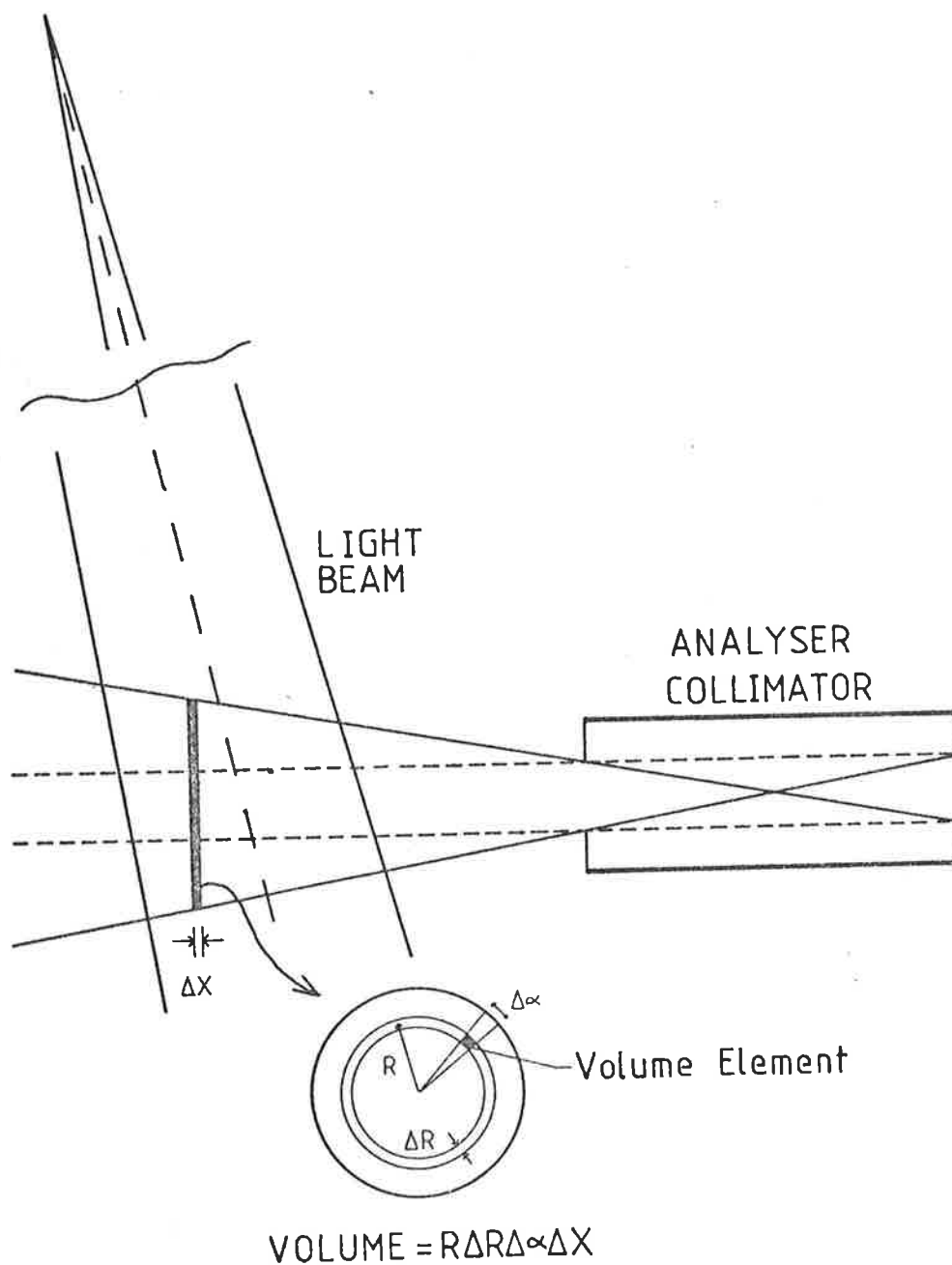


FIG. 2.17 Full size drawing of the interaction region showing the method of dissection into volume elements.

on the results but a crippling effect on the computing time and only the few values needed to analyse the data were done at .5 mm . Some idea of the size of the volume increments in relation to the size of the interaction region can be gained from Figure 2.17 which is drawn full size.

Only those volume elements whose centre was common to both cones were included. No attempt was made to determine if an element was bisected by a boundary. This will lead to some error, but since a large number of these elements will be on the edges of the analyser cone, they will have a very small solid angle and thus contribute little to the summation.

In addition, each volume element was divided by the square of its distance from the apex of the light beam cone to compensate for the reduced intensity per unit area as the beam diverges.

Whilst dimensional information about the analyser could be easily obtained, the size of the photon beam was not known. This is due to the use of the capillary to focus the beam with the unknown factor of how many reflections a light ray path can undergo and still have a useful intensity.

It was possible to measure the size of the beam by using a photocathode. This was achieved by attaching the photocathode to the front of the analyser and sweeping it through the beam. Since only horizontal movement was possible, the photocathode used was a narrow rod vertically orientated. In this way there could be no ambiguity in the beam measurement as might happen if a point photocathode was used and the scanning did not pass through the centre of the beam.

The cross section of the beam as a function of the angle measured from the centre of the capillary is given in Figure 2.18. This curve was obtained from the measured curve after correcting it for the increase that occurs simply from the use of a vertical rod. It is interesting that the extremities of the beam roughly coincide with the angle that would be obtained by a triple reflection in the capillary. This implies that it is at maximum two reflections that can occur and the light still have useful intensity. It must be pointed out though that there has been no discrimination between 30.4 nm and 58.4 nm radiation.

Rather than take the light beam as a cone with a half angle equal to the maximum measured, it was approximated by the step function also shown in Figure 2.18. The beam was then taken to be the superposition of five uniform conical beams which when added formed the step function. The values of $A(\theta)$ and $B(\theta)$ were calculated for each of the conical beams and summed.

2.7.2 RESULTS

Shown in Tables 2.1 and 2.2 are the computed values of $B(\theta)/A(\theta)$ and $A(\theta)$ respectively. Also shown for comparison, are the equivalent functions when the $\sin(\theta)$ correction is used. That is, $(1-3 \cos^2 \theta)/4$ compared with $B(\theta)/A(\theta)$ and $1/\sin(\theta)$ compared with $A(\theta)$. It can be seen that the difference between the computed functions and those for the $\sin(\theta)$ correction is about 1-2%. Also to be noticed is the slight asymmetry about 90° . Incidentally, the reason $B(\theta)/A(\theta)$ is given rather than just $B(\theta)$ is that $B(\theta)/A(\theta)$ can be compared directly with $(1-3 \cos^2 \theta)/4$ without any scaling being necessary. This is not the case however with the comparison

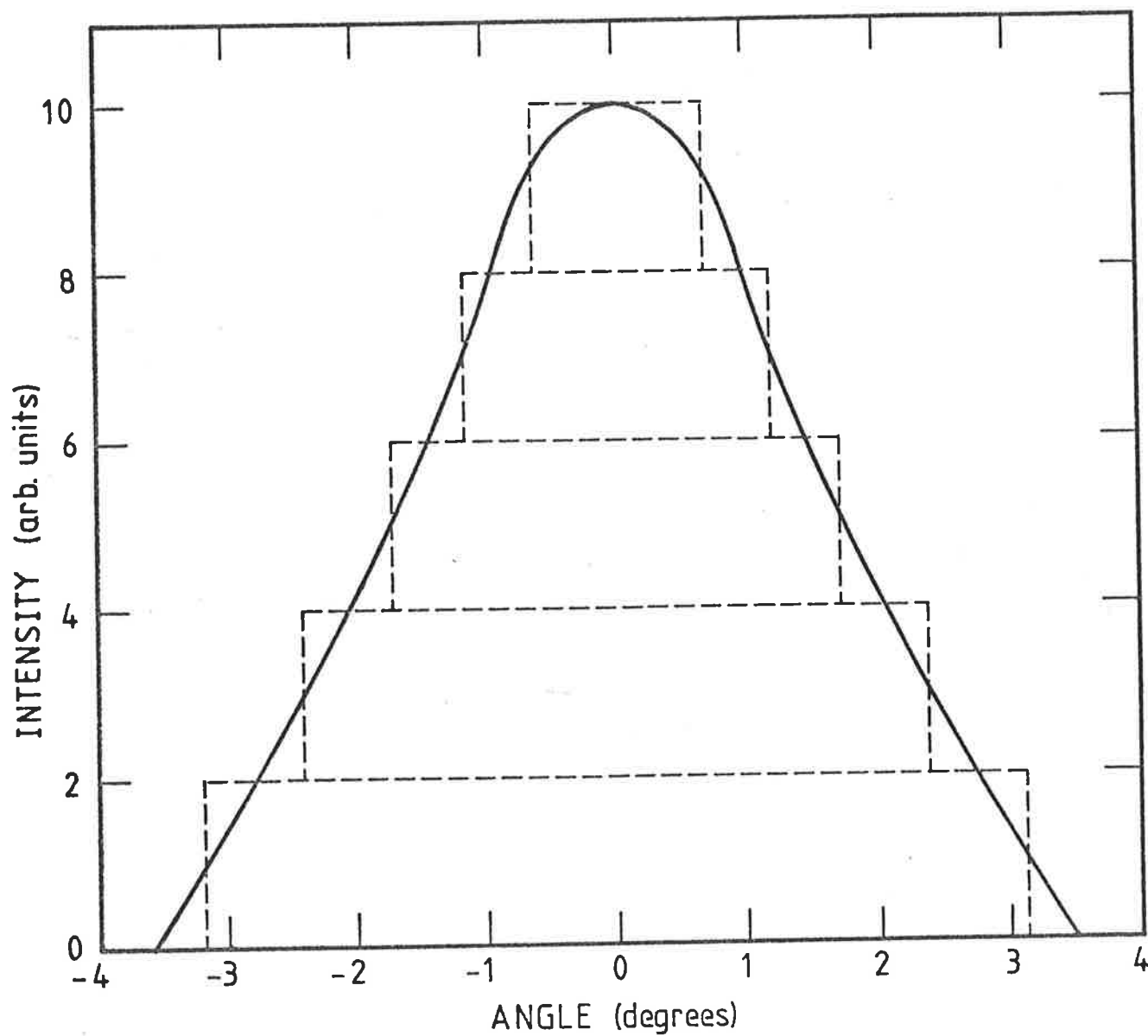


FIG. 2.18 Cross section of the photon beam as a function of the angle from the apex of the beam. The dotted lines show the five cones it was approximated by for the calculation.

θ	$B(\theta)/A(\theta)$	$(1-3 \cos^2 \theta)/4$
30	- .3113	- .3125
40	- .1898	- .1901
50	- .0605	- .0599
60	.0609	.0625
70	.1598	.1623
80	.2243	.2274
90	.2466	.2500
100	.2239	.2274
110	.1590	.1623
120	.0597	.0625
130	- .0621	- .0599
140	- .1917	- .1901
150	- .3133	- .3125

TABLE 2.1 A comparison of the computed values $B(\theta)/A(\theta)$ with the function $(1-3 \cos^2 \theta)/4$.

θ	$A(\theta)$	$1/\sin\theta$
30	2.0071	2.0
40	1.5585	1.5557
50	1.3082	1.3054
60	1.1564	1.1547
70	1.0653	1.0642
80	1.0161	1.0154
90	1.0	1.0
100	1.0164	1.0154
110	1.0663	1.0642
120	1.1565	1.1547
130	1.3099	1.3054
140	1.5628	1.5557
150	2.0194	2.0

TABLE 2.2 A comparison of the calculated values of $A(\theta)$ with $1/\sin\theta$. Note that the $A(\theta)$ values have been normalised to the value 1 at $\theta = 90^\circ$.

between $A(\theta)$ and $1/\sin(\theta)$ and the values of $A(\theta)$ have been scaled such that $A(90^\circ) = 1$. For this reason, it is difficult to gain any insight from the tables as to the effect the difference between the computed values and the $\sin(\theta)$ correction values might have on β . This was investigated in the following way. From the values of $A(\theta)$ and $B(\theta)$, the expected count rate as a function of angle could be calculated for any value of β . These numbers were then analysed assuming the $\sin(\theta)$ correction to give a new value β' . The difference $\Delta\beta = \beta - \beta'$ is the error that would occur if the data was analysed simply by the $\sin(\theta)$ correction.

A graph of $\Delta\beta$ against β is shown in Figure 2.19. This has been calculated with values of $A(\theta)$ and $B(\theta)$ in 10 degree increments between 30° and 150° inclusive. As can be seen, the worst error is about .015 which as will be seen in Chapter Three is much less than the experimental error encountered. However, the asymmetry about ninety degrees can be seen if the calculation is repeated for the two quadrants separately. This is shown in Figure 2.20.

There are two conclusions that can be drawn from this. Firstly, and most importantly, the use of the large aperture in the analyser is expected to give reasonable results and secondly, there is a very slight difference between the two quadrants as expected.

It is also possible to include in the calculations the 1 mm mis-alignment that exists in the present apparatus between the centre of rotation of the analyser and the centre of the beam. This is shown in Figures 2.21(a) and 2.21(b) and has the effect of slightly increasing $\Delta\beta$.

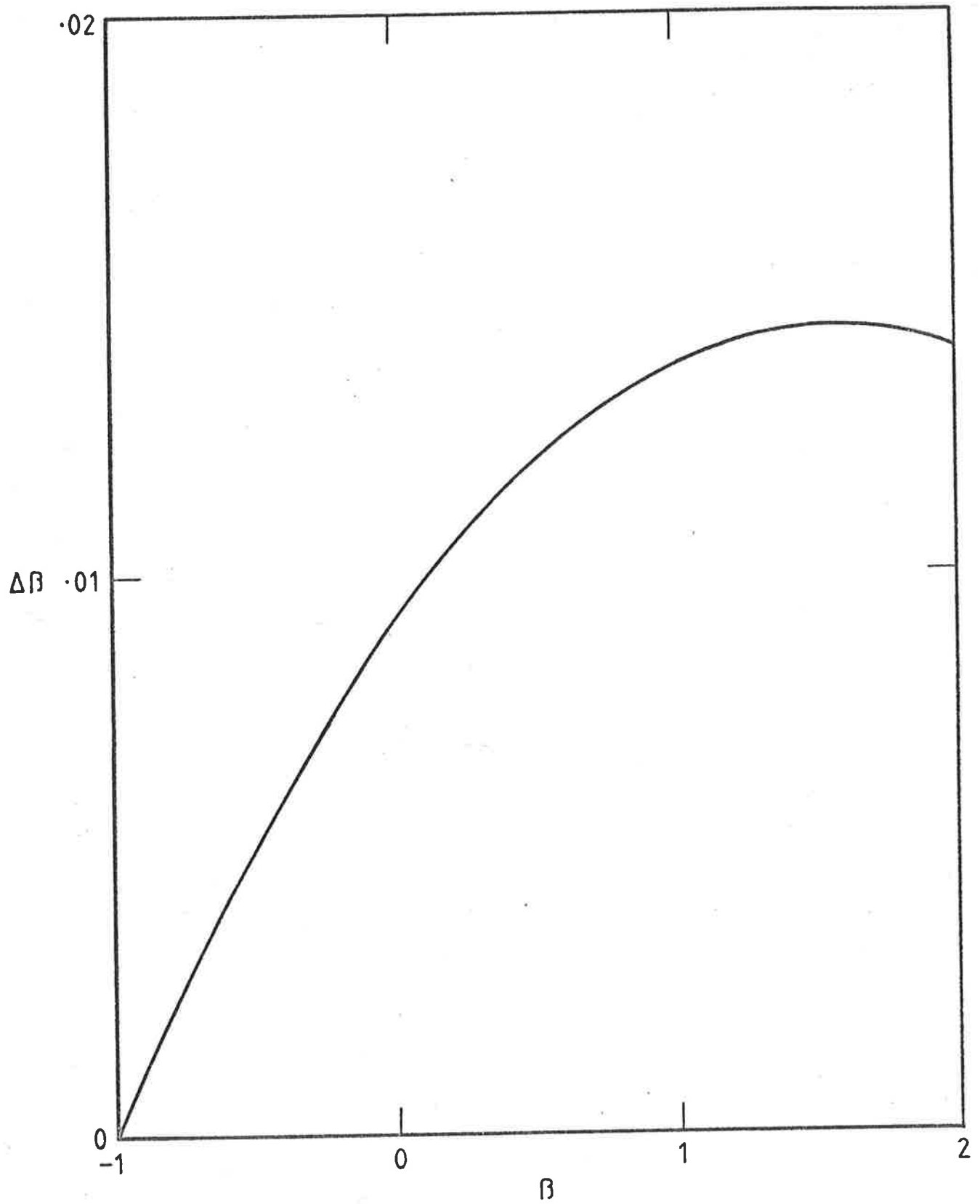


FIG. 2.19 The difference in β when simulated data is analysed using the $\sin(\theta)$ correction plotted as a function of β .

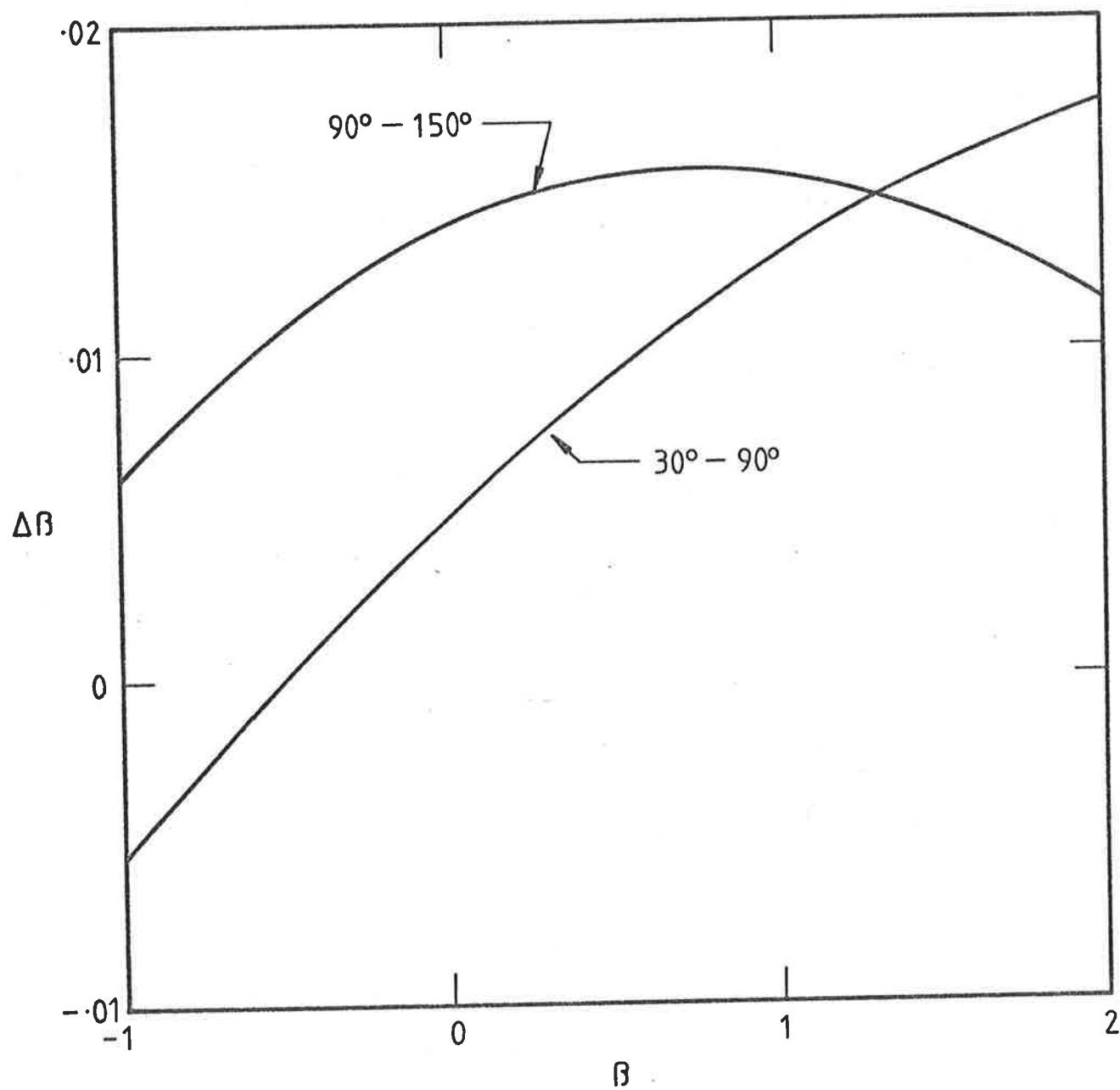


FIG. 2.20 The difference in β when simulated data is analysed using the $\sin(\theta)$ correction. Each quadrant has been considered separately.

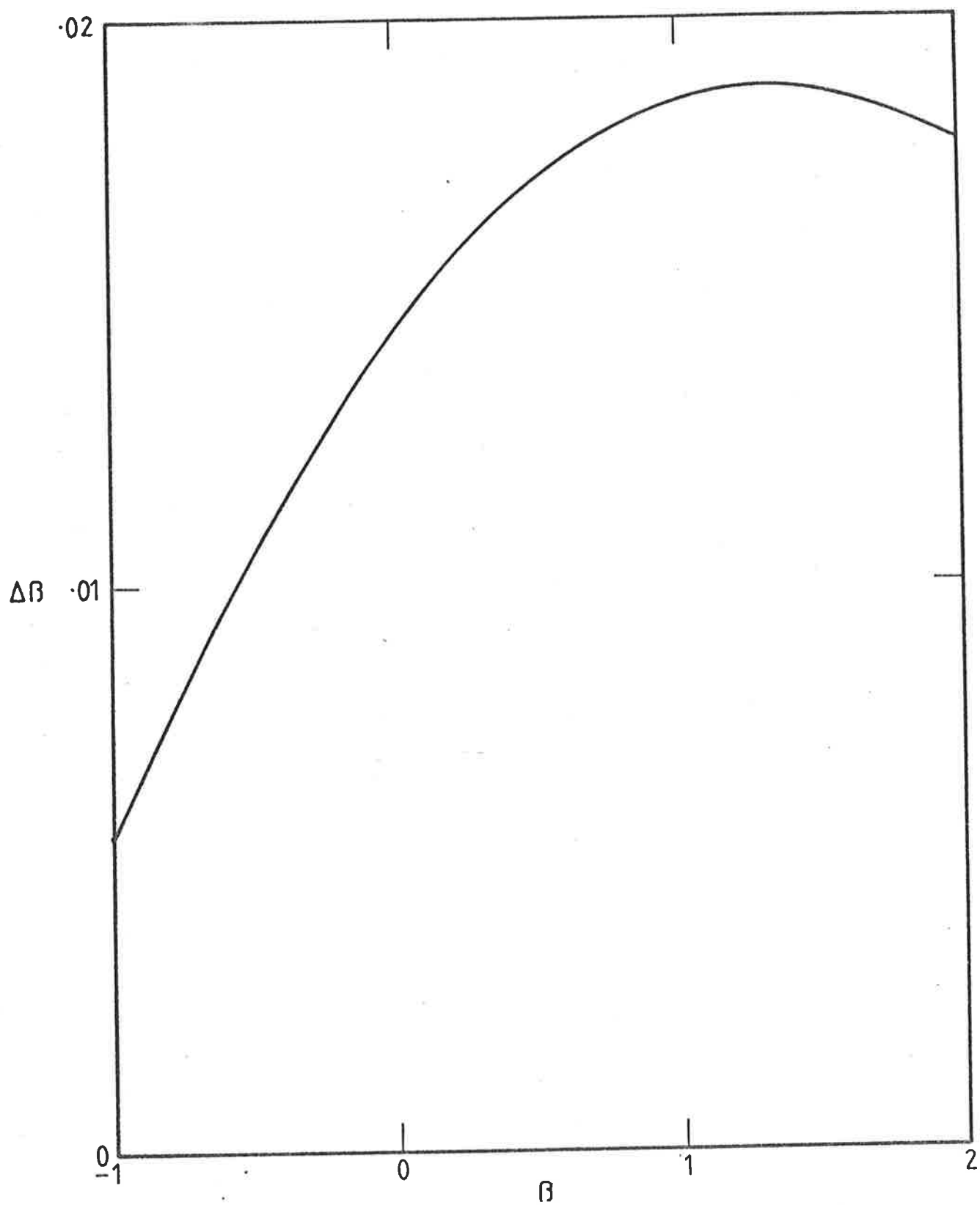


FIG. 2.21(a) The difference in β when simulated data is analysed by the $\sin(\theta)$ correction, assuming a 1 mm mis-alignment in the analyser.

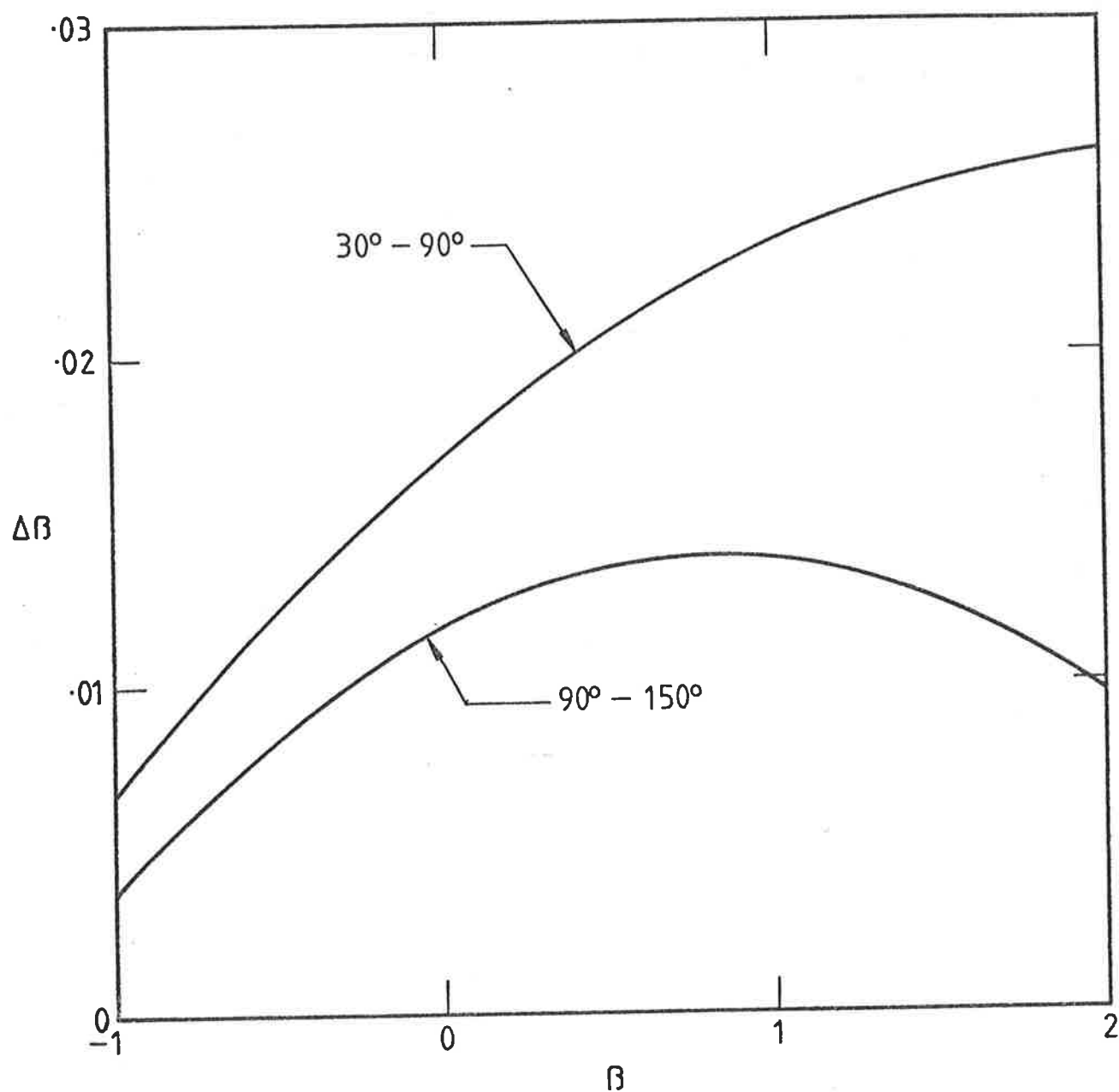


FIG. 2.21(b) The difference in β when simulated data is analysed by the $\sin(\theta)$ correction, assuming a 1 mm mis-alignment in the analyser. Each quadrant has been considered separately.

However, unanswered so far is the question of the accuracy of the calculations. When the work was commenced, it was thought the effect might be large enough to check the results with the data. However, this is not the case with the β value for helium photoelectrons being measured as $2.01 \pm .05$ using $A(\theta)$ and $B(\theta)$ and $1.98 \pm .05$ with $\sin(\theta)$, both adequately overlapping the value of 2.

With a computer program of this kind, it is difficult to define a single test for errors. A number of checks of individual parts of the program were carried out and these provided confidence in the results.

A general conclusion from these calculations is that if the simple $\sin(\theta)$ correction had been used, the error involved would have been very small. This was a most surprising result. When the work was commenced, the equipment was giving an incorrect value of β for the helium photoelectrons and this was one of a number of avenues explored to understand the problem. The error we were searching for was about 10% and it seemed reasonable that the true volume correction factor could differ from the $\sin(\theta)$ by about that amount. However, the program showed otherwise.

Nevertheless, it would be incorrect to refer to the $\sin(\theta)$ as a volume correction in this case. This is shown in Figure 2.22 which gives the volume of the interaction region for both the full width and FWHM of the beam. Also shown is the $\sin(\theta)$ volume change and all three have been normalised to 1 at 90° .

The volume was calculated from the program described above. As can be seen, on the 30-90 degree side, the calculated volume is

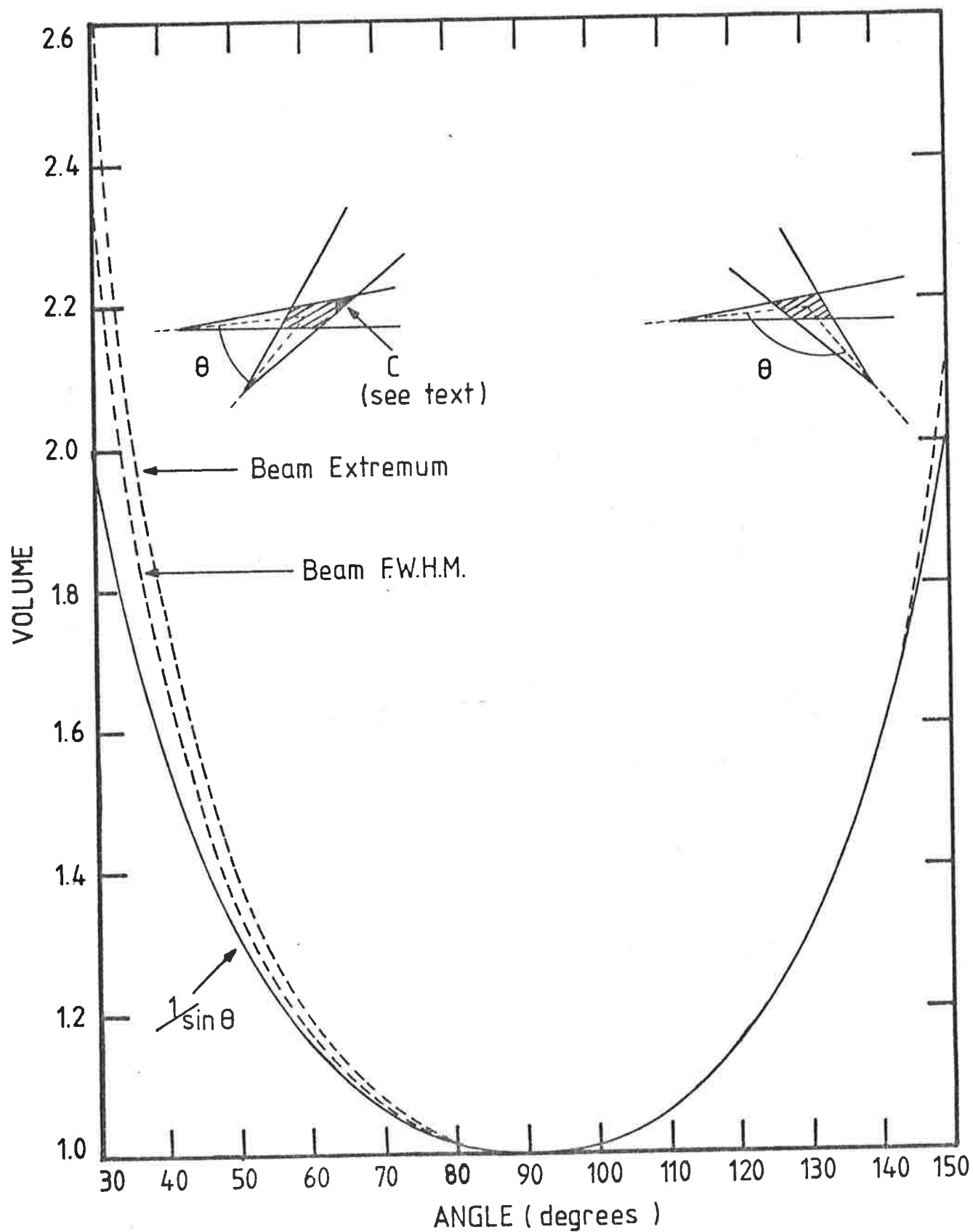


FIG. 2.22 Volume of intersection of two cones as a function of the angle between their axes. The volumes have been normalized to unity at 90°.

much larger than the $1/\sin(\theta)$ curve, while for the 90-150 degrees, there is little deviation. This difference is presumably due to the increase in volume in the corner of the interaction region in the 30-90 degree region. This is labelled 'c' in Figure 2.22. The fact that when the full calculation for the correction is performed, the values closely approach the $\sin(\theta)$, indicates that this corner region has a low weighting when the solid angle is taken into account. This is sensible since the corner would be in the penumbra of the analyser's field of view as well as being furthest away from the analyser.

It is difficult to carry this discussion further due to the complex three-dimension geometry. Nevertheless, the above does provide some insight into the reason the calculated and $\sin(\theta)$ corrections are so close.

2.8 SYSTEM OPERATION

The collection of sufficient data to evaluate an angular distribution can require the equipment to run for many hours. This necessitates complete automation to alleviate the tedium that would otherwise result from manual operation.

The electronics to be described was designed with this aim in mind and at one stage in the system development this was the case. However, a major change in the data collection technique necessitated changes in the electronics that have not yet been implemented. The majority of results contained in this thesis were collected in a semi-automatic fashion and it is this arrangement which will be described.

The electronics consists of two distinct units. The first chooses an angle from one of a set of preselected angles and advances

the analyser to it. This is described in Section 2.8.1. The second unit is a multi-channel store that collects the electron spectra and this is described in Section 2.8.2. Each of these is completely automatic in itself but the interface is human and at present requires manual switching between them.

2.8.1 ANGLE DRIVE

The shaft supporting the analyser is rotated by a motor through a reduction gear box to give a final drive rate of .1 radians per second. The motor can be driven in either direction, although a change in direction is accompanied by a delay due to back lash in the gears.

The gear attached to the shaft which is driven by the motor, in turn rotates a potentiometer. A voltage is applied to each end of the potentiometer and the voltage on the wiper then is directly proportional to the angle of rotation of the shaft. A particular angle is selected by comparing this voltage with that from a pre-settable potentiometer. The voltages on both potentiometers are derived from the same reference voltage to minimise drift errors.

The voltage range of the preset potentiometer can be adjusted so that the complete rotation of the potentiometer corresponds to any angle range from 360 degrees down to 10 degrees. This means that if only one quadrant is to be used, as was generally the case, the preset potentiometer could be configured so that the whole rotation corresponded to that one quadrant. This eased the task of setting a potentiometer for a particular angle. The output of the preset potentiometer and the output of the driven potentiometer pass to a

comparator which controls the motor. This is shown in Figure 2.23.

To prevent hunting, a wide comparator window is used. This means that for reproducibility of angles, the analyser is always tracked towards a chosen angle from the same direction. Despite this precaution, it is still occasionally possible for the mechanism to experience difficulty attaining the desired angle either due to mechanical problems or a poor contact on the potentiometer wiper. To prevent this affecting the results, the electronics is arranged to require the drive to have settled for 8 seconds after reaching an angle before continuing with the data collection. By "settled" is meant that once the comparator output has changed state, indicating the angle has been reached, it is not allowed to change again during that period. If it does, the eight second timer is re-started up to a maximum time of 90 seconds. After either of these limits is reached, the motor drive is turned off to prevent any noise pulses on the comparator lines re-starting the motor during the data collection. The extra timing cycles were rarely required and the reproducibility of the drive is better than .25 degrees.

A maximum of twelve preset angles can be set up on twelve individual potentiometers, although the use of the multichannel store in the latter stages of the work limited the number to four. These are selected in turn with an analog multiplexer. Since the drive is constructed to track towards the angle only in one direction, the preset angles must be initially set up in a sequentially increasing order. There is one further angle, a reset position. The analyser always starts an angle sequence from this position to ensure the first angle is approached from the correct direction.

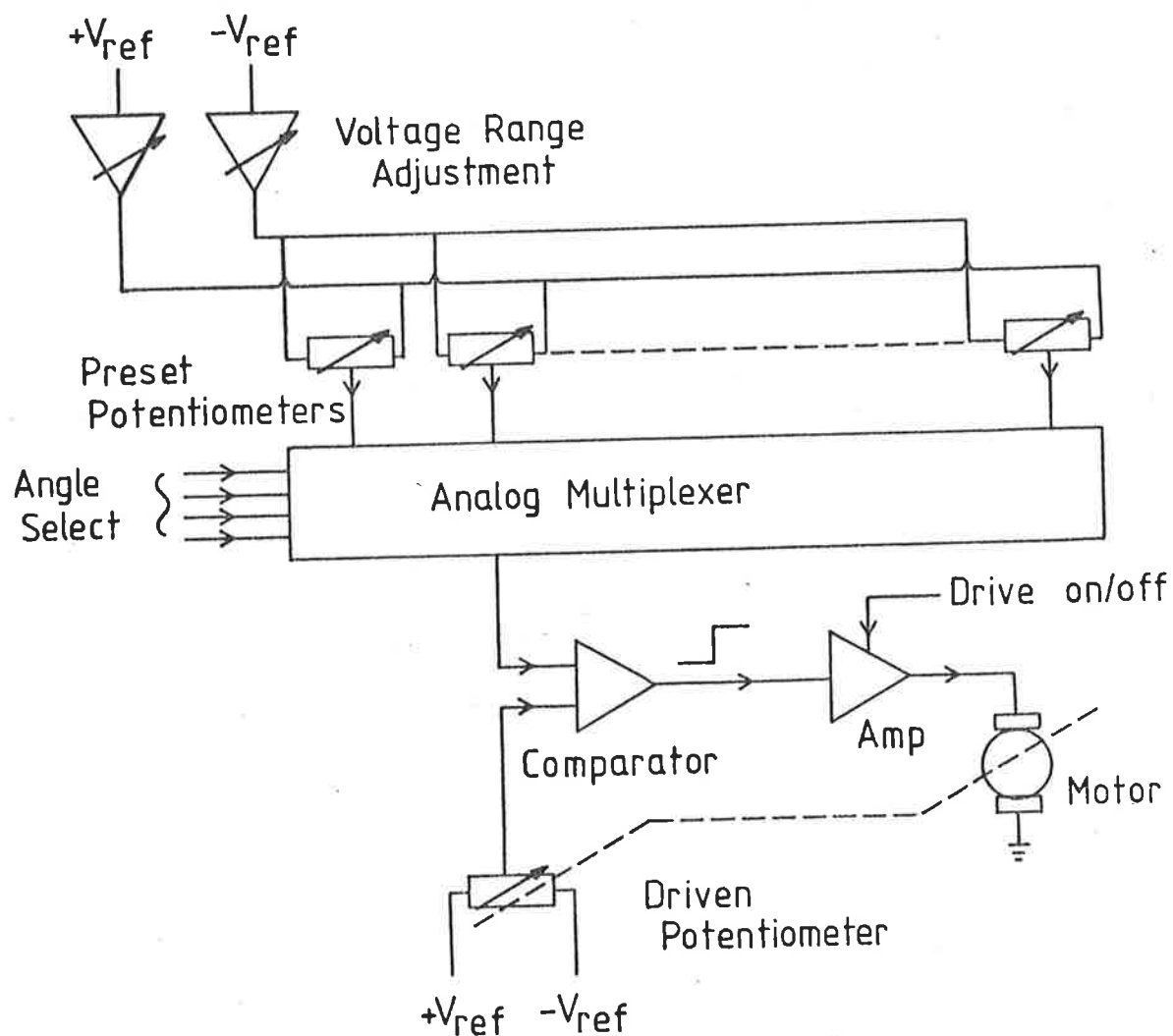


FIG. 2.23 Schematic of the angle drive electronics.

If the angles need to be scanned in the opposite direction, then the drive has to track back to the reset position and then forward to the new angle each time. In fact each angular distribution measurement consisted of an equal number of forward and backward runs. That is, if four angles were to be scanned, the sequence would be something like 30° , 40° , 70° , 90° , 90° , 70° , 40° , 30° . This helped compensate for any slow monotonic drift in the gas pressure or lamp intensity.

The angular range of the analyser is limited to 190 degrees due to the positioning of the scattering shields as mentioned in Section 2.3.4. The travel is restricted by two microswitches which prevent the analyser moving outside the region, but still allow it to reverse away.

2.8.2 DATA COLLECTION

The instrument used to accumulate the electron counts is a multichannel store. This consists of 400 channels each capable of storing 100K counts and can be configured as one block of 400 channels, two blocks of 200 channels or four blocks each of 100 channels. The channel electron multiplier pulses are first amplified to TTL logic level as explained in Section 2.3.3 and then fed into the multichannel store into a channel number which depends on the retarding voltage on the analyser grid. The final result then in a block of say, 100 channels, would be the electron counts as a function of retarding voltage.

A block diagram of the electronics is shown in Figure 2.24. The control logic is largely concerned with generating the necessary timing pulses. The sequence is to first output a pulse to a counter

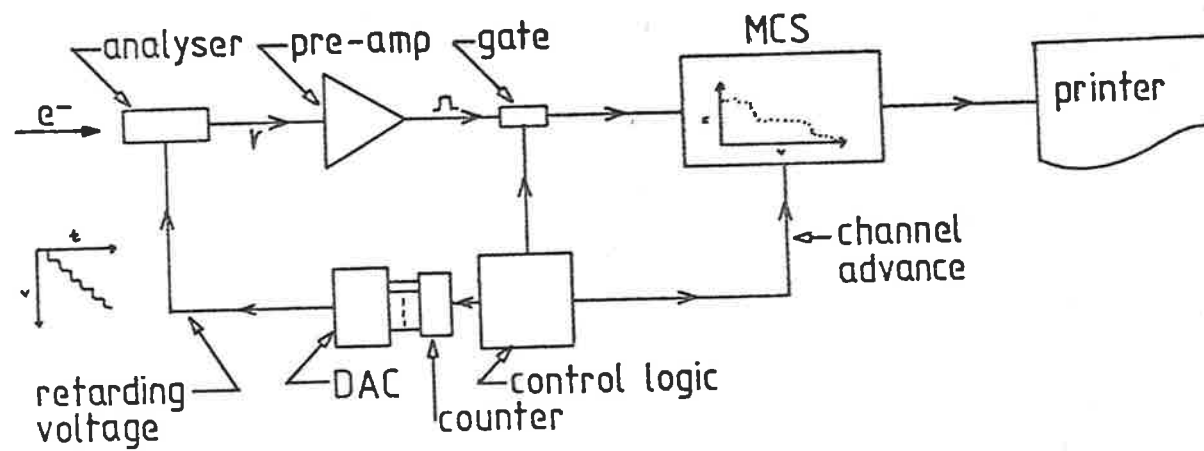


FIG. 2.24 Block diagram of the electronics for recording the electron count as a function of retarding voltage.

which controls a digital to analog converter (DAC) to produce the retarding voltage. The gate controlling the entry of pulses into the multichannel store is then opened and pulses counted into a specific channel for a certain fixed time. Then the gate is closed, another pulse output to the counter to advance the DAC to the next retarding voltage, the gate opened and pulses admitted to the next channel of the multichannel store. The sequence can be repeated a number of times to accumulate a spectrum. Once this is finished, the data can be printed out.

In addition, the DAC voltage passes through an amplifier of which the gain and offset can be adjusted to produce the desired voltage range.

Angular distribution measurements were generally taken with the multichannel store configured as 4×100 channels. In this way each block of 100 channels corresponded to one angle. This limited each measurement to four angles.

2.8.3. TARGET GAS PRESSURE

The target gas enters the chamber through a 2.2 cm diameter tube which passes through the centre of the rotating head. By using a comparatively large bore tube and terminating it about 10 cms above the analyser, it was hoped to eliminate any pressure variations across the interaction region. The gas leak rate into the tube was controlled by an adjustable needle valve.

The pressure was monitored with an ionization gauge. Base pressure of the system was about 10^{-5} torr. Normal operating pressure was generally about 4×10^{-4} torr with an upper limit of

10^{-3} torr in order to avoid breakdown in the channel electron multiplier. The background pressure of helium leaking into the chamber from the lamp was insignificant. This is due to the low conductance of the pyrex capillary.

Care was taken to ensure that the pressure was very stable during data collection. It was not possible to monitor the pressure during this period as the ionization gauge was turned off to prevent either its electric field or the electrons it produced from interfering with the results. However, before and after measurements showed the pressure to be the same within the resolution of the ionization gauge. In general, once the gas pressure had been set, the system was left for at least an hour before starting data collection to ensure the pressure had stabilised. As well, the forward/backward ordering of the angles as explained in Section 2.8.1 was such as to help compensate for any monotonic drift in pressure.

The question which arises, though, is what gas pressure should be used? Obviously this should be as high as possible to provide good statistics. However, an upper limit is set by the problem of electrons scattering off the gas molecules and affecting the results. This ignores for the moment, the upper limit on pressure set by the CEM. It is difficult to know how much scattering can be tolerated and still give reasonable results. Possibly the only sure method is to take each β value at a range of pressures. However, where a range of gases is being investigated, this is a very long and tedious process. This is especially so in the present work since the data collection was only semi-automatic.

The only gas on which pressure dependent measurements were made was helium. The helium results were normally taken at a pressure reading of 4×10^{-4} torr and the pressure was varied about this value, from 2×10^{-4} torr up to 4.5×10^{-4} torr without affecting the value of β . It should be pointed out though, that the value 4×10^{-4} is the pressure as read on the ionization gauge which is NOT the absolute pressure. This will be explained further on. It is sufficient to state at this stage that the conclusion of these measurements was that at a pressure reading of 4×10^{-4} torr, the β value for the helium photoelectrons was not influenced by electron scattering. The data for the other gases was then taken in such a way that this one conclusion concerning helium could be extrapolated to the other gases. This will now be explained.

Having obtained the above conclusion for helium, we wish to examine the electron scattering in the other gases relative to that in helium. For a gas density n , scattering cross section σ , and path length x , the fraction of electrons scattered is $(1 - \exp^{-\sigma n x})$. Therefore, if we assume that all the electrons travel the same distance, the quantity we are interested in when comparing different gases is (σn) or rather for a gas of pressure p , the quantity (σp) .

As mentioned previously, the gas pressure was measured with an ionization gauge. This operates by producing electrons from a filament which accelerate towards a high voltage anode. Collisions between electrons and gas molecules produce ions which are collected. This ion current is then proportional to the gas pressure provided the electron current is constant. However, the constant of

proportionality depends on the nature of the gas since the probability of ionization will be different for different gases. The gauge is normally calibrated for dry air, and if other gases are measured, the pressure reading must be multiplied by a correction factor. For the gases investigated in this work, the correction factors are shown in Table 2.3 and labelled k . Therefore it can now be seen that when the pressure reading for helium was 5×10^{-4} torr, the actual pressure was about 3.6×10^{-3} torr. Incidentally, this is somewhat higher than the recommended operating pressure for the CEM, but no problems were encountered in this respect when using helium.

Returning to the question of scattering, if the reading on the ionization gauge is P' , then the measure of scattering is now $\sigma k P'$. Typical values of the total scattering cross section σ for electron energies appropriate to this work are shown in Table 2.3. Also shown is the product $k\sigma$. If all measurements are made with the gas pressure such that the ionization gauge has the same reading each time, then the product $k\sigma$ gives a direct measure of the amount of scattering.

And in fact this is what was done. The majority of the measurements were made in the pressure measurement range $4-5 \times 10^{-4}$ torr. It can then be seen that from Table 2.3, the product $k\sigma$ is the highest for helium, and since no pressure effects were observed for helium, then scattering was not expected to be a problem for the other gases. An exception was xenon, where the small photoionisation cross section meant using a pressure of 10^{-3} torr, although even at that pressure, the amount of scattering would still only be comparable to helium.

Gas	k	$\sigma_{\text{SCAT}} (\pi a_0^2)$	$k\sigma$
He	7.2	4	28.8
Ne	4.0	4	16.0
Ar	.75	25	18.75
Kr	.6	30	18.0
Xe	.33	45	14.9
O ₂	1.25	12	15.0
N ₂	1	15	15.0
CO	.95	15	14.3
CO ₂	.73	20	14.6

TABLE 2.3 Table showing ;

k - the correction factor for an ionization gauge.

σ_{SCAT} - total electron scattering cross section for the electron energy appropriate to this work (from Massey and Burhop, 1952).

$k\sigma$ - the product of the above two parameters.

The advantage of the above argument is that it does not depend on the calibration of the vacuum gauge, and in fact no absolute calibration was made. Similarly the values of k were simply read from the manufacturers data and although the absolute values may be slightly in error, nevertheless the trend will be the same and the above conclusions still apply.

Thus it was concluded that the results were not affected by electron scattering. In fact, the conclusion was strengthened in a comparison of the present results with other measurements (see Chapter Three). The effect of scattering is to make the distribution more isotropic and hence lower the value of β . No such trend in the data was evident.

2.9 DATA ANALYSIS

The method of collection of the data and the form it takes have been discussed in Sections 2.3.2 and 2.8.2. This section describes the techniques used to analyse that data and to extract from it the value of β for the angular distribution of particular energy electrons.

The first step is to analyse the retarding voltage curves to find the number of electrons at each angle. The method involved has already been mentioned briefly in Section 2.3.2 in describing the operation of the analyser. However, it will be considered in more detail in Section 2.9.2.

Once the data is reduced to a set of electron counts each at a particular angle, it must then be analysed to find β . This is described in Section 2.9.3.

The methods discussed in both these sections rely strongly on the technique of fitting a straight line to a series of points. In order to avoid repetition, this will be described separately in Section 2.9.1.

2.9.1 LINEAR FITTING

The process of linear fitting asks the following question. Given a set of N two dimensional data points (x_i, y_i) , what are the best values of the parameters m and b such that the line

$$y_i = mx_i + b \quad 2.22$$

fits the data ?

The technique used is the method of least squares. It is a standard analytic technique and the details are covered by many texts, for example, Meyer (1975). As such the following description will be limited to just quoting the relevant formulas and avoid the unnecessary derivations.

The method of least squares is to minimise the sum,

$$\chi^2 = \sum_{i=1}^N (y_i - mx_i - b)^2 / (\Delta y_i)^2 \quad 2.23$$

with respect to m and b . The quantity Δy_i which weights the sum is the error in y_i . If the error in x_i must be included, then the denominator of Equation 2.23 becomes

$$(\Delta y_i)^2 + m^2 (\Delta x_i)^2 \quad 2.24$$

where Δx_i is the error in x_i . However it will be shown in the following sections, that where the linear fit was used it was sufficient to consider just Δy_i .

The minimisation of χ^2 requires,

$$\frac{\partial \chi^2}{\partial m} = \frac{\partial \chi^2}{\partial b} = 0 \quad 2.25$$

This results in a pair of simultaneous equations with the following solution (Meyer, 1975).

$$m = (EB - CA)/(DB - A^2) \quad 2.26(a)$$

$$b = (DC - EA)/(DB - A^2) \quad 2.26(b)$$

where,

$$A = \sum_{i=1}^n \frac{x_i}{(\Delta y_i)^2} \quad 2.27(a)$$

$$B = \sum_{i=1}^n \frac{1}{(\Delta y_i)^2} \quad 2.27(b)$$

$$C = \sum_{i=1}^n \frac{y_i}{(\Delta y_i)^2} \quad 2.27(c)$$

$$D = \sum_{i=1}^n \frac{x_i^2}{(\Delta y_i)^2} \quad 2.27(d)$$

$$E = \sum_{i=1}^n \frac{x_i y_i}{(\Delta y_i)^2} \quad 2.27(e)$$

As mentioned before, no attempt has been made to derive these formulas, and their method of use is obvious. Thus values of m and b can be calculated.

It is also possible to calculate the variances in m and b and these are given by (Meyer, 1975),

$$\sigma_m^2 = B/(DB - A^2) \quad 2.28(a)$$

$$\sigma_b^2 = D/(BD - A^2) \quad 2.28(b)$$

and also the covariance representing the correlation between m and b ,

$$\sigma_{mb}^2 = -A/(BD - A^2) \quad 2.28(c)$$

The application of these formulas to the specific problems will be discussed in Sections 1.9.2 and 1.9.3.

2.9.2 RETARDING VOLTAGE CURVE ANALYSIS

The number of electrons of a particular energy can be found from the graph of electron count versus retarding voltage. The poor resolution of the analyser coupled with the asymmetric shape of the instrument function meant great care needed to be exercised in the fitting procedure, even for single well resolved peaks.

The retarding curve for such a peak is shown in Figure 2.25. This is for photoelectrons from the photoionization of helium by 30.4 nm radiation. A similar curve has already been used in the description of the analyser in Section 2.3.2, however helium is a useful starting point as the electrons are monoenergetic and a reasonable count rate of a few hundred counts per second ensures good statistics.

The two points on the curve that are of most importance are the full transmission and the total cut-off. However, the number of electrons is not simply the difference between the electron counts at these points. This is because, if there is a background which is constant with energy then the shape of the curve on the high voltage side of the cut-off will be a sloping line and it is the extrapolation of this line under the retarding curve which forms the base line. (Inherent in this is the assumption that the extrapolation is valid. This could not be proved, but no evidence was found to the contrary).

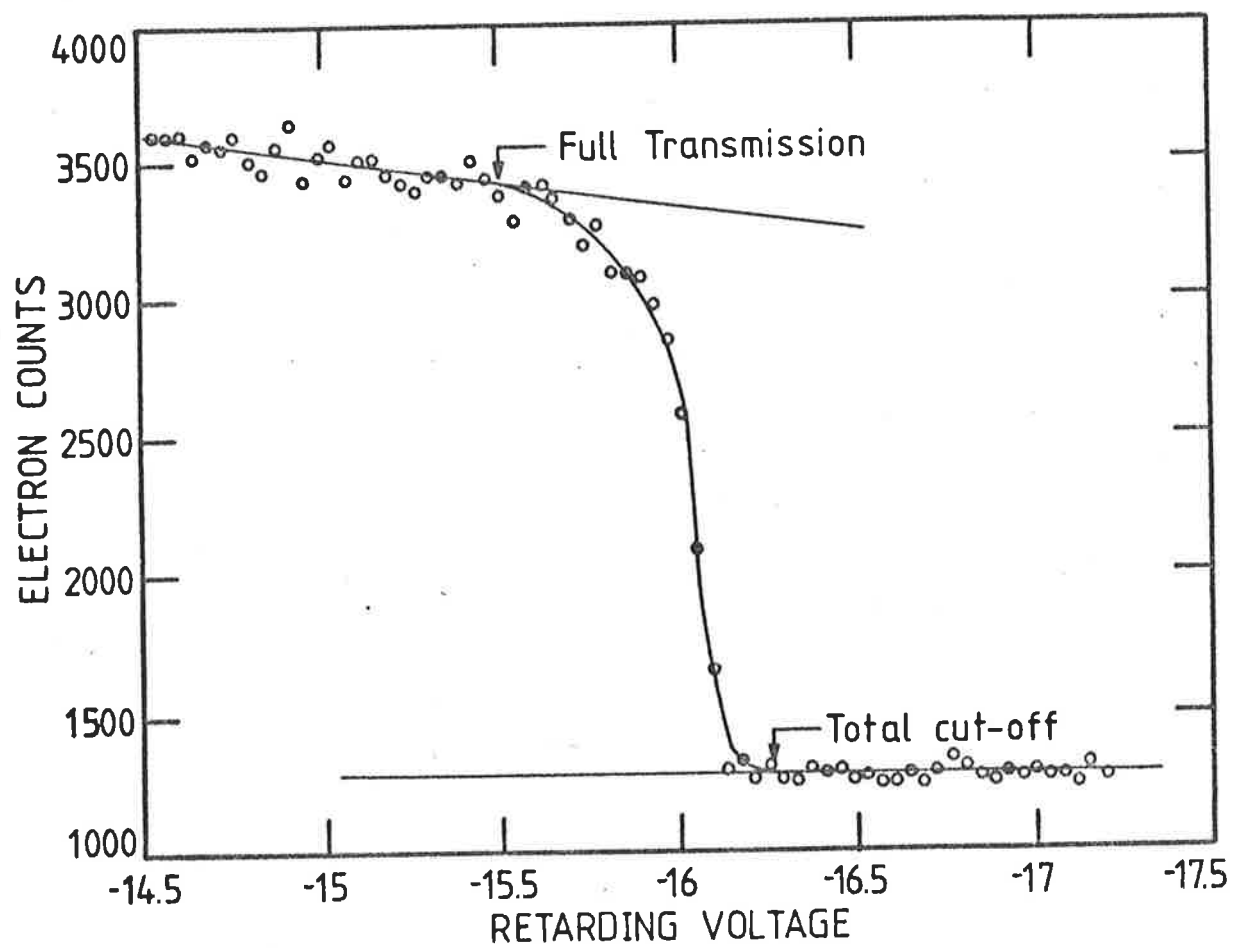


FIG. 2.25 Spectrum of photoelectrons from helium photoionized by 30.4 nm radiation.

Thus the number of electrons is the vertical height from this extrapolated line to the full transmission point.

The first step in the analysis then is to draw this line. Similarly on the low voltage side of the full transmission point, the curve is again a sloping straight line due to a background that is constant with energy. A straight line was fitted to these points and used to decrease the error in the location of the full transmission point. This will be explained further on.

The aim with both lines is to fit a straight line to a set of data points (x_i, y_i) where x_i is the retarding voltage and y_i the electron count at that voltage. Thus the formulas from Section 2.9.1 can be used. The electron counts were assumed to obey Poisson statistics and the error in y_i taken to be $(y_i)^{1/2}$. This was much larger than the .05% or so error in the retarding voltage and was assumed to be the only error. In general, the slopes of the lines were small and consequently the y_i 's not too different, thus the error was usually taken to be a constant equal to the error in the mean value of y_i . This significantly reduced the complexity of the formulas and allowed the calculations to be performed on a calculator.

Having fitted a straight line to each of the set of data points, it was then a simple matter to extrapolate the lines and calculate the value of the count at the full transmission point and at the point vertically below it on the extrapolated background.

The error in the extrapolated value (x_j, y_j) can also be calculated. This is given by,

$$\sigma_{y_j}^2 = \left(\frac{\partial y_j}{\partial b} \right) \sigma_b^2 + \left(\frac{\partial y_j}{\partial m} \right)^2 \sigma_m^2 + \left(\frac{\partial y_j}{\partial b} \right) \left(\frac{\partial y_j}{\partial m} \right) \sigma_{mb}^2$$

2.29

and since

$$\frac{\partial y_j}{\partial b} = 1 \quad \text{and} \quad \frac{\partial y_j}{\partial m} = x_j \quad \text{this becomes}$$

$$\sigma_{y_j}^2 = \sigma_b^2 + x_j^2 \sigma_m^2 + 2x_j \sigma_{mb}^2 \quad 2.30$$

Substituting the expressions given in Section 1.9.1 for σ_b^2 , σ_m^2 and σ_{mb}^2 yields,

$$\sigma_{y_j}^2 = \frac{(\Delta y)^2}{N} \left[\frac{x_j^2 + \bar{x}^2 - 2x_j \bar{x}}{\bar{x}^2 - (\bar{x})^2} \right] \quad 2.31$$

where

$$\bar{x} = \frac{1}{N} \sum_{i=1}^n x_i$$

and

$$\bar{x}^2 = \frac{1}{N} \sum_{i=1}^n x_i^2$$

and Δy is the error in the average of the y_i 's. Note that if the value of x_j is equal to the mean, that is the extrapolated value is in the centre of the equally spaced data points, then the expression reduces to the familiar formula,

$$\sigma_{y_j}^2 = (\Delta y)^2 / N \quad 2.32$$

It is now apparent why the full transmission point was located by extrapolation of the points beyond it. In that way, the N points help to reduce the error. However, also apparent from

Equation 2.31 is that the further the extrapolated point (x_j, y_j) is away from the cluster of points (x_i, y_i) , the larger the error. This is logical since a small error in the line at the set of data points will have a magnified error at a point some distance away. Thus it is apparent that in the method of analysis, the error in the point found by the extrapolation of the background beyond the cut-off can be comparable to the error in the value of the count at the full transmission point. The error in the electron count was the square root of the sum of the squares of the errors in the full transmission point and in the extrapolated background.

Thus far, no mention has been made of the problems associated with finding the points of full transmission and cut-off. Assuming a single well resolved peak, this was usually not too difficult. The cut-off was certainly relatively easy to locate since the curve ends quite rapidly at that point. In fact, to fit the line, it was only necessary to recognise a set of points beyond the cut-off.

However, at the full transmission point, the smooth slow termination of the curve made finding that point more difficult. It was usually possible to recognise points on the low voltage side of the full transmission point, even if the point itself was not apparent. The straight line could then be fitted. In instances where the full transmission point could not then be allocated by inspection, it was taken to be at a retarding voltage given by,

$$V = V_c \cos^2(10^\circ) \quad 2.33$$

where V_c is the retarding voltage at fifty percent transmission. This

assumes there is only one energy of photoelectrons contributing to the curve. The origin of the Equation (2.33) can be found in the discussion of the analyser in Section 2.3.2. Briefly, it arises from the fact that a retarding grid analyser only measures the component of energy normal to its surface. In the present analyser, the worst case possible is 10° away from the normal. If the electron has an energy E , the measured energy will then be $E \cos^2(10^\circ)$. Therefore this will define the minimum in the energy spread in the retarding curve and hence the point of full transmission.

Measurements made with good statistical data indicated that Equation 2.33 gave a reasonable estimate of the full transmission point. However, it was found that provided the two lines at the top and bottom of the curve could be drawn, error in assigning the full transmission point did not overly affect the value of β . This is shown for helium in Figure 2.26 where the β value is calculated at various points along the curve. It is seen that over the whole curve the difference is only .07 which can be compared with the $\pm .05$ absolute error in β . It is estimated that error in assigning the full transmission point would only increase the error in β by about $\pm .01$ and this has been taken into account in the final results.

A more difficult situation arises when there are two or more peaks that overlap. An example is shown in Figure 2.27 for the photoionization of krypton by 30.4 nm photons. There are two photoelectrons corresponding to the $^2P_{1/2}$ and $^2P_{3/2}$ states of the ion and they have an energy difference of .65 eV.

The first step in the analysis was simply to fit a straight

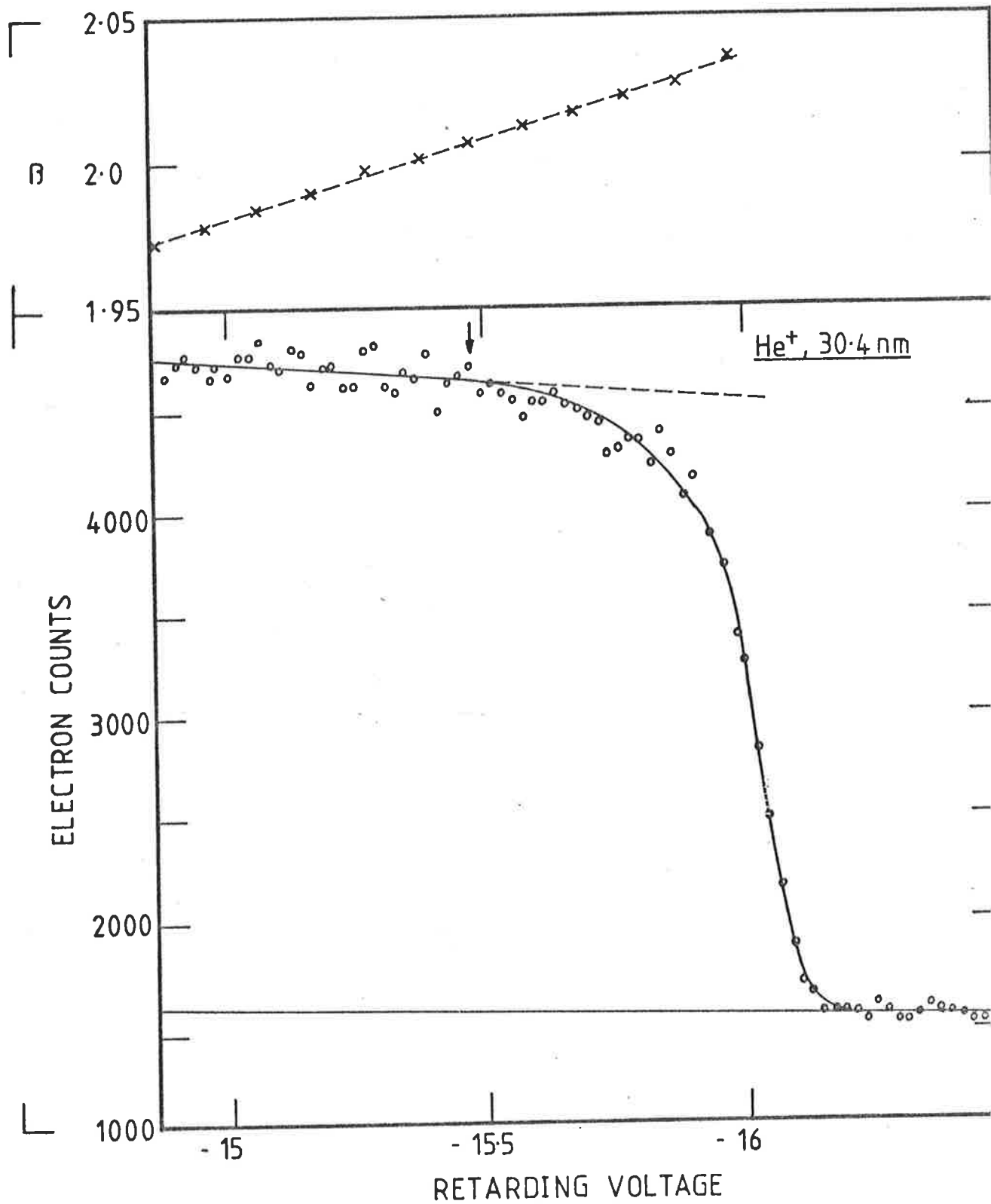


FIG. 2.26 Calculation of the angular distribution for photoelectrons from helium taking the height at different points along the curve. The arrow shows the assumed full transmission point.

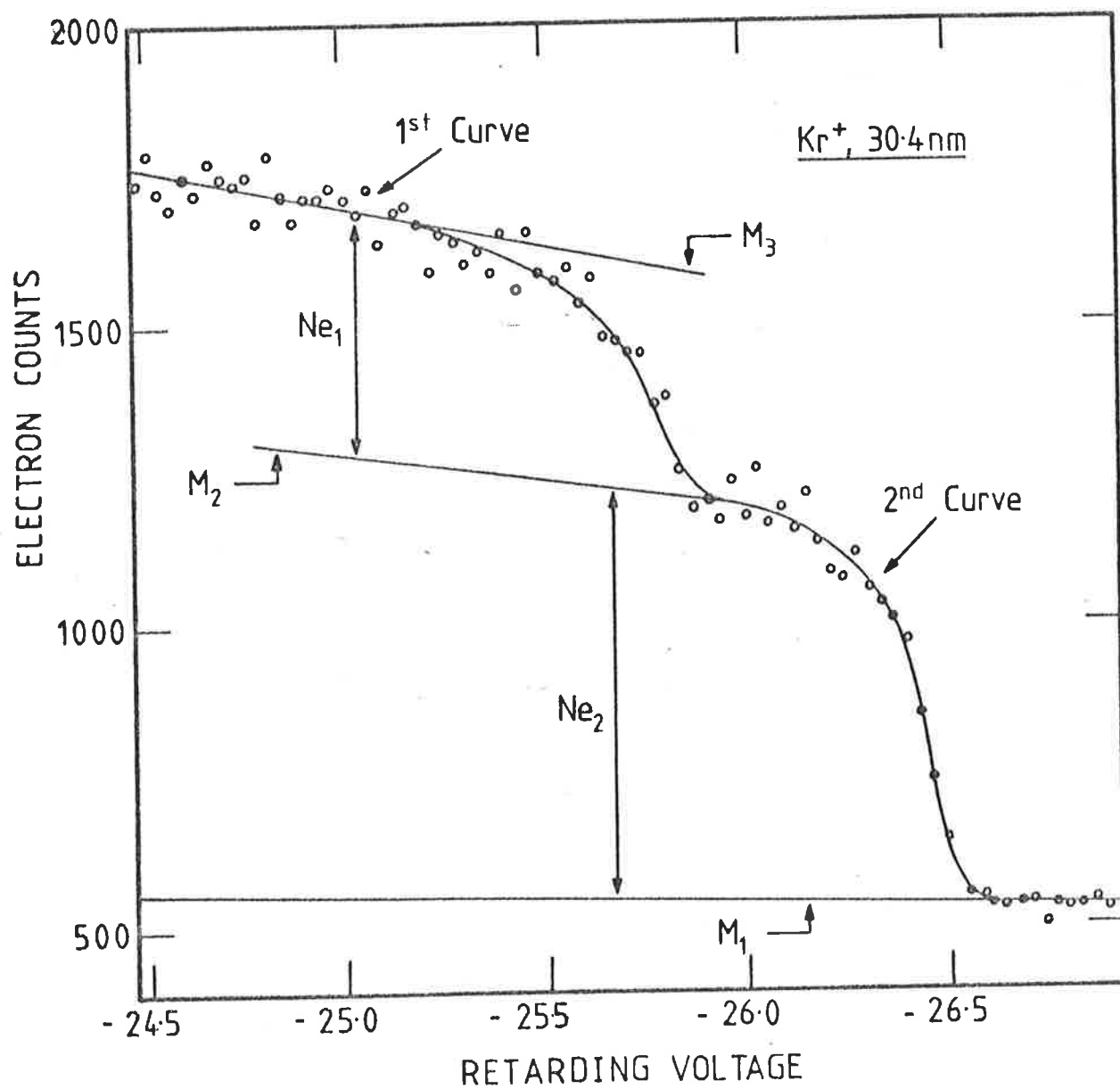


FIG 2.27 Photoelectron spectrum for krypton photoionized by 30.4 nm radiation. The notation refers to the text.

line to the points above the full transmission point of the first curve and below the cut-off of the second. The more difficult task was to draw in the extrapolated line between the two curves.

Firstly, from the shape of the curves it was possible to estimate the position of the full transmission point of the second curve. In cases where this was not possible, the curves were considered unresolved. Thus the electron count for the second curve could be found. However, to find the electron count for the first curve, the extrapolated background from this full transmission point was needed. This was difficult because there was no known relationship between the background and the step height. Consequently, the following algorithm was assumed; that any increase in the slope of the background above the retarding curve relative to that below it was proportional to the height of the step. This assumes that any increase in the background above the full transmission point is due to those electrons that are now transmitted. It was further assumed that for two steps that are energetically close, the constant of proportionality is the same.

Mathematically this was written,

$$\frac{Ne_1}{Ne_2} = \frac{\tan (\arctan M_3 - \arctan M_2)}{\tan (\arctan M_2 - \arctan M_1)} \quad 2.34$$

where Ne_1 , Ne_2 , M_1 , M_2 and M_3 are defined in Figure 2.27. The right hand side is the ratio of the angle between M_3 and M_2 to the angle between M_2 and M_1 . Whilst there are two unknowns, namely Ne_2 and M_2 in Equation 2.34, they are dependent on each other and the equation was easily solved iteratively.

Justifying Equation 2.34 is somewhat difficult. The statement that any change in the slope is due to the transmitted electrons was easily shown in practice by the fact that the gradient above the full transmission point was always greater than the gradient below the cut-off. This is an expected result. It arises from the addition to the signal of the scattered component of the now transmitted electrons. But to check Equation 2.34 requires data that can be analysed by this technique and at the same time for the steps to be sufficiently resolved to use the normal method. This was attempted, but the errors involved prevented a definitive proof. As such, it had to be assumed true but it was only needed in a few cases, and there is reasonable confidence that it gave a good estimate of the parameters.

All the data analysis was performed by hand and no attempt was made to perform any computer assisted curve fitting or deconvolution. One reason was because the data was only available in printed form and the time consuming procedure of converting it to punch cards was undesirable. However, more importantly, the asymmetric shape of the analyser function meant it was easier to analyse the data by hand than to try and convert the series of decision processes into a sequential program.

A further reason for by-passing the computer was to do with the calculation of errors. In a number of cases, especially where there were overlapping steps, the error formulas shown previously could not be used. The reason being that the formulas are only applicable for the straight line fitting at the top and bottom of the curve, while in some cases it was necessary to use the shape of the curve to help estimate the electron count. In these cases, an estimate of the error was obtained from an observation of the range of curves that could be drawn for the particular set of data points.

Once the primary data had been reduced to a set of electron counts at particular angles, a computer was used in the final estimation of β . The method used is described in the following section, 2.9.3.

2.9.3. ESTIMATION OF β

The collected data consists of a set of N electron counts C_i at particular angles θ_i . As discussed in Section 2.7, these are related to the asymmetry parameter by,

$$C_i = k (A(\theta_i) + \beta B(\theta_i)) \quad 2.35$$

where k is a constant of proportionality and $A(\theta_i)$ and $B(\theta_i)$ are the functions found in Section 2.7.

The data is first corrected by dividing by $A(\theta_i)$, that is

$$S_i = \frac{C_i}{A(\theta_i)} = k(1 + \beta B(\theta_i)/A(\theta_i)) \quad 2.36$$

Thus a graph of S_i versus $B(\theta_i)/A(\theta_i)$ is expected to be a straight line with any deviation from that line taken as due to experimental error. This error is assumed to be only in the electron count and not in the angle function. Thus each S_i has associated with it an error σ_i which is equal to the error in the electron count divided by $A(\theta_i)$.

The aim is to find parameters m and b such that the line,

$$y_i = m [B(\theta_i)/A(\theta_i)] + b \quad 2.37$$

is the best fit to the data. Then the asymmetry parameter is just,

$$\beta = m/b \quad 2.38$$

The method is to use a least squares fit as discussed in Section 2.9.1.

setting $B(\theta_i)/A(\theta_i)$ equal to x_i . Using the formulas given, values for m and b can be found. The error in β can also be calculated. Since β is a function of m and b , it is possible to write,

$$\sigma_{\beta}^2 = \left(\frac{\partial\beta}{\partial m}\right)^2 \sigma_m^2 + \left(\frac{\partial\beta}{\partial b}\right)^2 \sigma_b^2 + 2\left(\frac{\partial\beta}{\partial m}\right)\left(\frac{\partial\beta}{\partial b}\right) \sigma_{b,m} \quad 2.39$$

where σ_{β}^2 , σ_m^2 and σ_b^2 are the variances in β , m and b respectively and $\sigma_{b,m}$ is the covariant term representing the correlation between m and b . The partial derivatives of β with respect to m and b are,

$$\frac{\partial\beta}{\partial m} = \frac{1}{b}, \quad \frac{\partial\beta}{\partial b} = \frac{-m}{b^2}$$

and therefore

$$\sigma_{\beta}^2 = \frac{1}{b^4} (b^2 \sigma_m^2 + m^2 \sigma_b^2 - 2mb \sigma_{m,b}) \quad 2.40$$

and this can be calculated using the formulas for σ_m^2 , σ_b^2 and $\sigma_{m,b}$ given in Section 2.9.1.

All the data was analysed in this way using the functions $A(\theta)$ and $B(\theta)$. As well, it was also analysed using the $\sin(\theta)$ correction with the simpler forms,

$$A(\theta) = 1/\sin(\theta)$$

$$\text{and } B(\theta) = (1-3 \cos^2 \theta)/4\sin(\theta)$$

All the above formulas still apply simply by replacing $B(\theta)/A(\theta)$ by $(1-3 \cos^2 \theta)/4$. It is also apparent that in this situation, a plot of the corrected data against $\cos^2(\theta)$ is a straight line. All data was quickly checked in this way and closeness of fit to the straight line used as a test of the quality of the data. Satisfactory data was then

transferred to computer cards for more detailed analysis.

However, the data analysis technique discussed above depends on the hypothesis that the data can be fitted to a straight line of the form of Equation 2.36. Deviation from this immediately invalidates the technique. In the first instance this will happen if an interaction other than electric dipole occurs, but that will not be considered here. A second possibility is the introduction of non-linearity due to the method of data collection. This may be due to irregular motion of the analyser or perhaps to stray fields. However, the linearity can only be tested to within the accuracy of the data and if checked at one energy, may not apply to others. The tests that have been applied in the present system are discussed in Section 2.10, but they are limited by the energies and β values available. Thus inherent in this work is the basic assumption that all data can be characterised by an expression of the form $A(\theta) + \beta B(\theta)$.

2.10 QUALITY OF DATA

One of the more difficult aspects of photoelectron angular distribution measurements is ascertaining whether the values of β obtained are accurate. There are a number of techniques of differing reliability which can be used and these will now be discussed.

The first and most obvious check is the symmetry of the distribution about 90° . In fact, if accessible, all four quadrants can be checked. However, this only indicates that the angle drive mechanism has no irregularities and in itself it is not a definitive test. It must be coupled to a test which can give at least one known β value.

The first possibility then is to compare measured values with other published results, of which the most plentiful are for photoelectrons from inert gases photoionized by 58.4 nm radiation. However, even if we consider the most commonly measured of these, namely argon, it can be seen in Table 2.4 that there is a sufficiently large spread in values to make it difficult to obtain a representative value for comparison. Thus whilst a comparison with other published results is always necessary and of benefit, it is not necessarily a definitive test.

However, there is one photoelectron angular distribution that appears to be accurately predicted and hence useful as a standard. This is the photoionization of the 1s shell of helium. The resulting photoelectron, since from an s shell, has a β value of 2 which is well supported by theory (Johnson and Lin, 1977). The difficulty though is that the ionization potential is 24.50 volts and thus inaccessible with 58.4 nm radiation. Failing the availability of a synchrotron, the alternative is to use an undispersed light source capable of producing 30.4 nm radiation.

In the present work, the source described in Section 2.4 was constructed with this in mind. The resulting angular distribution is shown in Figure 2.28 and, as can be seen, the β value is $2.01 \pm .05$. Figure 2.29 shows the same data but analysed using the $\sin(\theta)$ correction and yielding a β value of $1.98 \pm .05$. It should be pointed out, though, that this was only attained after considerable time spent tracking down errors in the alignment and the data analysis technique which pointed out the necessity of having a reference.

Reference	β value	
	$^2P_{1/2}$	$^2P_{3/2}$
Dehmer <i>et al</i> (1975)		$.89 \pm .04$
Hancock and Samson (1976)		$.95 \pm .02$
Niehaus and Ruf (1972)		$.95 \pm .02$
Carlson and Jonas (1971)	$.85 \pm .05$	$.85 \pm .05$
McGowan <i>et al</i> (1969)	$.9$	
Leng and Nyberg (1977)	$1.02 \pm .01$	$1.03 \pm .01$
Mason <i>et al</i> (1977)	$.86 \pm .02$	$.88 \pm .05$

TABLE 2.4 A collection of various measurements of the β value for Argon photoelectrons produced by 58.4 nm radiation.

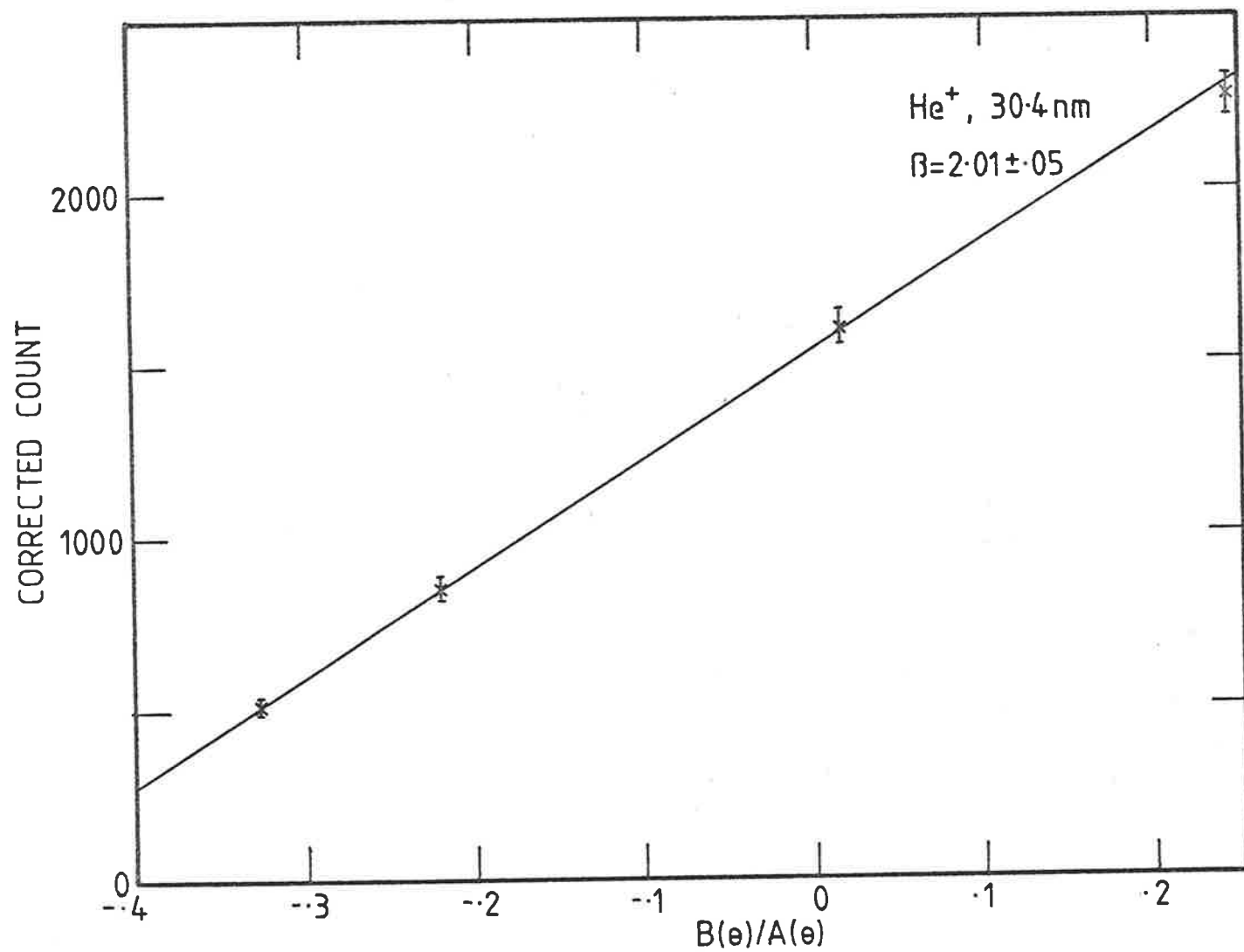


FIG. 2.28 Corrected counts for helium photoelectrons plotted against $B(\theta)/A(\theta)$.

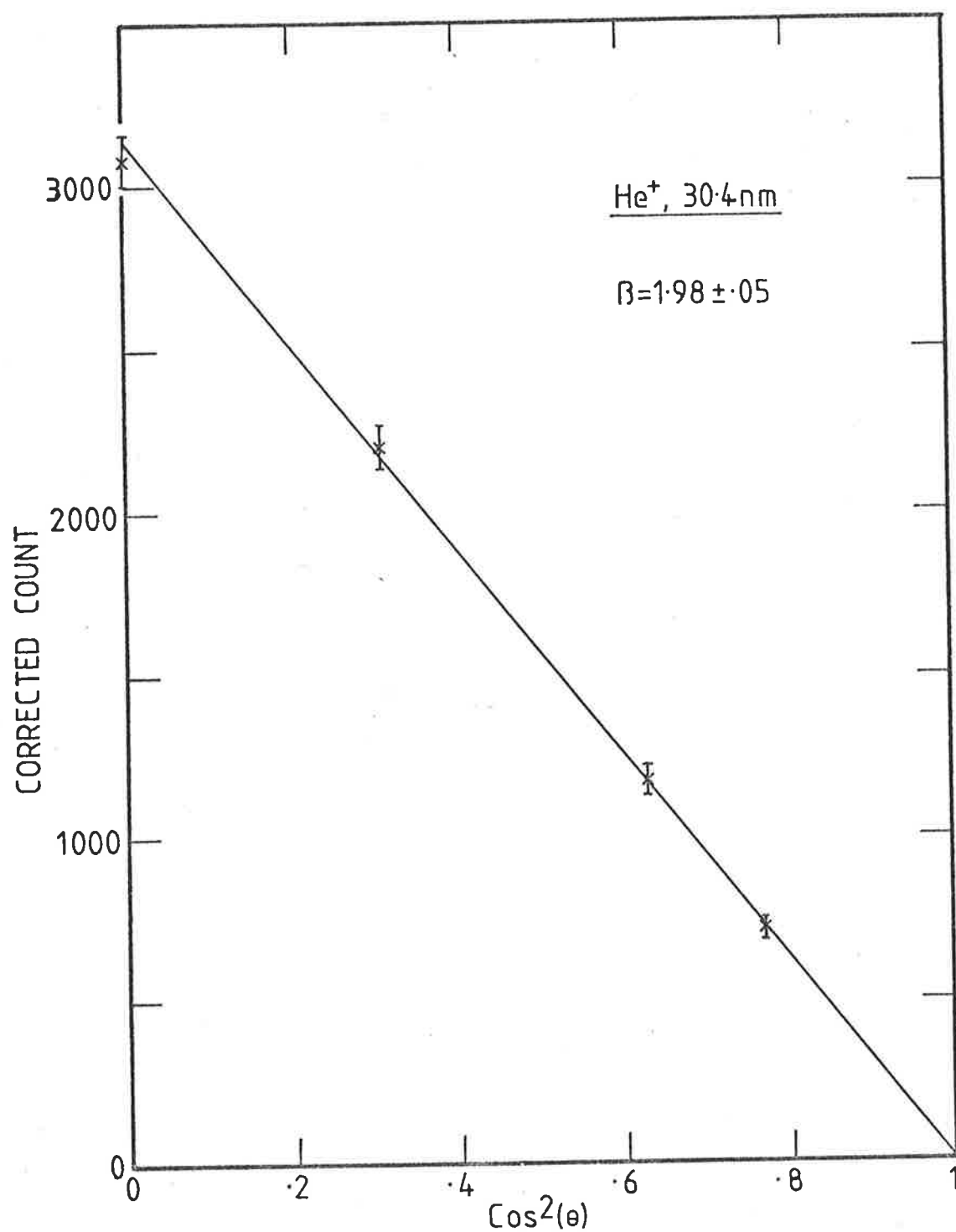


FIG. 2.29 Corrected counts for helium photoelectrons plotted against the square of the cosine of the angle.

A further necessary but not sufficient test of the equipment is that when the angle corrected data is plotted against the angle function, the result should be a straight line. The details of this have already been given in Section 2.9. The paucity of this test was demonstrated in the present work when at one stage, all data fitted the straight line, the β value for argon photoelectrons was within those quoted in Table 2.4, but the β value for the helium photoelectrons was consistently 1.88. The error was eventually traced to the method of analysing the retarding curves.

However, a difficulty arose in the present apparatus in trying to attain symmetry. The helium result given in Figure 2.28 is for data taken in the $0^\circ - 90^\circ$ sector and this quadrant consistently gave good results. However, the $90^\circ - 180^\circ$ quadrant gave inconsistent results that generally differed from the $0^\circ - 90^\circ$ sector and also failed the straight line plot test. At the time of writing, this asymmetry had not been properly solved but it is believed due to some form of wear in the rotatable head as there is some evidence that it only occurred in the later stages of the work. The indecision here is due to the fact that very few measurements were made over the two quadrants and then only at low statistics. Generally, test runs involved taking data for helium photoelectrons at just a few angles in one quadrant.

Despite this difficulty, the results presented in this thesis, all of which were taken in the $0^\circ - 90^\circ$ quadrant, are believed to be accurate. This is predominantly based on the β value obtained for the helium photoelectron but also supported by a comparison with other published results as will be seen in Chapter Three.

A rider that must accompany the use of the β value of helium photoelectrons at 30.4 nm is that this only applies to one energy. It is possible that at very low energies stray electric fields may affect the results. In the present work, the lowest energy photoelectrons were 5.3 eV from argon photoionized by 58.4 nm radiation. It is believed that these are sufficiently energetic to be largely unaffected by stray fields.

CHAPTER 3 : RESULTS.

3.1 INTRODUCTION

This Chapter will describe the photoelectron angular distributions that were measured using the apparatus described in Chapter Two. The measurements fall into the two categories of inert gases and molecules.

Photoelectrons from the inert gases neon, argon, krypton and xenon, were produced by both 58.4 nm and 30.4 nm radiation. The measurement with 58.4 nm radiation were done primarily as a check on the equipment by comparing the results with other measurements. However, as will be shown, in some cases there is still sufficient difference between the measurements of other groups for the addition of an extra measurement to be of use.

The measurements with 30.4 nm radiation have more importance since there has been only one other set of measurements using a resonance source of this wavelength, namely those of Dehmer *et al* (1975). The present results are compared with these and also with results taken using synchrotron radiation. The strength of the synchrotron radiation data lies in its giving the value of β as a function of wavelength. However this does not negate the usefulness of the discrete wavelength data which at the very least provides an extra and independent data point. In addition the errors in the β values measured using a line source are generally smaller than for the synchrotron radiation due to the requirement in the latter of measuring the polarization of the beam. Thus the synchrotron data and the line

source data complement one another to produce an enhanced experimental picture. In all cases a comparison between the experimental data and the various theoretical treatments will be shown.

In Section 3.3, the measurement of the β values for a number of molecules photoionized by 30.4 nm radiation will be discussed. Four molecules were investigated namely, nitrogen, oxygen, carbon monoxide and carbon dioxide. The energy analyser had insufficient resolution to resolve the vibrational structure and the β value was measured for photoelectrons from the whole vibrational envelope.

The results presented are compared where possible with both the synchrotron radiation measurements and the line source measurements of Katsumata *et al* (1979). Again a comparison between the experimental picture and the various theoretical results is made.

Finally, Section 3.4 presents some conclusions based on an overview of all the data as opposed to the microscopic step by step examination that is pursued in Sections 3.2 and 3.3.

3.2 INERT GASES

The angular distributions measured were for photoelectrons from the 1s subshell of helium and the outer p subshell of neon, argon, krypton and xenon. The ionization potentials of these states and the energies of the resulting photoelectrons when the atoms are ionized by 58.4 nm or 30.4 nm radiation are shown in Table 3.1. For neon, argon, krypton and xenon, separate ionization potentials corresponding to the $^2P_{1/2}$, $^3/2$ spin orbit states of the ion are shown.

The β values obtained using 58.4 nm radiation are shown in Table 3.2. The results are shown for both analysis using the $A(\theta)$

ION	STATE	IONIZATION POTENTIAL (eV)	PHOTOELECTRON $h\nu = 58.4 \text{ nm}$	ENERGY (eV) $h\nu = 30.4 \text{ nm}$
He ⁺	$2S_{1/2}$	24.59	-	16.22
Ne ⁺	$2p_{1/2}$	21.66	-	19.15
	$2p_{3/2}$	21.56	-	19.25
Ar ⁺	$2p_{1/2}$	15.94	5.28	24.87
	$2p_{3/2}$	15.76	5.46	25.05
Kr ⁺	$2p_{1/2}$	14.65	6.57	26.16
	$2p_{3/2}$	14.0	7.22	26.81
Xe ⁺	$2p_{1/2}$	13.43	7.79	27.38
	$2p_{3/2}$	12.13	9.09	28.68

TABLE 3.1 Ionization potentials for the inert gases with the ion left in the state shown. Also included is the photoelectron energy for photoionization by 58.4 nm and 30.4 nm radiation.

PRESENT RESULTS			OTHER RESULTS									
ION	A(θ), B(θ)	Sin(θ)	1	2	3	4	5	6	7	8	9	10
Ar ⁺ 2P _{1/2}	} .90±.04	.88±.04	.89±.04	.95±.02	.95±.02	.85±.05	1.02±.01		.86±.02			
Ar ⁺ 2P _{3/2}					.95±.02	.85±.05	1.03±.01		.88±.05	.4	.9	.3
Kr ⁺ 2P _{1/2}	1.19±.05	1.17±.05	1.25±.05		1.37±.03	1.20±.05		1.23±.05				
Kr ⁺ 2P _{3/2}	1.33±.05	1.31±.05	1.29±.05		1.37±.02	1.20±.05		1.30±.05		} .6	1.1	
Xe ⁺ 2P _{1/2}	1.67±.05	1.65±.05	1.63±.05	1.64±.04	1.64±.06	1.35±.05						
Xe ⁺ 2P _{3/2}	1.80±.05	1.77±.05	1.77±.05	1.78±.04	1.71±.02	1.45±.05				} .8	1.2	

1. Dehmer *et al* (1975)
2. Hancock and Samson (1976)
3. Niehaus and Ruff (1972)
4. Carlson and Jonas (1971)
5. Leng and Nyberg (1977)

6. Karlsson *et al* (1976)
7. Mason *et al* (1977)
8. Berkowitz *et al* (1967), Berkowitz and Ehrhardt (1966)
(the values attributed to these references were taken from reference 4 above)
9. McGowan *et al* (1969)
10. Samson (1970)

TABLE 3.2 The value of β for photoelectrons from argon, krypton and xenon photoionized by 58.4 nm radiation.

and $B(\theta)$ functions as discussed in Section 2.7, and using the $\sin(\theta)$ correction. The former are considered to be the "correct" values.

Commencing with argon, the two photoelectrons corresponding to the ion being left in the $^2P_{1/2}$ and $^2P_{3/2}$ states could not be resolved and the β value given is for the combination of the two. However, this is not a serious deficiency as relativistic effects are small in argon (Johnson and Cheng, 1979). The value of $.9 \pm .04$ that was obtained overlaps most other values within the error bars. Exceptions are the measurements of Berhowitz *et al* (1967) and Samson (1970), however, they are very early values and are somewhat outside of the more recent results. A similar statement can be made concerning the results of Berkowitz *et al* (1967) for krypton and xenon and they won't be considered further. The results of McGowan *et al* (1969) can also be considered "early values". Their argon value agrees quite well with more recent results, the krypton value slightly less so, and the xenon value not at all. These results, as well, will not be considered further.

Returning now to the argon data, another value which disagrees with the present results is that of Leng and Nyberg (1977). However, there is evidence (Kibel *et al*, 1979) that their results are in error due to scattering and that the value 1.02 should be closer to .97.

Although all the remaining values do overlap with the present value, they do not overlap between themselves and despite the large number of measurements made it is still difficult to provide a definitive value for β for electrons from the 3p subshell of argon. As such it is not difficult to justify the addition of this extra measurement.

The β value obtained for photoelectrons from krypton when the ion is in the $^2P_{1/2}$ state was $1.19 \pm .05$. This overlaps most other values within the sum of the errors. The exception is the value $1.37 \pm .03$ obtained by Niehaus and Ruf (1972). The β value of $1.33 \pm .05$ when the ion is left in the $^2P_{3/2}$ state also overlaps all other values with one exception, this time the value $1.20 \pm .05$ of Carlson and Jonas (1971).

As can be seen the value $\beta(^2P_{3/2})$ was found to be greater than $\beta(^2P_{1/2})$ which agrees with the measurements of Dehmer *et al* (1975) and Karlsson *et al* (1976). However, the .14 difference found in the present work is greater than the .04 of Dehmer *et al* (1975) or the .07 of Karlsson *et al* (1976), although if the errors in β are taken into account, this variation is not necessarily significant.

The β values for photoelectrons from xenon were found to be $1.67 \pm .05$ and $1.80 \pm .05$ corresponding to the $^2P_{1/2}$ and $^2P_{3/2}$ ionic states respectively. Both these values disagree with Carlson and Jonas (1971) and the $\beta(^2P_{3/2})$ value disagrees with that of Niehaus and Ruf (1972). However, good agreement is found with the values of Dehmer *et al* (1975) and Hancock and Samson (1976). Again the value of $\beta(^2P_{3/2})$ was found to be greater than the $\beta(^2P_{1/2})$ which agrees with the other authors.

Thus, it was concluded that considering the range of β value measurements with 58.4 nm radiation, a comparison with the present results showed there to be no gross errors in the equipment.

Continuing with the results, Table 3.3 summarises the values of the asymmetry parameter for photoionization with 30.4 nm radiation.

ION	PRESENT RESULTS		Dehmer <i>et al</i> (1975)
	A(θ), B(θ)	Sin θ	
He ⁺ 2S _{1/2}	2.01±.05	1.98±.05	1.97±.04
Ne ⁺ 2p _{1/2, 3/2}	.87±.04	.84±.04	.81±.04
Ar ⁺ 2p _{1/2, 3/2}	1.65±.1	1.63±.1	1.77±.04
Kr ⁺ 2p _{1/2}	1.92±.08	1.90±.08	1.93±.06
2p _{3/2}	1.94±.08	1.91±.08	1.90±.07
Xe 2p _{1/2}	1.41±.06	1.39±.06	1.58±.03
2p _{3/2}	1.24±.06	1.21±.06	1.28±.03

TABLE 3.3 The Asymmetry parameter for helium, neon, argon, krypton and xenon photoelectrons produced by 30.4 nm radiation.

The β value for the $1s$ electron from helium has already been discussed in the previous chapter and will not be considered further. Moving on to neon, this is a doublet $^2P_{1/2}, ^2P_{3/2}$ state which with ionization potentials of 21.66 eV and 21.56 eV respectively is inaccessible with 58.4 nm radiation. However with 30.4 nm radiation photoionization is possible although in the present work photoelectrons from the individual states could not be resolved. The value of β of $.87 \pm .04$ is slightly higher than the $.81 \pm .04$ of Dehmer *et al* (1975) although the error bars do overlap.

The photoelectrons from transitions in argon resulting in the $^2P_{1/2}$ and $^2P_{3/2}$ states could also not be resolved and a combined β value of $1.65 \pm .1$ was measured. A possible error in this value is due to photoelectrons resulting from the interaction of a small amount of 25.6 nm radiation produced by the lamp and any helium which leaks from the lamp into the chamber. The energy of these electrons is 23.84 eV which is close to the 24.96 eV average energy for the argon photoelectrons. However, measurements showed that this background was less than 10% of the argon signal which, assuming the value $\beta=2$ for the helium photoelectrons, would change the argon result by less than .01.

The value obtained of $1.65 \pm .1$ is less than the value $1.77 \pm .04$ of Dehmer *et al* (1975). The large error bar reflects the poor counting statistics that were obtained.

The values of β for the krypton photoelectrons agree well with those of Dehmer *et al* (1975). However in the present work the value of $\beta(^2P_{1/2})$ is found to be less than $\beta(^2P_{3/2})$ while for Dehmer

et al (1975) the reverse is true. Since in both measurements the difference in the β 's is significantly smaller than the error bars on the individual β values, the difference is at present insufficiently established.

However, for xenon, the β difference between photoelectrons from the $5p_{1/2}$ and $5p_{3/2}$ subshells is amply shown by the data and the direction of change found agrees with Dehmer *et al* (1975). However the β value of $1.41 \pm .06$ for photoelectrons with the ion left in the $^2P_{1/2}$ state is somewhat less than the value $1.58 \pm .03$ found by Dehmer *et al* (1975), while for the $^2P_{3/2}$ state the present value of $1.24 \pm .06$ agrees well with the $1.28 \pm .03$ of Dehmer *et al* (1975).

Thus far no mention has been made of either the synchrotron radiation measurements or how the data fits the theory. This will now be discussed within the context of figures 3.1 through to 3.7 which show the wavelength dependent nature of β for the outer p subshell of the inert gases already discussed. The graphs show the present results together with examples of other results and the theoretical calculations.

Neon is the simplest of the gases in that it is adequately described by LS coupling and β can be found by the Cooper-Zare model. Recalling Chapter One, this means that the photoionization of a p electron consists of outgoing s and d waves and the expression for β contains the matrix elements for these waves weighted by functions of ℓ , the orbital angular momentum, and the cosine of the phase difference between them. Figure 3.1 shows the variation of the asymmetry parameter with photoelectron energy. Shown are the present data, the synchrotron radiation measurements of Codling *et al* (1976), the line source data of Dehmer *et al* (1975) and a data point from the

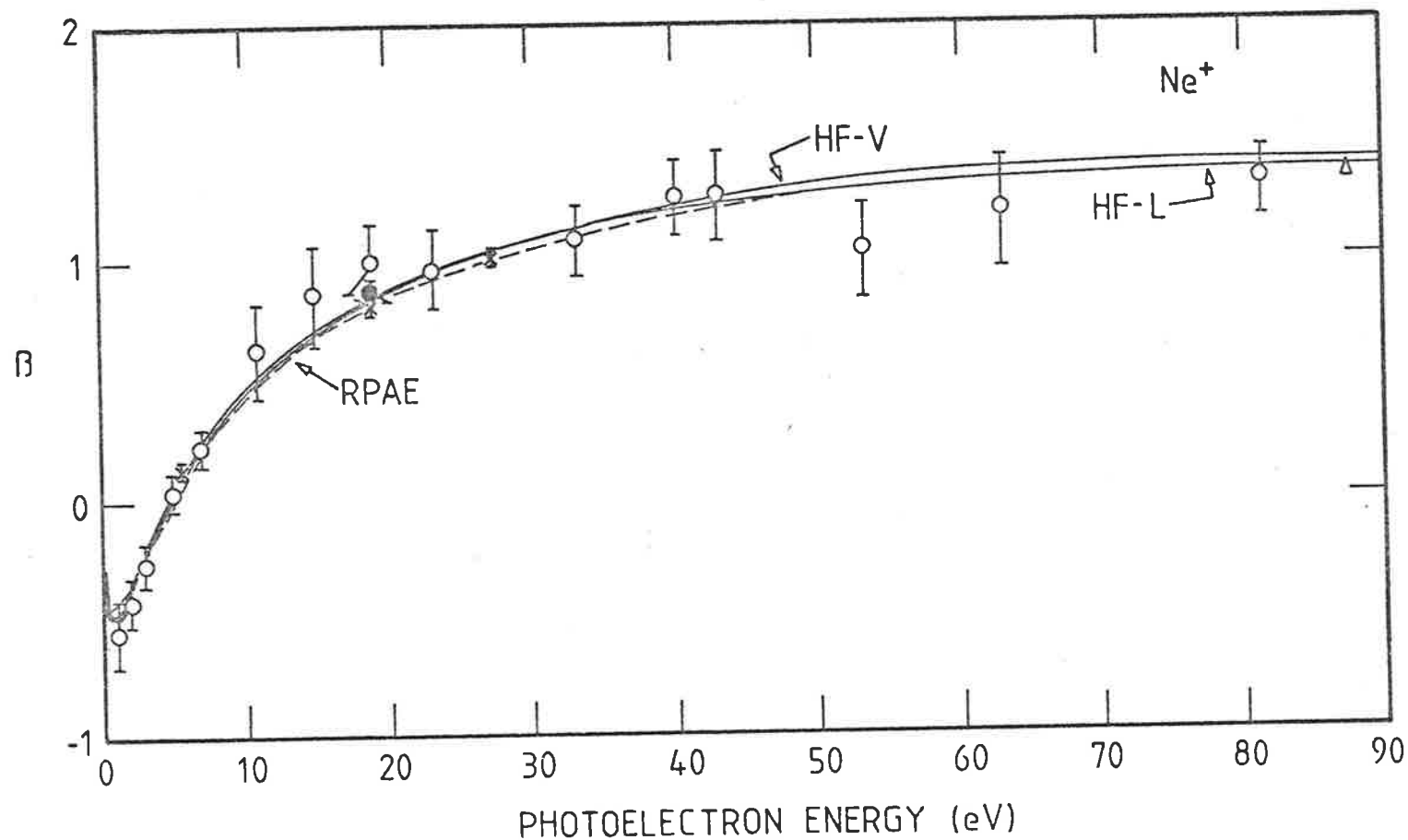


FIG 3.1 The value of the asymmetry parameter for photoelectrons from the 2p shell of neon as a function of the photoelectron energy (adapted from Codling *et al* (1976)). Experimental results shown are : ● present result; ○ Codling *et al* (1976); x Dehmer *et al* (1975); Δ Wuilleumier and Krause (1974). The HF-V and HF-L calculations are from Kennedy and Manson (1972) and the RPAE from Amusia *et al* (1972).

soft X-ray data of Wuilleumier and Krause (1974). All the data adequately fits both velocity and length forms of the Hartree-Fock calculations of Kennedy and Manson (1972) and the RPAE calculations of Amusia *et al* (1972) thus indicating that correlations are not important for neon.

The only significant difference between the theories is near threshold where the Hartree-Fock calculations show a slight trough but the RPAE do not. However, experimentally this is a difficult region since the low energy electrons are easily affected by stray fields and as yet, the correct shape in this region is undecided.

In Figure 3.2, the same experimental data is plotted with two further theoretical calculations, namely, the relativistic random phase approximation calculation (RRPA) of Johnson and Cheng (1979) and the R-matrix calculation of Taylor (1977). This diagram is taken from an article by Johnson and Cheng (1979) where it is stated that "the RRPA predictions agree well with R-matrix values, as well as with experimental determinations". However, it seems to the author, that whilst the R-matrix does indeed fit the experimental data, the RRPA deviates from the experiments below about 20 eV photoelectron energy. This seems strange since the RRPA calculations would be expected to give a good fit to the data and would seem to warrant investigation. Not shown in the diagram is that the R-matrix calculation shows a similar trough at about 1 eV above threshold as do the Hartree-Fock calculations.

To date there have been no measurements of β for the individually resolved $^2P_{1/2}$, $^2P_{3/2}$ components of neon. However, they are expected to have very close β 's and this is confirmed by the

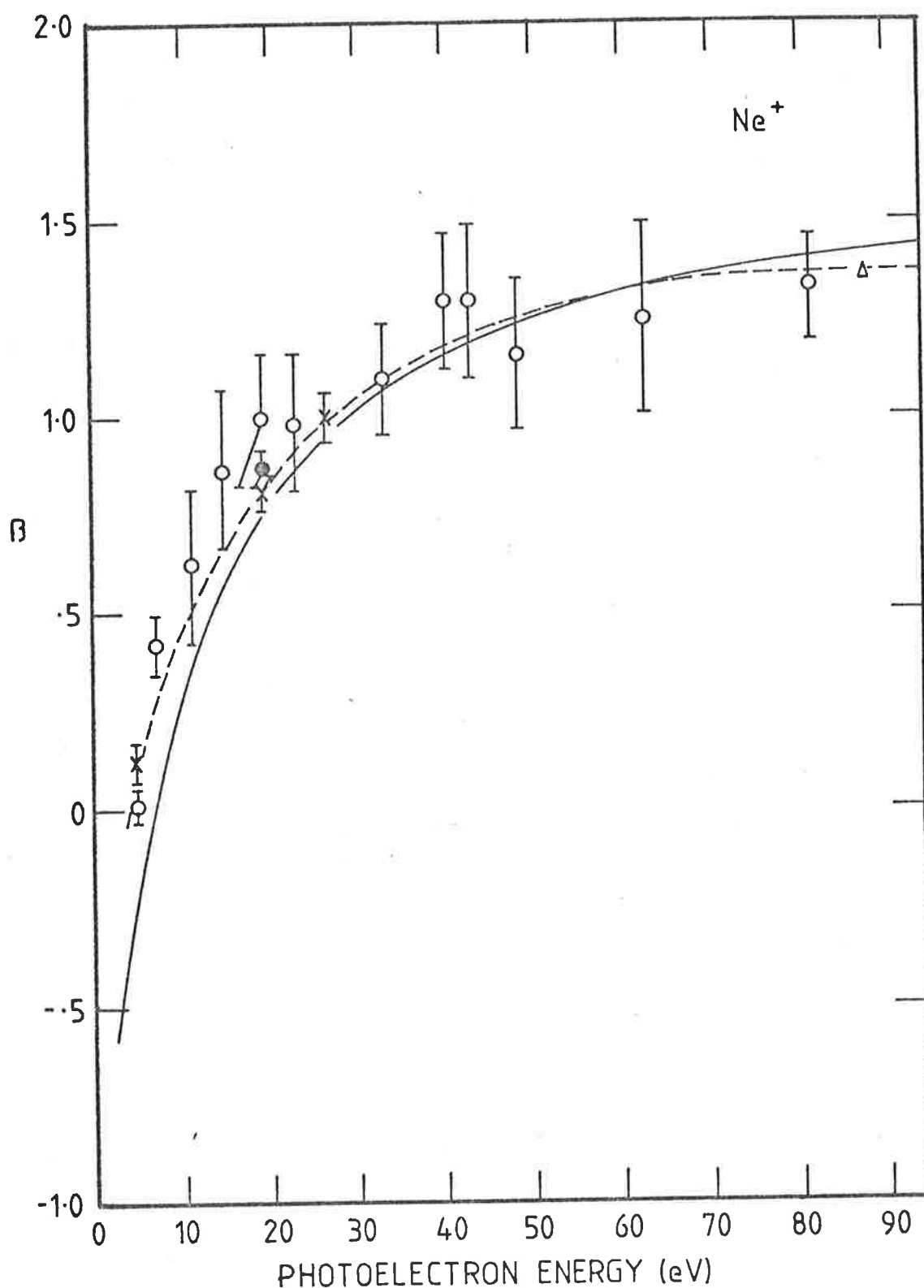


FIG 3.2 The value of the asymmetry parameter for photoelectrons from the $2p$ shell of neon as a function of the photoelectron energy (adapted from Johnson and Cheng, 1979).

Experimental results: $\bullet$ present result: O, Codling *et al* (1976); X Dehmer *et al* (1975); Δ Willeumier and Krause (1974).

Theoretical results: solid line, RRPA results of Johnson and Cheng (1979); broken line, R-matrix results of Taylor (1977).

RRPA calculations (Johnson and Cheng, 1979).

The angular distribution for photoelectrons from the 3p subshell of argon are shown in Figure 3.3. The present results agree well with the wavelength dependent results of Watson and Stewart (1974) and Houlgate *et al* (1976). Not shown, to avoid confusion, are the relative measurements of Mitchell and Codling (1972) and the pseudo-photon data of Branton and Brion (1974). Of the large amount of resonance radiation measurements, only those of Dehmer *et al* (1975) are shown, since they cover the largest number of wavelengths.

Theoretical results shown are both velocity and length forms of the Hartree-Fock (Kennedy and Manson, 1972), the random phase approximation with exchange (RPAE) of Amusia *et al* (1972) and the relativistic random phase approximation (RRPA) of Johnson and Cheng (1979). Not shown is the R-matrix calculation of Taylor (1977) but this closely follows the RRPA curve.

In the first part of the curve, the asymmetry parameter increases to a maximum at about 22 eV photoelectron energy. Up to about 8 eV all theories follow the experimental data well with the exception of the RPAE. However, Houlgate *et al* (1976) point out that Amusia in a private communication has stated that later calculations do follow the Hartree-Fock in this region. Above about 15 eV, the Hartree-Fock length curve begins to move away from the data and this deviation is even more extreme beyond the β maximum where the asymmetry parameter rapidly decreases as it approaches the region of the Cooper minimum. Recalling Chapter One, the Cooper minimum is due to the radial matrix element for the $3p \rightarrow \epsilon d$ channel becoming zero, and β is then determined predominantly by the s wave. In this region, electron correlation effects must be included and thus

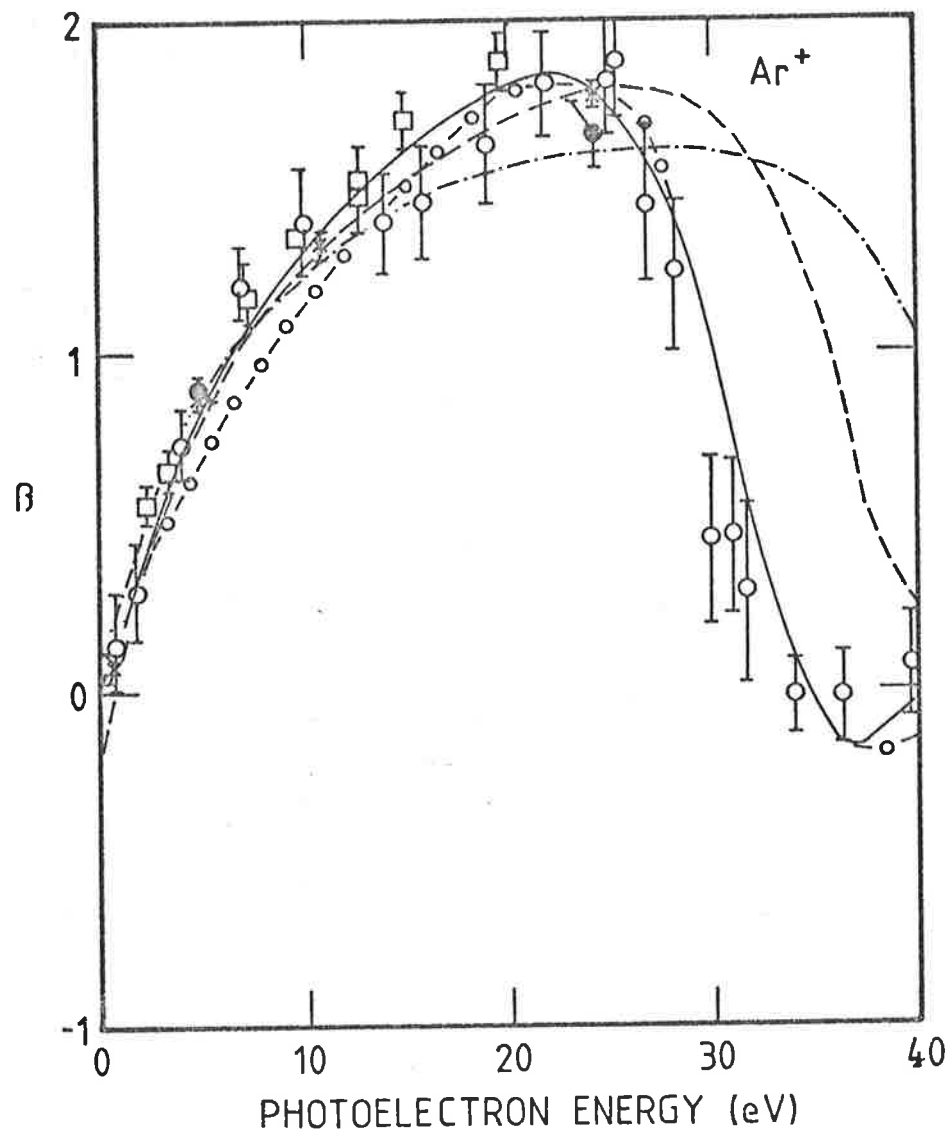


FIG 3.3 The asymmetry parameter for electrons from the 3p shell of argon as a function of the photoelectron energy (adapted from Houlgate *et al.* (1976))

Experimental results: ● present data; X Dehmer *et al* (1975); □ Watson and Stewart (1974); ○ Houlgate *et al* (1976).

Theoretical results: -○-○- RPAE, Amusia *et al* (1972); - - - - HF-V, Kennedy and Manson (1972); - · - · - HF-L, Kennedy and Manson (1972); solid line, RRPA, Johnson and Cheng (1979).

while both forms of the Hartree-Fock deviate strongly from the data, it is seen that the RPAE and RRPA results follow the data reasonably well. Nevertheless, in this region, the experiments still show a slightly lower value of β than is predicted by the theory, indicating that still further theoretical sophistication is required.

With regard to the present data, the β value at 5.37 eV agrees well with both the synchrotron data and the theoretical models. However at 24.96 eV the data point seems to be slightly below the RRPA calculation and also below small clusters of experimental points, although the error bars do overlap.

Referring to Table 3.2, only a few experimenters have measured separate β 's for the $^2P_{1/2,3/2}$ electron pair from argon and then only at 58.4 nm. The difference found, if any, is very small which is confirmed theoretically in the RRPA calculation of Johnson and Cheng (1979) since relativistic effects are also small in argon.

However, this is not the case for krypton where the $^2P_{1/2,3/2}$ electrons are separated by .65 eV and hence more easily resolved experimentally and as will be seen, relativistic effects are sufficient for there to be an observed difference in the $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ values.

In Figure 3.4, the present results and those of Dehmer *et al* (1975) show separate β values corresponding to the $^2P_{3/2}$ and $^2P_{1/2}$ final ionic state. This also applies to the synchrotron results of Miller *et al* (1977) up to about 5 eV, while beyond that combined β values are shown. The data of Watson and Stewart (1974) is also a weighted average of the β values for the two photoelectrons as are

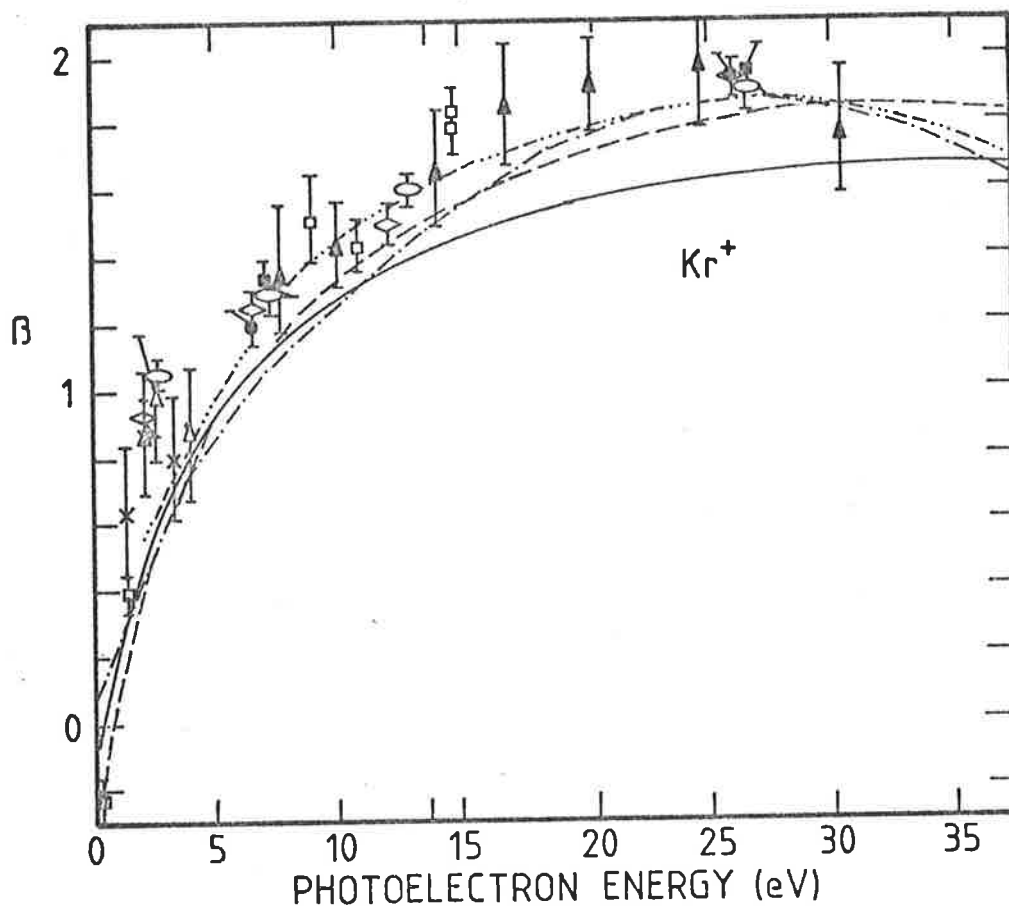


FIG 3.4 The asymmetry parameter for an electron from the 4p shell of krypton as a function of the photoelectron energy.

Experimental results: $\times$ $^2P_{1/2}$, Δ $^2P_{3/2}$, $\blacktriangle$ unresolved $^2P_{1/2}$ and $^2P_{3/2}$ from Miller *et al* (1977); $\square$ Watson and Stewart (1974); $\diamond$ $^2P_{1/2}$, $\circ$ $^2P_{3/2}$, Dehmer *et al* (1975); $\bullet$ $^2P_{1/2}$, $\blacksquare$ $^2P_{3/2}$, present work.

Theoretical results: solid line, HF-L, Kennedy and Manson (1972); ----- HF-V, Kennedy and Manson (1972); -.-.-.- RPAE, Amusia *et al* (1972); RRPA (4s + 4p), Johnson and Cheng (1979).

the theoretical results shown. These are the Hartree-Fock (Kennedy and Manson, 1972), the RPAE (Amusia *et al.*, 1972) and the RRPA (Johnson and Cheng, 1979). It is apparent that the RRPA calculation which includes two shell (4s + 4p) correlations provides the best fit to the data.

An RRPA calculation that includes three shell (4s + 4p + 4d) correlations is shown in Figure 3.5 and in this case individual curves for $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ are given. Whilst the three shell correlation would be expected to be superior to the two shell, this is not shown clearly in Figures 3.4 and 3.5. However, when the experimental data beyond 35 eV is considered, where the β value decreases to the position of the Cooper minimum, then the advantage of the three shell correlation is evident (Johnson and Cheng, 1979).

The RRPA calculation given in Figure 3.5 shows the $\beta(^2P_{1/2})$ value to be less than the $\beta(^2P_{3/2})$ up to about 44 eV photon energy where they cross over. The present results agree with this ordering as do the results of Dehmer *et al.* (1975) with the exception of their data at 41 eV which shows the inverse order to both the present results and the theoretical calculation. However, the difference in the $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ values at that point is much less than the error bars and so the discrepancy is not serious.

The synchrotron measurements, where the individual $\beta(^2P_{1/2})$, $\beta(^2P_{3/2})$ values have been given, unfortunately have rather large error bars. Nevertheless, the ordering agrees with the theoretical calculations.

Of the present data, the measurements at 21 eV(58.4 nm) fit the theory reasonably well, although the $\beta(^2P_{3/2})$ value is slightly above the theoretical line. At 41 eV(30.4 nm) the error bars of both data points overlap the theory although they do seem to be slightly above the RRPA curves. This trend is also seen in the data of Dehmer

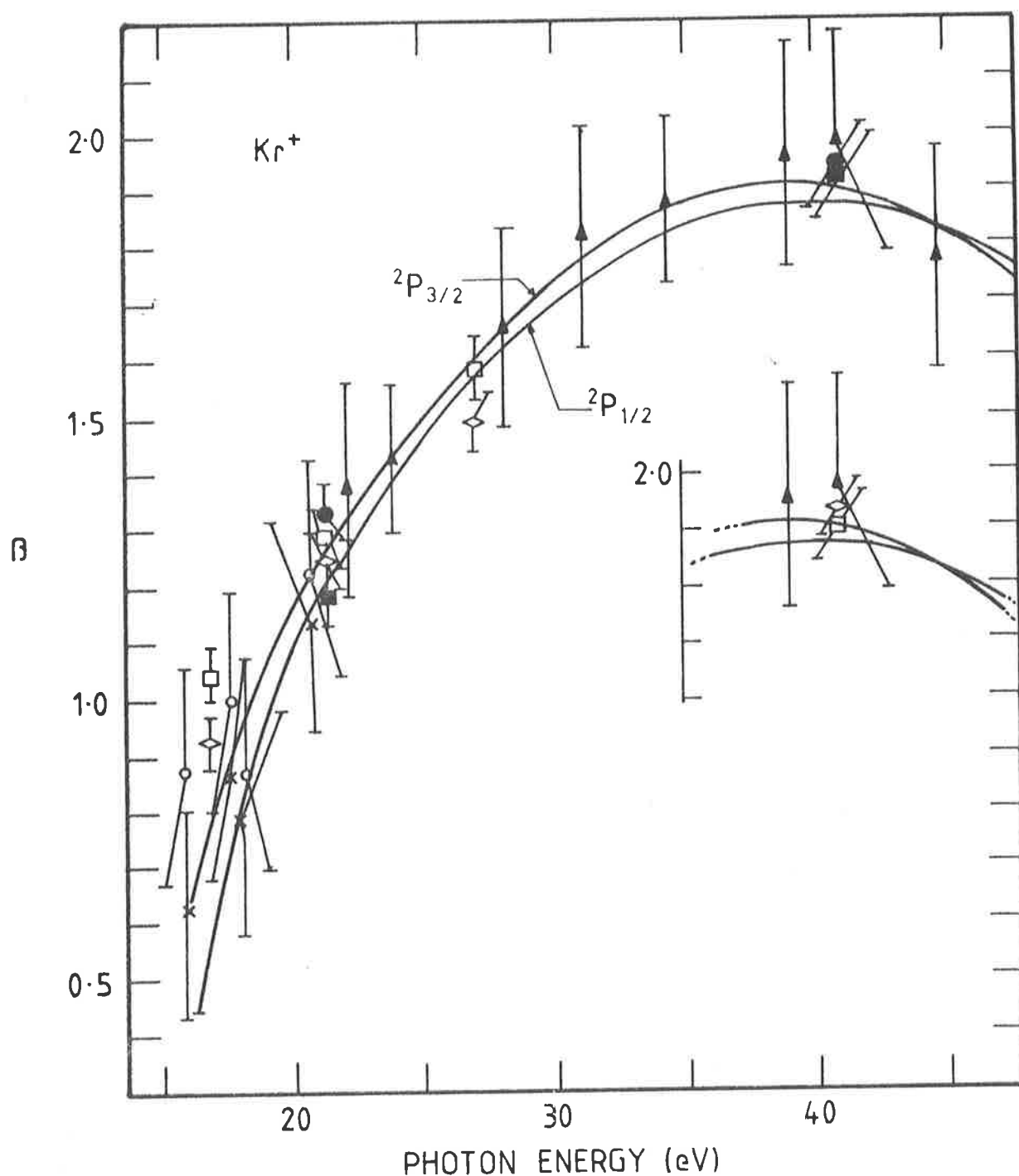


FIG 3.5 The asymmetry parameter for an electron from the 4p shell of krypton as a function of the photon energy (adapted from Johnson and Cheng (1979)).

Experimental results: $\times$ $^2P_{1/2}$, $\circ$ $^2P_{3/2}$, $\blacktriangle$ unresolved $^2P_{1/2}$ and $^2P_{3/2}$ from Miller *et al* (1977); $\diamond$ $^2P_{1/2}$, $\square$ $^2P_{3/2}$, Dehmer *et al* (1975); $\blacksquare$ $^2P_{1/2}$, $\bullet$ $^2P_{3/2}$, present results.

Theoretical result is the RRPA calculation with (4s + 4p + 4d) correlations, (Johnson and Cheng, 1979).

[NOTE: the insert is to show the results of Dehmer *et al* (1975) separately from the present work to avoid confusion]

et al (1975) and may indicate that further refinement of the theory is necessary, although much higher resolution data is required to confirm this. Nevertheless, one anomaly that is clear is near threshold where the β values of Dehmer *et al* (1975) are significantly above the RRPA curves.

The final inert gas investigated was xenon. Figure 3.6 shows a range of experimental and theoretical results. The present results and those of Dehmer *et al* (1975) show the individual β values corresponding to the ion being left in the $^2P_{1/2}$ or $^2P_{3/2}$ state. The relative synchrotron data of Lynch *et al* (1973) is for the combination of the two states. This data differs from the results actually given in Lynch *et al* (1973) in that it has been corrected for instrumental effects and is as presented in Dehmer *et al* (1975).

The theoretical results are all a weighted average of the $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ values and shown are Hartree-Fock velocity and length calculations (Kennedy and Manson, 1972) and three RPAE calculations. The first of these, denoted RPAE(a), is given in Amusia *et al* (1972) while RPAE(b) and (c) are from Amusia and Ivanov (1976). Of the last two, the RPAE(c) curve is the calculation of β for the $5p^6$ subshell including the effect of the $4d^{10}$ subshell while RPAE(b), from the same paper, is said to be the same calculation but without this included. However, the earlier calculation RPAE(a) also does not include the $4d^{10}$ subshell and it would seem reasonable to think that RPAE(a) and (b) should be the same. However this is not the case, and neither article provides any indication of why this is so.

The large error bars on the synchrotron data renders it somewhat ineffective in determining the appropriate theory. However,

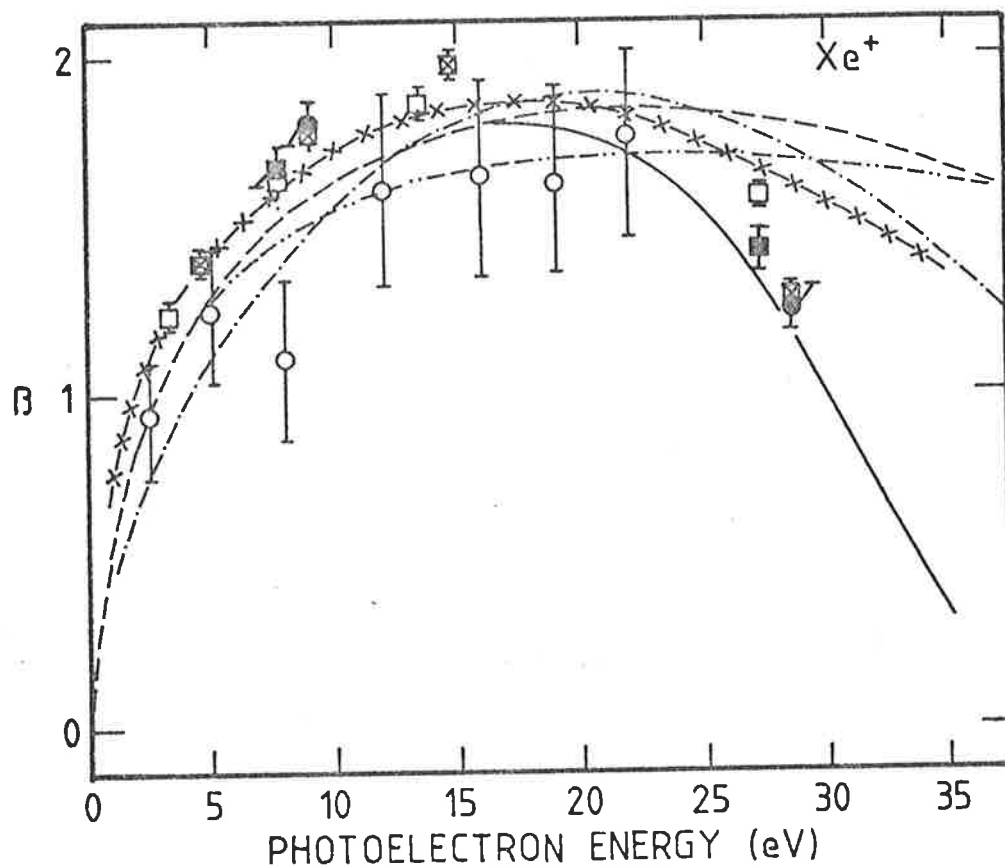


FIG 3.6 The asymmetry parameter for an electron from the $5p$ shell of xenon as a function of the photoelectron energy (adapted from Dehmer *et al.* (1975)).

Experimental results: $\blacksquare$ $2p_{1/2}$, $\bullet$ $2p_{3/2}$, present results; $\square$ $2p_{1/2}$, $\boxtimes$ $2p_{3/2}$, Dehmer *et al.* (1975); $\circ$ Lynch *et al.*, (1973) [as given in Dehmer *et al.* 1975.]

Theoretical results: ——— HF-V, Kennedy and Manson (1972); - - - - - HF-L, Kennedy and Manson (1972); RPAE(a), Amusia *et al.* (1972); -x-x-x- RPAE(b), Amusia and Ivanov (1976); ——— RPAE(c), Amusia and Ivanov (1976).

the higher accuracy of the present data and that of Dehmer *et al* (1975) significantly narrows the choice. It is apparent that from threshold up to about 15 eV photoelectron energy, the RPAE(b) curve gives the best fit. However, beyond that, as the β value decreases in the vicinity of the Cooper minimum, the RPAE(c) calculation, which includes the influence of the $4d^{10}$ subshell, is required. However, this calculation only starts at about 16 eV and there is an unexplained discontinuity between the RPAE(b) and RPAE(c) curves at this point.

The present results at 7.8 eV and 9.1 eV (58.4 nm) agree well with those of Dehmer *et al* (1975) and the $\beta(^2P_{1/2})$ value agrees with the RPAE(b) calculation although the $\beta(^2P_{3/2})$ value is slightly above it. The values at 27.4 eV and 28.7 eV (30.4 nm) are very close to the RPAE(c) calculation. Since the data is plotted as a function of the photoelectron energy it is tempting to suggest that at that point the difference between the $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ values is predominantly the kinetic energy difference. However, despite this reasonable fit to the RPAE(c) curve, the data does not agree as well with the relativistic random phase approximation curves of Johnson and Cheng (1979) shown in Figure 3.7. The broken line shows the weighted average for the $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ values using two shell (5s + 5p) correlations. The solid lines are for each of the $\beta(^2P_{1/2})$ and $\beta(^2P_{3/2})$ values but with three shell (5s + 5p + 4d) correlations. This again shows the importance of including the effect of the $4d^{10}$ subshell in this region.

With regard to the present data points, they are in agreement with the calculations at 21.2 eV photon energy, but significantly below

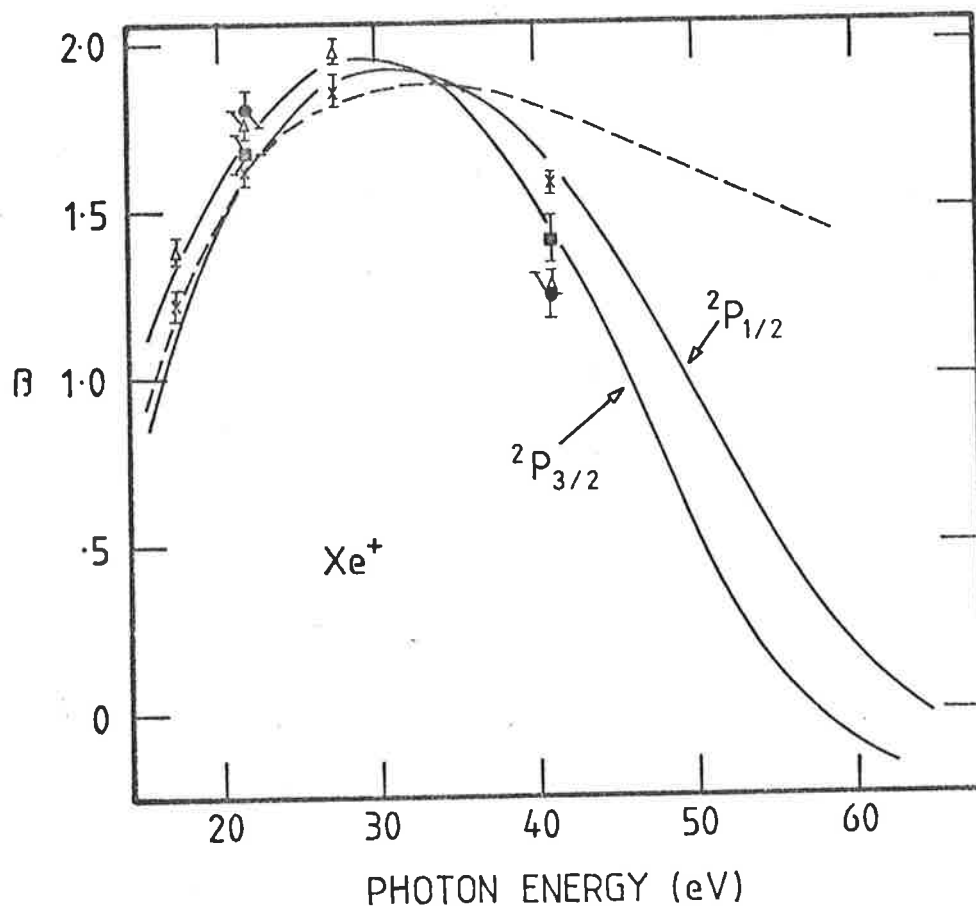


FIG 3.7 The asymmetry parameter for an electron from the 5p shell of xenon as a function of the photon energy (adapted from Johnson and Cheng (1979)).

Experimental results: $\blacksquare$ $^2P_{1/2}$, $\bullet$ $^2P_{3/2}$, present results;
 $\times$ $^2P_{1/2}$, Δ $^2P_{3/2}$, Dehmer *et al* (1975).

Theoretical results are the RRPA results of Johnson and Cheng (1979) with the solid line showing the individual β 's for the $^2P_{3/2}$ and $^2P_{1/2}$ components using 3 shell (5s + 5p + 4d) correlations, and the broken line is an averaged calculation with two shell (5s + 5p) correlations.

the curve at 41 eV. The present $\beta(^2P_{3/2})$ value at 41 eV is in agreement with Dehmer *et al* (1975), but the $\beta(^2P_{1/2})$ value is not. This is obviously a region where further measurements are required to accurately test the theory. However, since the present result for $\beta(^2P_{3/2})$ agrees with Dehmer *et al* (1975) and both are significantly below the calculated curve, this seems sufficient evidence that as yet the calculations are incomplete.

3.3 MOLECULES

Four molecules were investigated, namely oxygen, nitrogen, carbon monoxide and carbon dioxide. Only 30.4 nm radiation was used and the spectra are shown in Figure 3.8 through to 3.11. The states are labelled according to Turner *et al* (1970) and Gardner and Samson (1973).

There are a number of features of the photoelectron spectra of molecules that served to complicate the measurements of the asymmetry parameter. The most difficult problem was due to the photoelectron transition leaving the ion in a range of vibrational states. Thus the spectrum for a particular transition was not just a single energy, but rather an envelope of vibrational peaks. Since the analyser had insufficient resolution to resolve these, it was necessary to measure over the whole of the envelope and it was often difficult to estimate the points of total cut-off and full transmission. Coupled to this is that the assumption of the extrapolated background being constant is stretched further due to the increased effective width of the peak.

A further problem that occurred was due to the use of an integral analyser. For photoelectrons leaving the ion in an excited

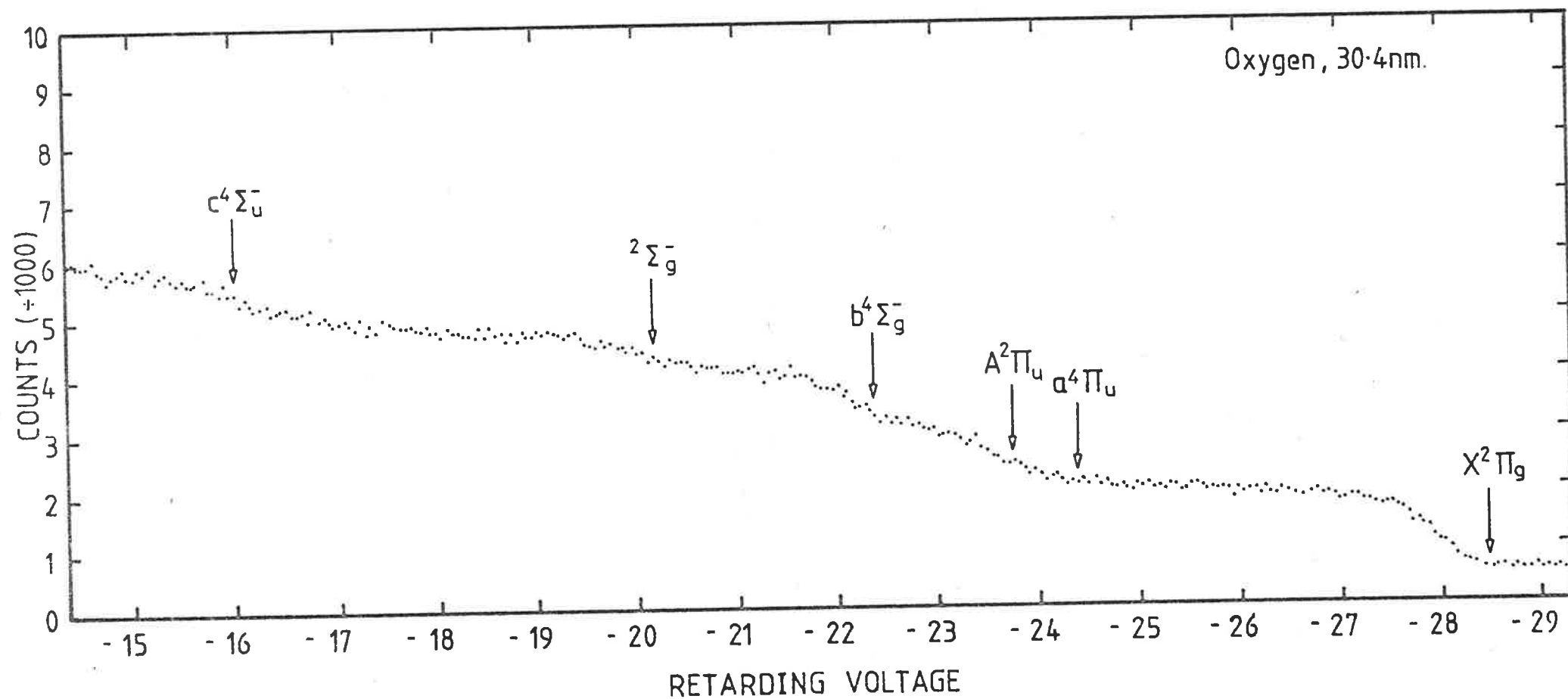


FIG 3.8 Photoelectron spectrum of molecular oxygen using 30.4 nm radiation.

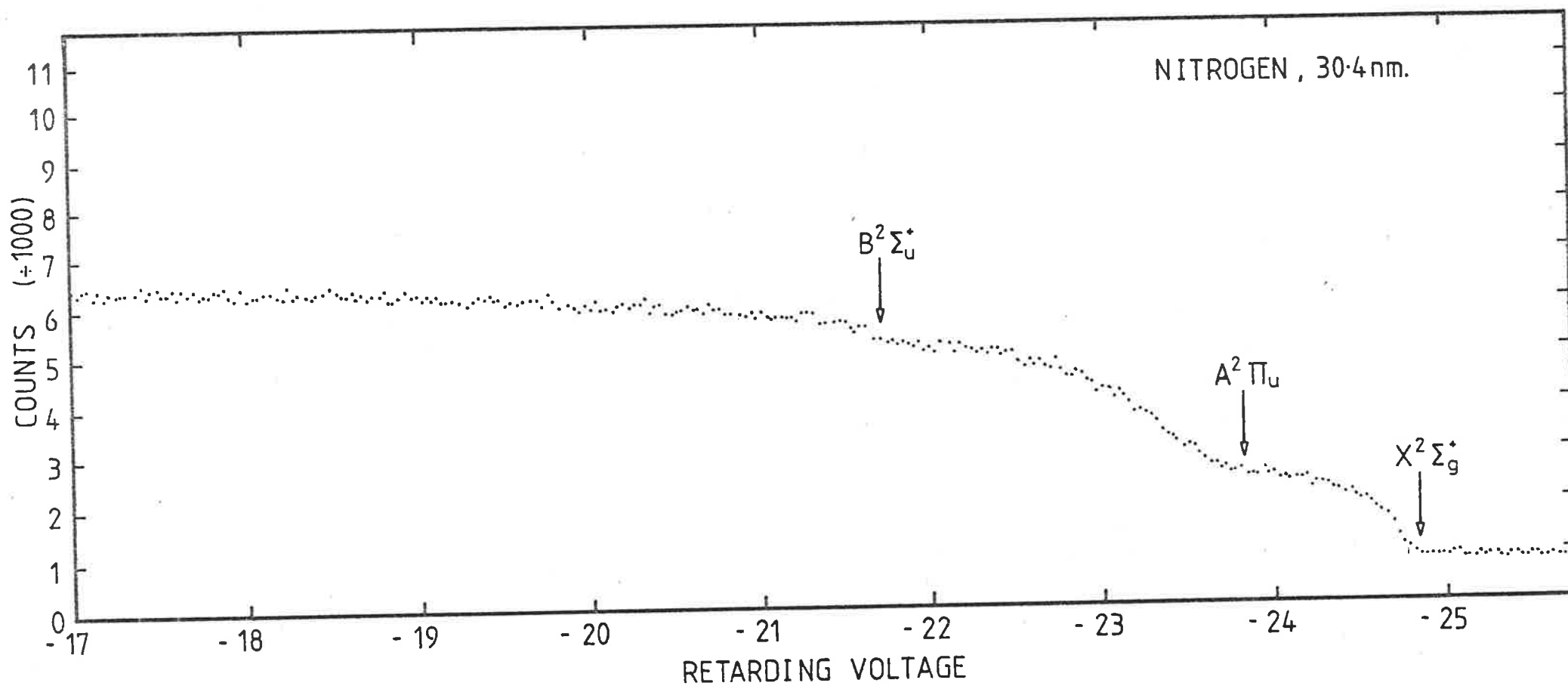


FIG 3.9 Photoelectron spectrum of molecular nitrogen using 30.4 nm radiation.

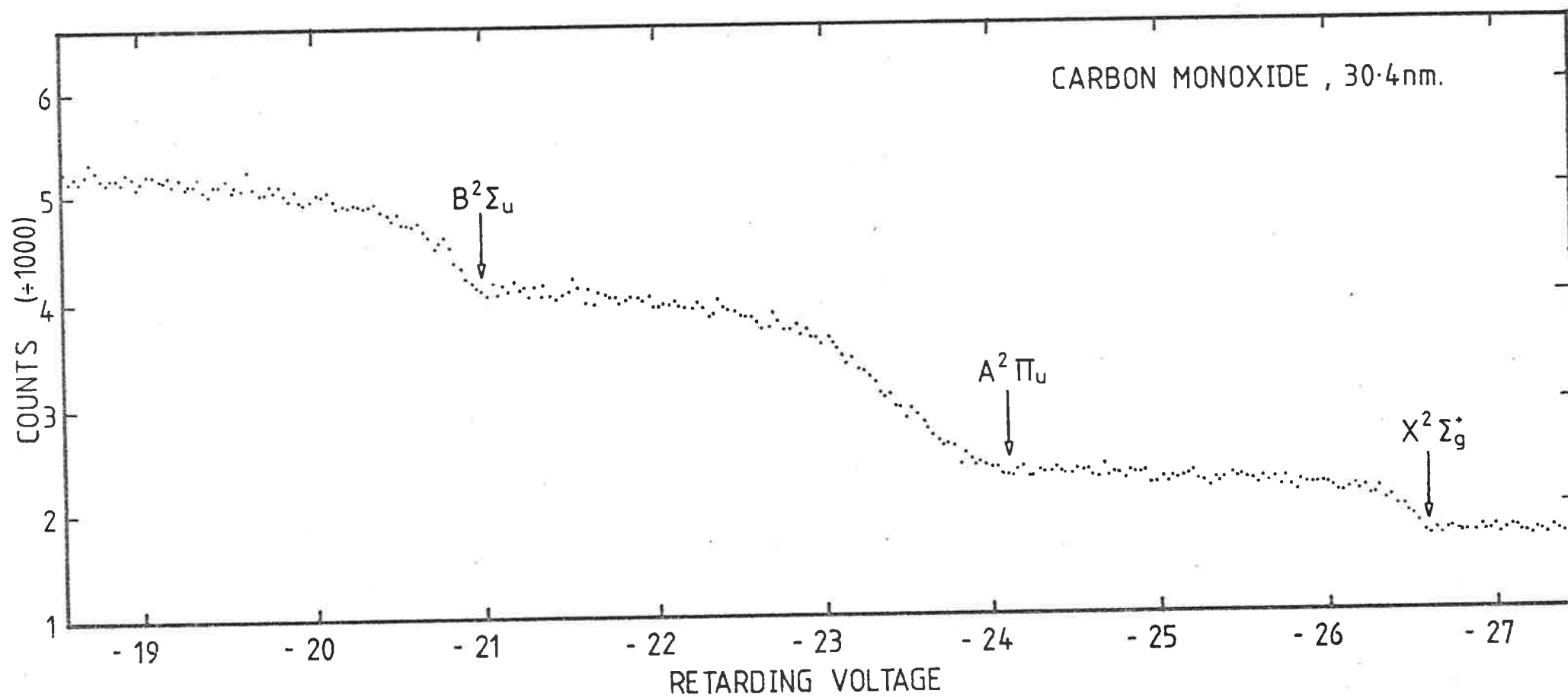


FIG 3.10 Photoelectron spectrum of carbon monoxide using 30.4 nm radiation.

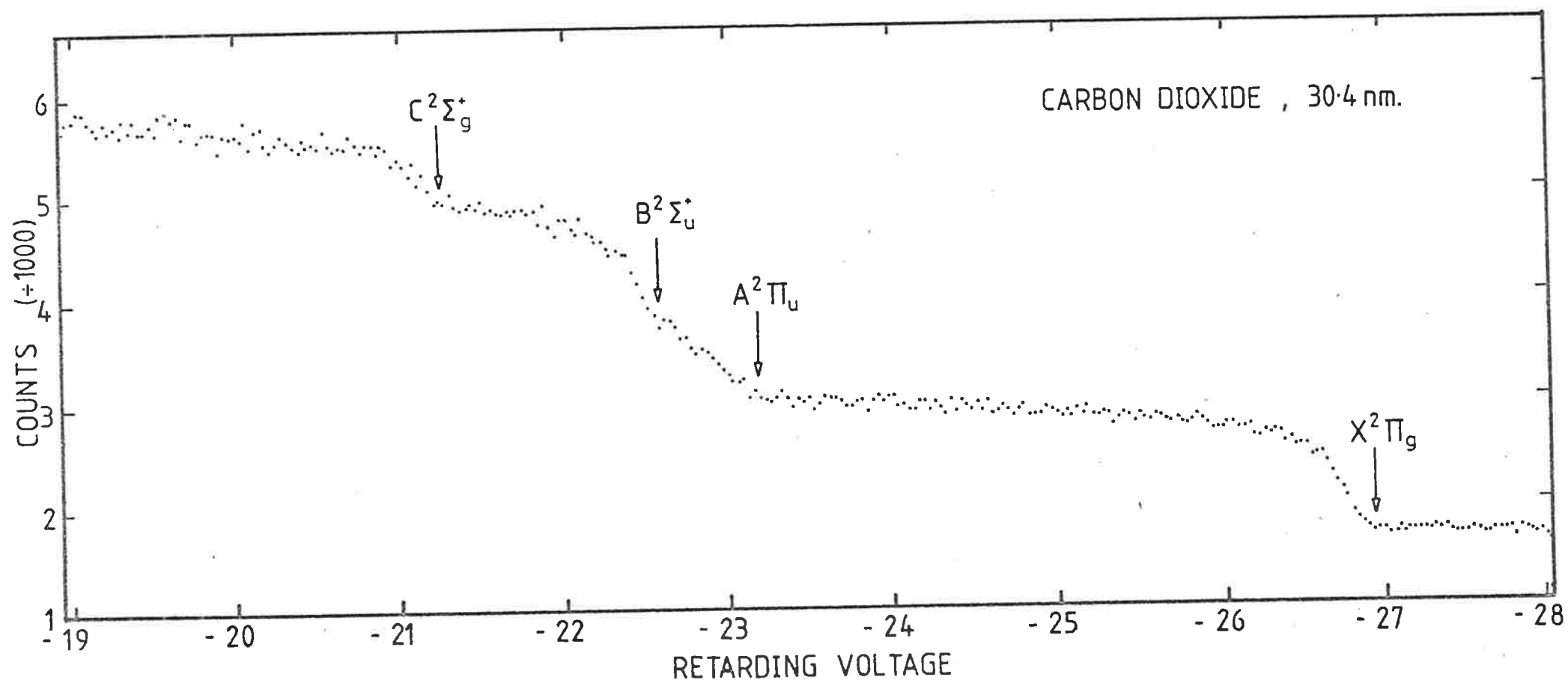


FIG 3.11 Photoelectron spectrum of carbon dioxide using 30.4 nm radiation.

state, the step height was often the difference of two quite large numbers and thus the errors are in general larger than encountered with atoms.

Referring now to Figures 3.8 through to 3.11, it can be seen that the largest number of states of the ion occurs with oxygen, but it was considered that the resolution of the analyser was sufficient only to investigate photoelectrons leaving the ion in the ground state. For nitrogen the asymmetry parameter was measured for photoelectrons leaving the ion in the ground state and in the A and B states. Similar measurements were made for carbon monoxide. For carbon dioxide the asymmetry parameter was measured for photoelectrons leaving the ion in the ground state and the first excited state but it was considered that the next excited state, $^2B \Sigma_u^+$ state could not be separated from the $A^2\Pi_u$ state and a combined angular distribution for photoelectrons leaving the ion in these two states was measured. Photoelectrons corresponding to the $C^2 \Sigma_g^+$ ionic state of carbon dioxide were also measured.

The results are summarised in Table 3.4 and compared with the resonance line results of Katsumata *et al* (1979). The results of Marr *et al* (1979a) and McCoy *et al* (1978) which are also shown were obtained with synchrotron radiation. However, the numbers given were not actually measured at 30.4 nm but have been obtained from an interpolation of their wavelength dependent data. They are given only as a guide and a more accurate comparison between the present results and the synchrotron radiation measurements will be given further on.

In general there is disagreement between the present results and those of Katsumata *et al* (1979). The two exceptions are for

	PRESENT RESULTS		OTHER RESULTS		
ION	A(θ), B(θ)	sin(θ)	Katsumata <i>et al</i> (1979)	Marr <i>et al</i> ^{ϕ} (1979a)	McCoy <i>et al</i> ^{ϕ} (1978)
N ₂ ⁺ X ² Σ_g^+	.89 $\pm$.07	.86 $\pm$.07	.58 $\pm$.06 ⁺ (.5 $\pm$.2 [*])	.82	1.12
A ² Π_u	1.22 $\pm$.08	1.20 $\pm$.08	1.16 $\pm$.15 ⁺	1.21	
B ² Σ_u^+	1.58 $\pm$.12	1.56 $\pm$.12	1.43 $\pm$.13 ⁺	1.46	
O ₂ ⁺ X ² Π_g	1.14 $\pm$.05	1.12 $\pm$.05	.92 $\pm$.1 [*]		
CO ⁺ X ² Σ_g^+	1.24 $\pm$.05	1.22 $\pm$.05		.98	
A ² Π_u	1.23 $\pm$.05	1.20 $\pm$.05		1.26	
B ² Σ_u	1.02 $\pm$.1	.99 $\pm$.1		.95	
CO ₂ X ² Π_g	1.02 $\pm$.08	1.00 $\pm$.08	.63 $\pm$.07		
A ² Π_u	1.40 $\pm$.1	1.37 $\pm$.1	1.04 $\pm$.13		
A ² Π_u + B ² Σ_u^+	.89 $\pm$.11	.87 $\pm$.11			
C ² Σ_g^+	1.65 $\pm$.5	1.62 $\pm$.5	.76 $\pm$.09		

+ $v = 0$ * $v = 1$ ϕ (see text)

TABLE 3.4 The β values for photoelectrons from nitrogen, oxygen, carbon monoxide and carbon dioxide produced by 30.4 nm radiation.

photoelectrons corresponding to the $A^2\Pi_u$ ionic state of nitrogen where the agreement is quite good and for the $B^2\Sigma_u^+$ state of the same ion where the large error bars are sufficient to ensure overlap. The reason for the disagreement for the other values is not known and is especially difficult to understand for transitions in carbon dioxide and oxygen which leave the ion in the ground state. Here the photoelectron peak is well separated from the other transitions and the data analysis free of the problems associated with the more closely packed peaks.

For photoelectrons corresponding to the ground state of the nitrogen ion, one possible reason for the difference between the present results and those of Katsumata *et al* (1979) is that Katsumata *et al* (1979) measured β for the $v = 0$ vibrational line, while in the present results the measurements were made over the whole vibrational envelope. However $v = 0$ and $v = 1$ are the only two lines of consequence within the envelope (Gardner and Samson, 1978) and as can be seen in Table 3.4, Katsumata *et al* (1979) also measured β for $v = 1$ and obtained a similar value to that for $v = 0$. In any case, since the intensity of the $v = 0$ transition is almost eight times the strength of the $v = 1$ (Gardner and Samson, 1978), the β value for $v = 0$ would be expected to be close to the β value for the whole envelope. Therefore this is not considered to be a possible reason for the difference.

Photoelectrons corresponding to the ground state of the oxygen ion provide another example where Katsumata *et al* (1979) have measured β for just a single vibrational peak. This time it is for $v = 1$ which is the strongest of five vibrational peaks that appear in

the envelope (Gardner and Samson, 1978). It is not possible though to draw the same conclusions as was done for nitrogen above. The relative intensities of the five vibrational peaks are (55 : 100 : 81 : 32 : 8) (Gardner and Samson, 1978) and therefore it is not possible to make any statement about the β value for $v = 1$ as compared with the β value for the whole envelope. Thus if the discrepancy between the present data and that of Katsumata *et al* (1979) is true, this may indicate an anomalous difference in the β values across the vibrational envelope.

For the carbon dioxide results, Katsumata *et al* (1979) measured β for the vertical ionization peaks and again, in the present work, the measurement was over the whole envelope. Therefore again it is necessary to investigate whether this difference can possibly explain the difference in the two measured values.

Figure 3.12 shows the photoelectron spectrum of carbon dioxide at 30.4 nm adequately displaying the vibrational structure (Gardner and Samson, 1973). It is apparent that for photoelectrons corresponding to the $X^2\Pi_g$ and $C^2\Sigma_g^+$ ionic states, that the β value obtained for the vertical ionization peak would be representative of the β value for photoelectrons corresponding to the state as a whole. Thus the difference between the present results and those of Katsumata *et al* (1979) for photoelectrons corresponding to these states must remain an anomaly.

Incidentally, the β value for the photoelectrons corresponding to the $C^2\Sigma_g^+$ ionic state was difficult to measure in the present work since it was close to photoelectrons from the $B^2\Sigma_u^+$ state. This is reflected in the very large error bar.

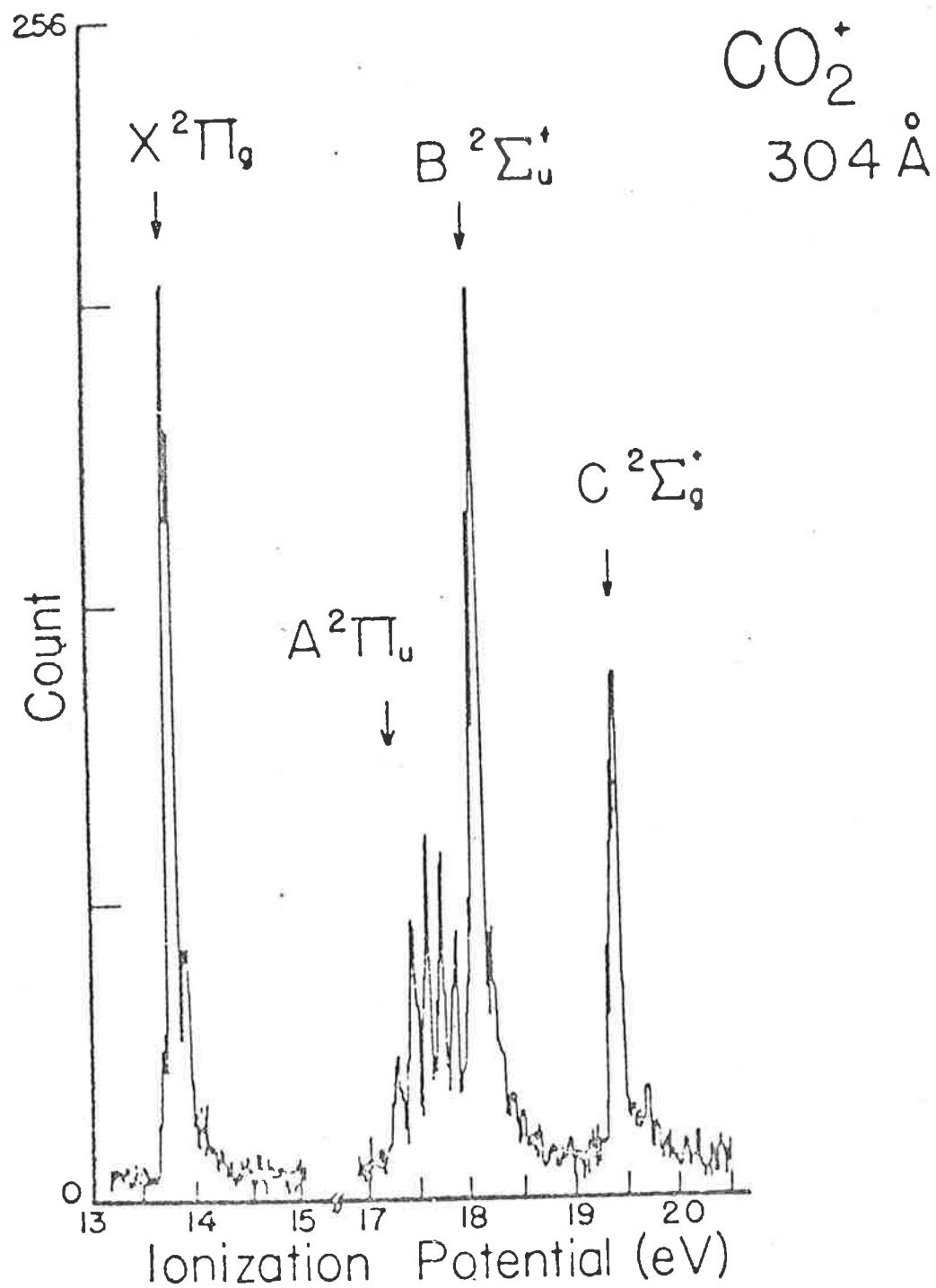


FIG. 3.12 Photoelectron spectrum of carbon dioxide produced by 30.4 nm radiation (from Gardner and Samson, 1973).

Referring again to Figure 3.12, it can be seen that for the $A^2 \Pi_u$ state, there is considerable vibrational structure and that part of it overlaps the $B^2 \Sigma_u^+$ state. In the present measurement, this created a difficulty in that the point in the retarding curve corresponding to full transmission for photoelectrons from the $A^2 \Pi_u$ state was beneath the retarding curve for electrons from the $B^2 \Sigma_u^+$ ionic state. The electron count corresponding to the $A^2 \Pi_u$ state was thus taken from the cut-off point to a point part way up the retarding curve. Therefore the β value measured will be for a partial sum of the vibrational peaks. This is not expected to affect the β value provided the value of β is constant for the vibrational peaks. However, since Katsumata *et al* (1979) measured β for only the vertical ionization peak, then if β does have a vibrational dependence, it is possible that this is the cause of the difference between the present result and that of Katsumata *et al* (1979).

In the present work a β value for photoelectrons from the combined $A^2 \Pi_u$ and $B^2 \Sigma_u^+$ ionic states of carbon dioxide was measured. As can be seen in Table 3.4, this combined β value is lower than for the A state, implying that β for photoelectrons corresponding to the B state is lower than the β for the A state. In fact, since the two ionic states have approximately equal branching ratios (Gardner and Samson, 1973), it is possible to calculate an approximate β value for the B state. This was found to be .38 which is greater than the $.05 \pm .08$ measured by Katsumata *et al* (1979).

Therefore in general, there is poor agreement between the measured results and those of Katsumata *et al* (1979). In a number of

cases, a possible reason has been given based on a difference in the vibrational peaks measured. However, in general, it is unlikely that this can explain the differences, especially as there is also disagreement in cases where this explanation isn't appropriate.

A comparison of the present results with those from synchrotron radiation is given in Figure 3.13 through to 3.19. These graphs are based on those given by Marr *et al* (1979a) and McCoy *et al* (1978) and have been expanded to include the present results and those of Katsumata *et al* (1979). Also included have been the multiple scattering calculations of Wallace *et al* (1979).

Figures 3.13, 3.14 and 3.15 show the variation of β with photon energy for nitrogen corresponding to the ion being left in the $X^2 \Sigma_g^+$, $A^2 \Pi_u$ and $B^2 \Sigma_u^+$ state which are due to the removal of an electron from $(\sigma_g 2p)^2$, $(\pi_u 2p)^2$ and $(\sigma_u 2s)^2$ orbitals respectively (Turner *et al*, 1970). The ionization potentials are 15.57 eV, 16.69 eV and 18.75 eV respectively (Turner *et al*, 1970). Apart from the above mentioned results, also shown are the orthogonalised plane wave calculations of Huang and Ellison (1974), the pseudo-potential approximation calculation of Duzy and Berry (1976) and the deformed coulomb calculations of Hirota (1976).

Referring firstly to the case where the ion is left in the ground state, it can be seen in Figure 3.13 that the present data point fits well into the general trend shown by the synchrotron data. There is also very good agreement between the data at that photon energy and both the pseudopotential approximation calculations of Duzy and Berry (1976) and the multiple scattering method of Wallace *et al* (1979).

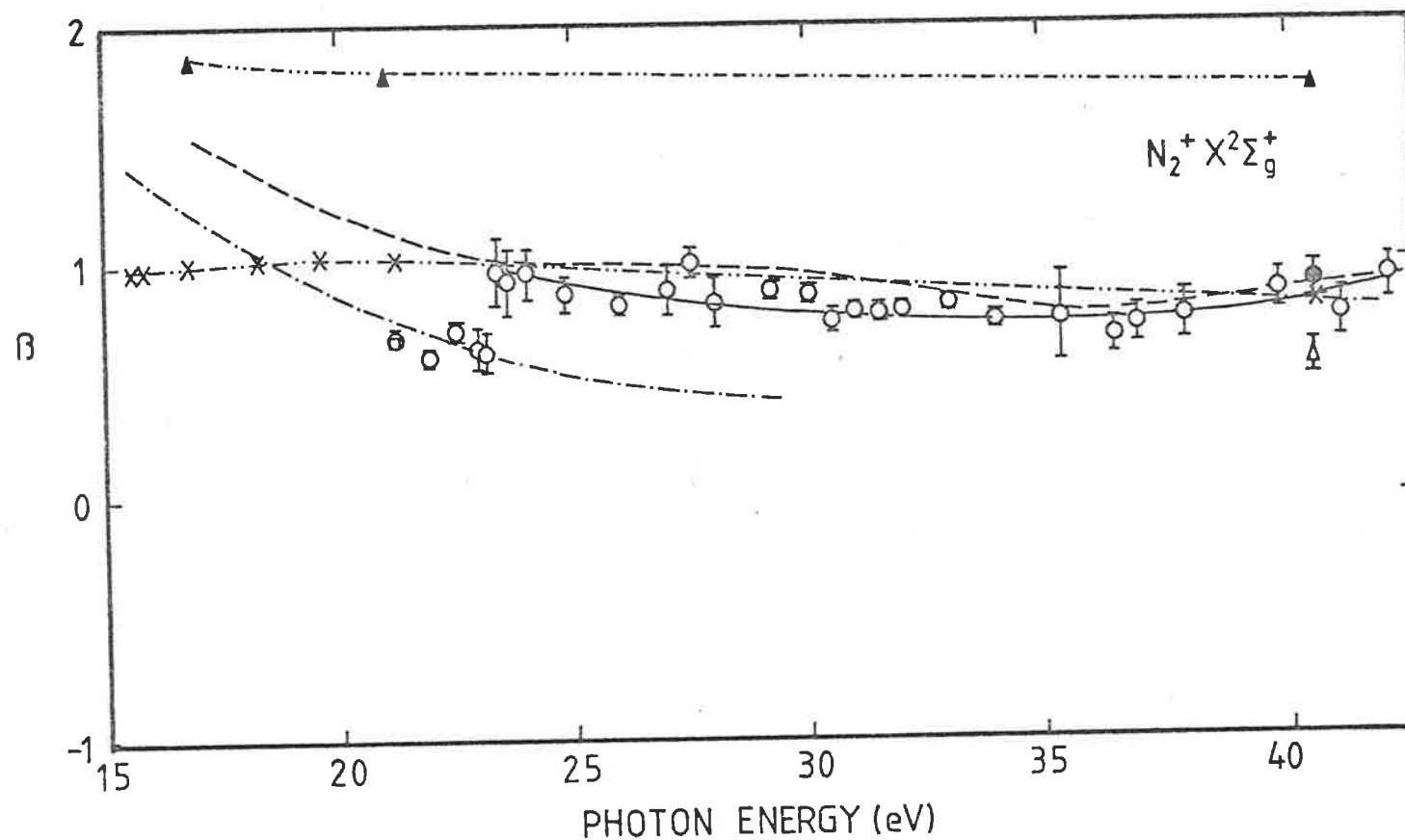


FIG 3.13 The β value as a function of photon energy for molecular nitrogen with the ion left in the ground state (adapted from Marr *et al*, (1979a))

Experimental results: ● present results; ○ and the solid line, Marr *et al* (1979a)
 □ Hancock and Samson (1976); Δ Katsumata *et al* (1979);
 Theoretical results: ▲-----▲ Huang and Ellison (1974); x-----x Duzy and Berry (1976);
 ----- Hirota (1976); ----- Wallace *et al* (1979)

Both theories follow the trend of the data down to about 23 eV photon energy although they are somewhat outside of the experimental error bars. The discontinuity at about 23 eV can be associated with the 23.56 eV threshold for the $C^2 \Sigma_u^+$ excited state of the nitrogen ion (Marr *et al*, 1979a). As can be seen, the data at photon energies below this is well fitted by the Coulomb potential calculation of Hirota (1976).

Figure 3.14 shows a graph of β versus photon energy for the nitrogen ion left in the $A^2 \pi_u$ state. Again the present data point at 41 eV photon energy agrees well with the trend of the synchrotron data. However agreement with theory is poor with the multiple scattering results of Wallace *et al* (1979) providing the closest approach.

Referring to Figure 3.15 which shows β as a function of the photon energy when the ion is left in the $B^2 \Sigma_u^+$ state, it can be seen that the present data point is slightly above the trend of the synchrotron data, although the error bars do overlap significantly. As for the theoretical calculations, at present there is little agreement with the experimental data.

Figure 3.16 shows the asymmetry parameter for photoelectrons from oxygen where the ion is left in the ground state. This occurs by the removal of a π_g 2p electron and has an ionization potential of 12.07 volts (Turner *et al*, 1970). The present data point is in good agreement with the trend in the synchrotron data. This makes the anomalous data point at a photon energy slightly above the present data

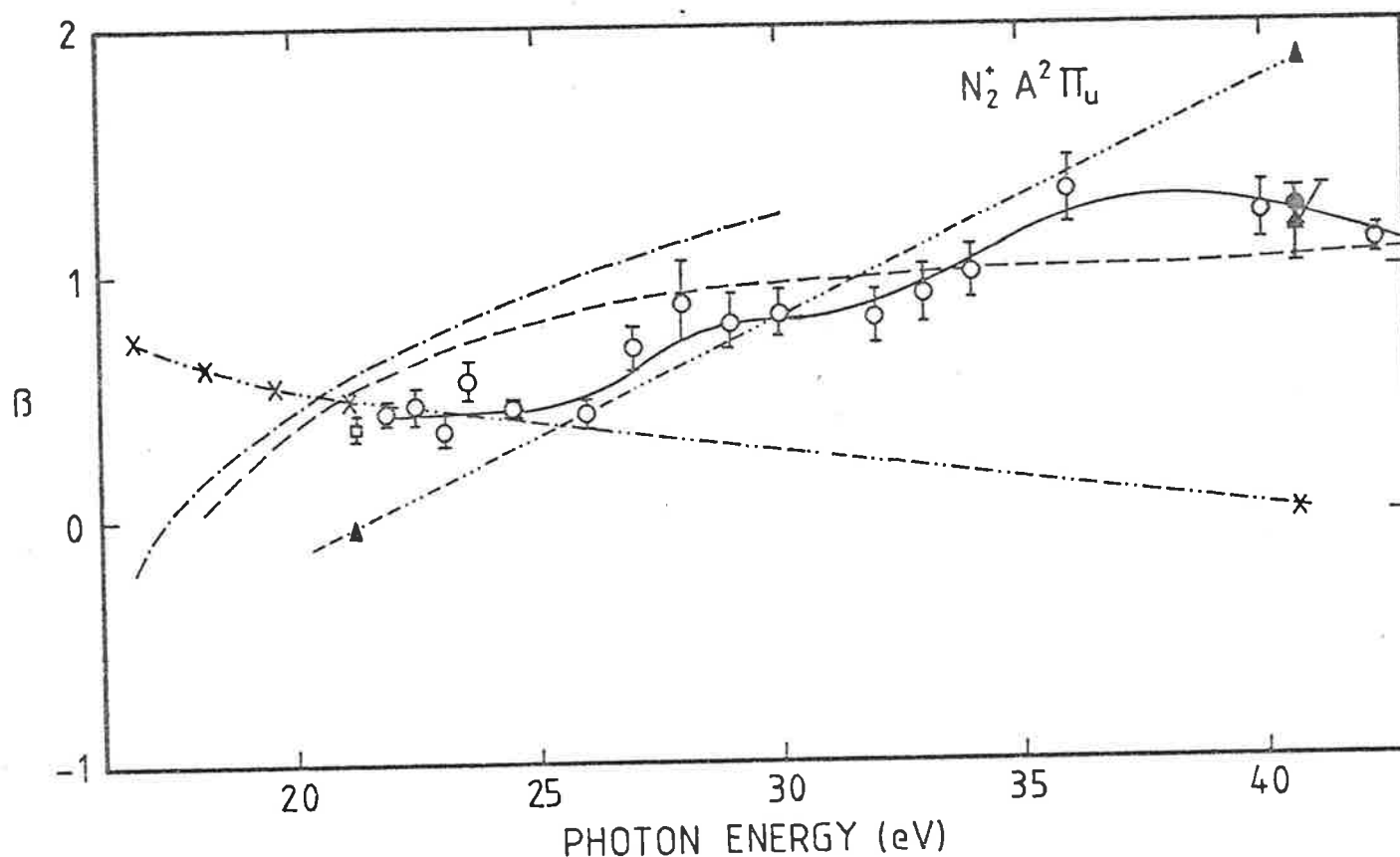


FIG 3.14 The value of β as a function of the photon energy for molecular nitrogen where the ion is left in the $A^2 \Pi_u$ state (adapted from Marr *et al.* 1979a))

Experimental results: ● Present result; ○, and solid line, Marr *et al.* (1979a);
□ Hancock and Samson (1976); ▲ Katsumata *et al.* (1979).

Theoretical results: ▲-----▲ Huang and Ellison (1974); x----- Duzy and Berry (1976);
----- Hirota (1976); ----- Wallace *et al.* (1979).

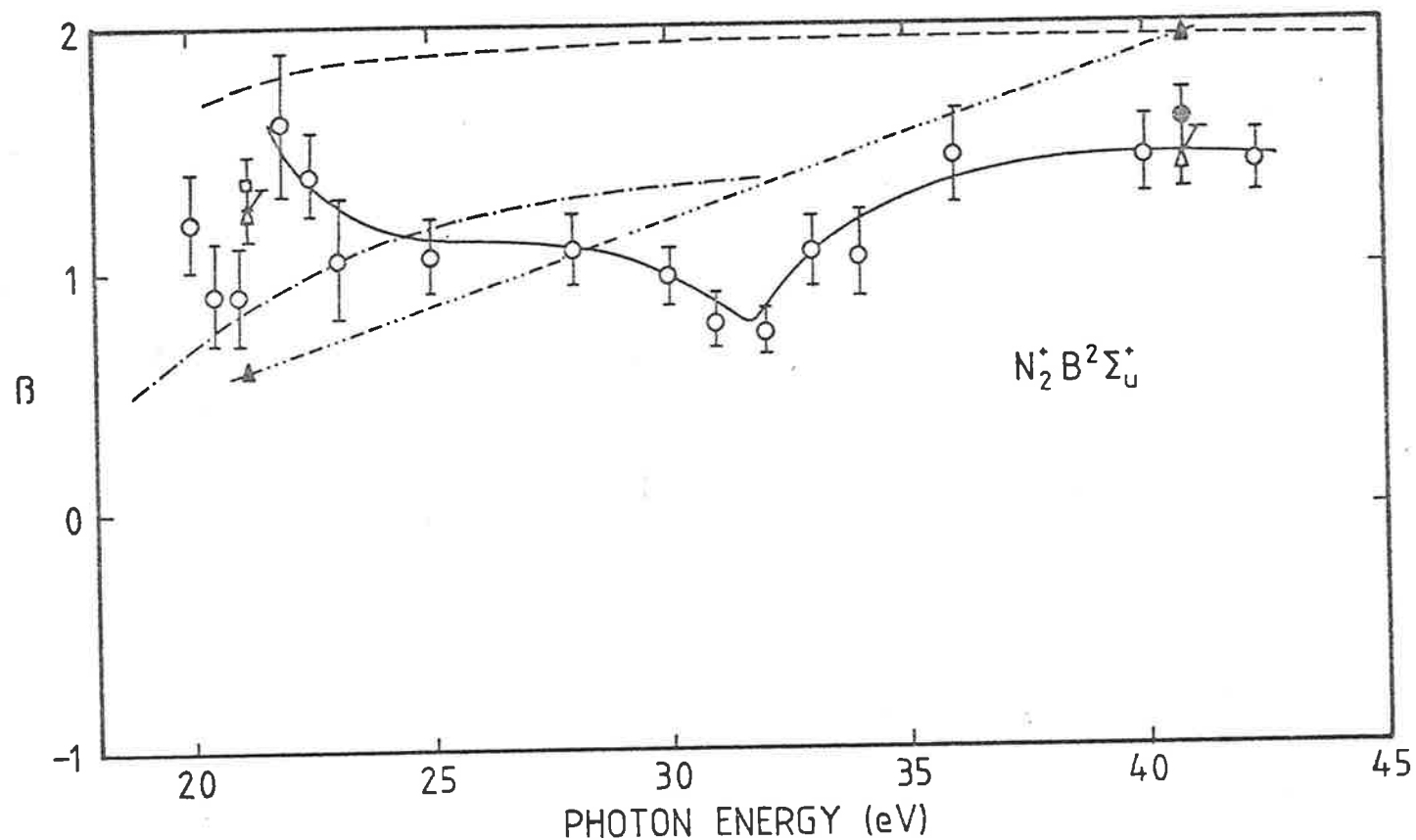


FIG 3.15 The value of β as a function of the photon energy for molecular nitrogen where the ion is left in the $B^2\Sigma_u^+$ state (adapted from Marr *et al* (1979a))

Experimental results: ● present result; o, and solid line, Marr *et al* (1979a)
 □ Hancock and Samson (1976); Δ Katsumata *et al* (1979).

Theoretical results: ▲-----▲ Huang and Ellison (1974); -.-.-.- Hirota (1976);
 ----- Wallace *et al* (1979).

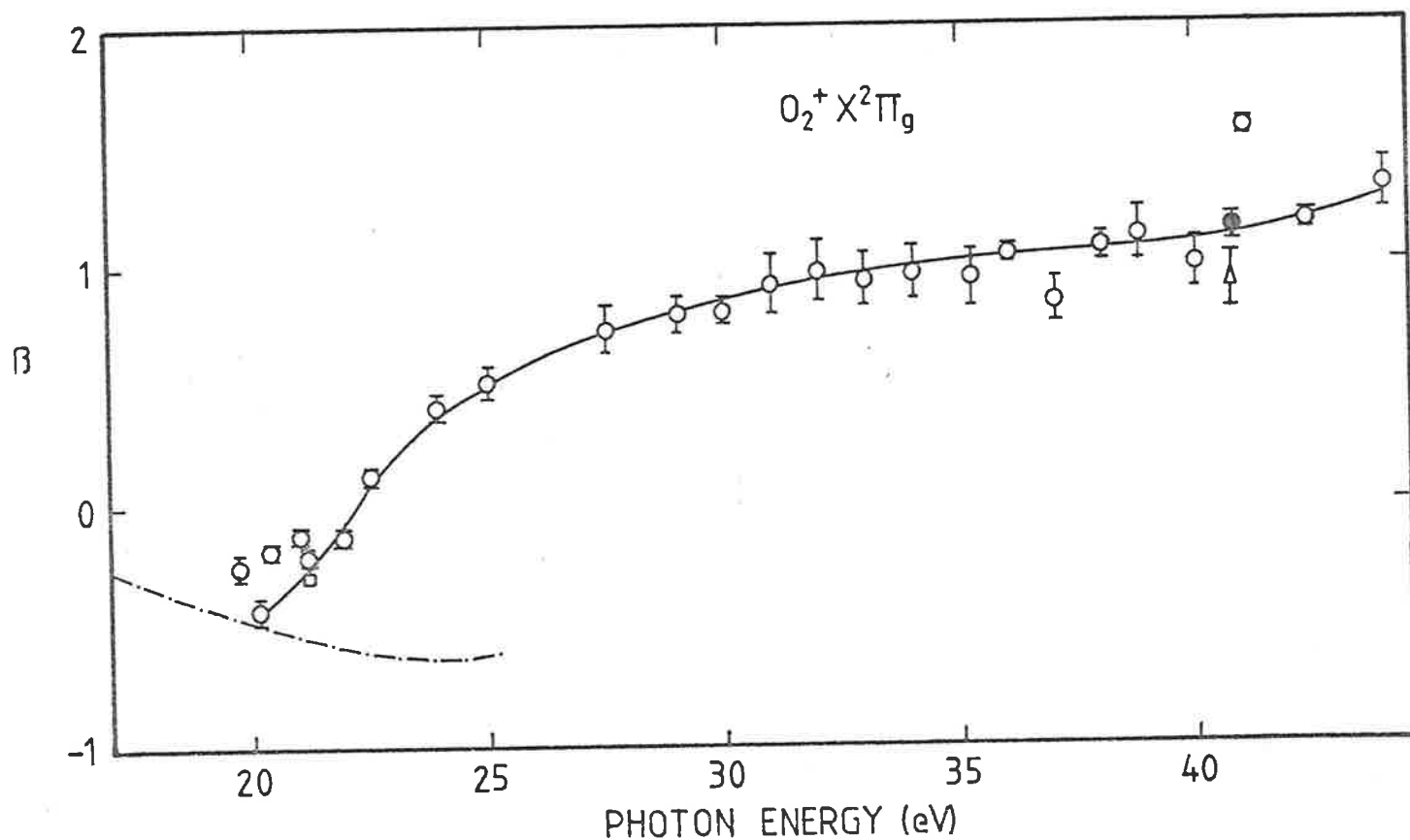


FIG 3.16 The value of β as a function of the photon energy for molecular oxygen where the ion is left in the ground state (adapted from McCoy *et al* (1978)).

Experimental results: ● present results; ○ , and the solid line, McCoy *et al* (1978);
 □ Hancock and Samson (1976); Δ Katsumata *et al* (1979).

Theoretical results: - · - · - Hirota (1976).

point difficult to understand. If this indicates a discontinuity then it is very sharp indeed.

The photoelectron spectrum obtained from carbon monoxide is similar to the isoelectronic molecule nitrogen, and also results in three bands corresponding to the ion being left in the $X^2 \Sigma_g^+$, $A^2 \Pi_u$ and $B^2 \Sigma_u$ states. These have ionization potentials of 14.01 eV, 16.53 eV and 19.68 eV respectively (Turner *et al*, 1970).

Figure 3.17 shows the asymmetry parameter as a function of photon energy for the ion left in the ground state. The present value is slightly higher than the general trend of the synchrotron data but no reason for this is known. In this case the multiple scattering method of Wallace *et al* (1979) gives a good fit to the data.

The variation of the asymmetry parameter when the ion remains in the $A^2 \Pi_u$ state is shown in Figure 3.18. The present data point agrees well with the synchrotron data. The theoretical calculation of Wallace *et al* (1979) largely follows the trend in the data but far more structure appears in the data than predicted by theory.

Finally, Figure 3.19 shows the asymmetry parameter as a function of photon energy for photoelectrons corresponding to the $B^2 \Sigma^+$ ionic state. Again the present data conforms with the trend in the synchrotron data. The theoretical calculation of Wallace *et al* (1979) follows the shape of the data but the calculated β value is displaced from the measured.

3.4 CONCLUSIONS

The aim of this final section is to present some conclusions and observations that have arisen when an overview is taken of the results in the preceding two sections.

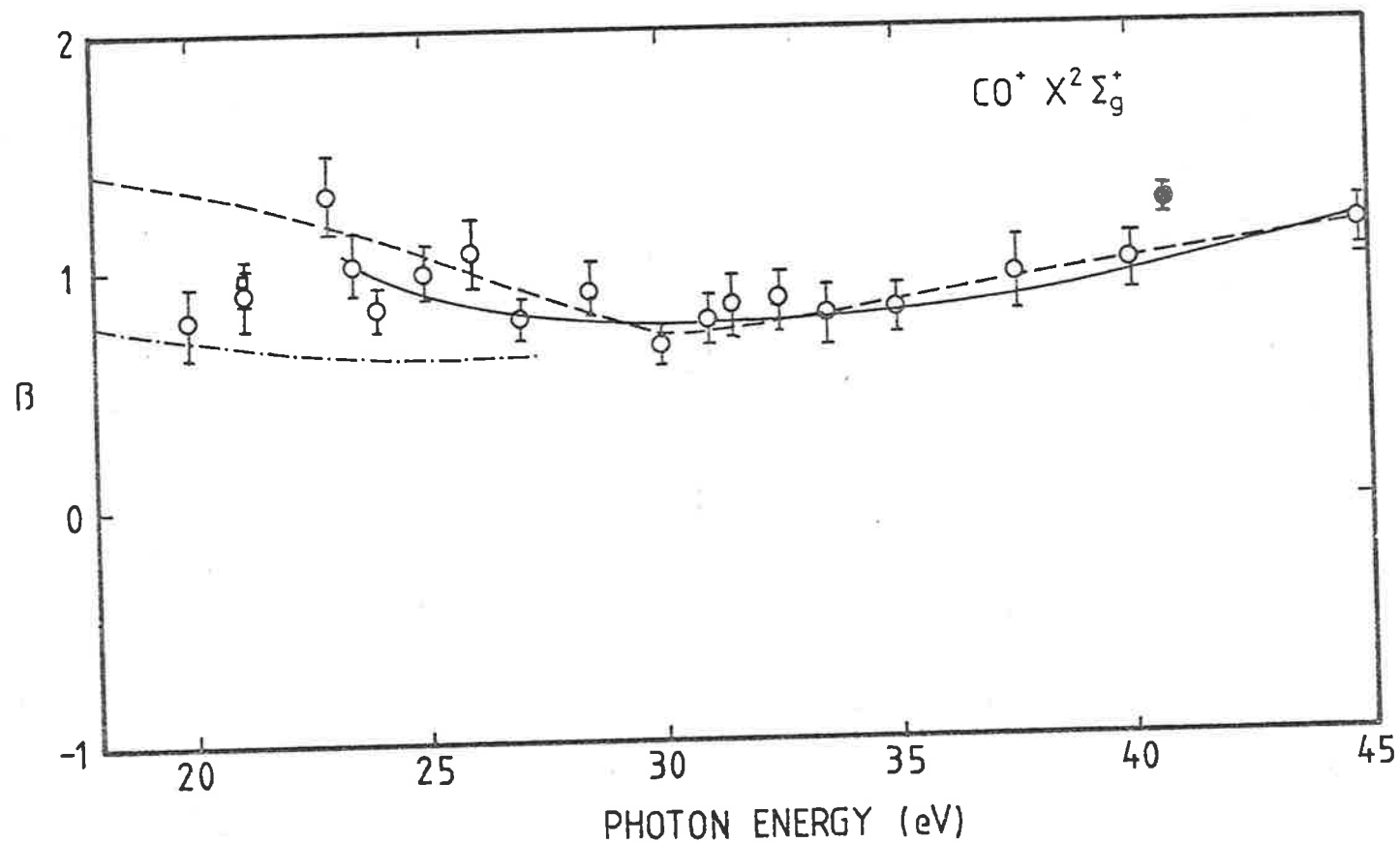


FIG 3.17 The value of β as a function of the photon energy for carbon monoxide where the ion is left in the ground state (adapted from Marr *et al.* (1979a))

Experimental results: ● present result; ○, and the solid line, Marr *et al.* (1979a);
□ Hancock and Samson (1976).

Theoretical results: -.-.- Hirota (1976); ---- Wallace *et al.* (1979).

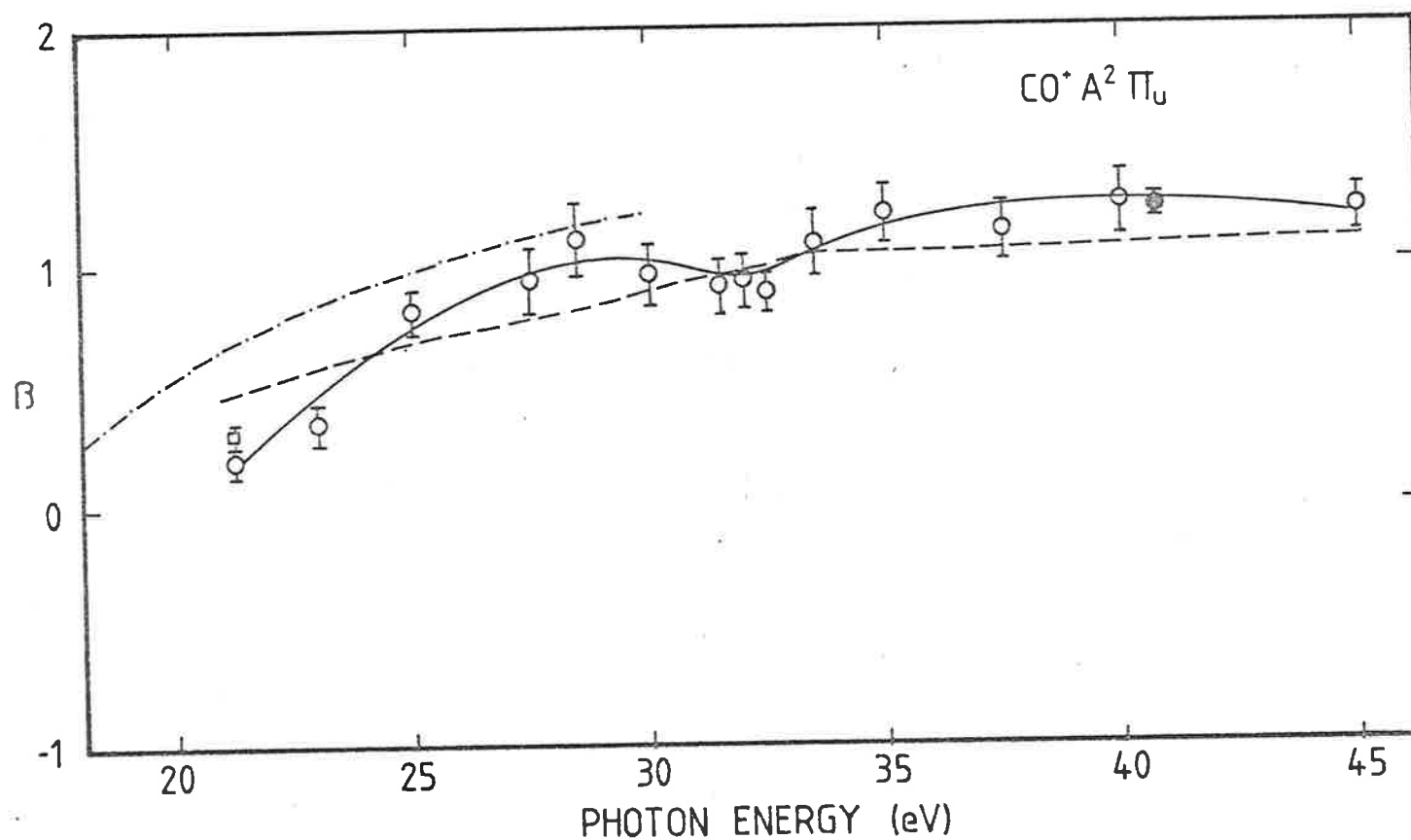


FIG 3.18 The value of β as a function of the photon energy for carbon monoxide when the ion is left in the $\text{A}^2\Pi$ state (adapted from Marr *et al.* (1979a))

Experimental results: ● present result; ○, and the solid line, Marr *et al.* (1979a);
□ Hancock and Samson (1976).

Theoretical results: - · - · - Hirota (1976); - - - - - Wallace *et al.* (1979).

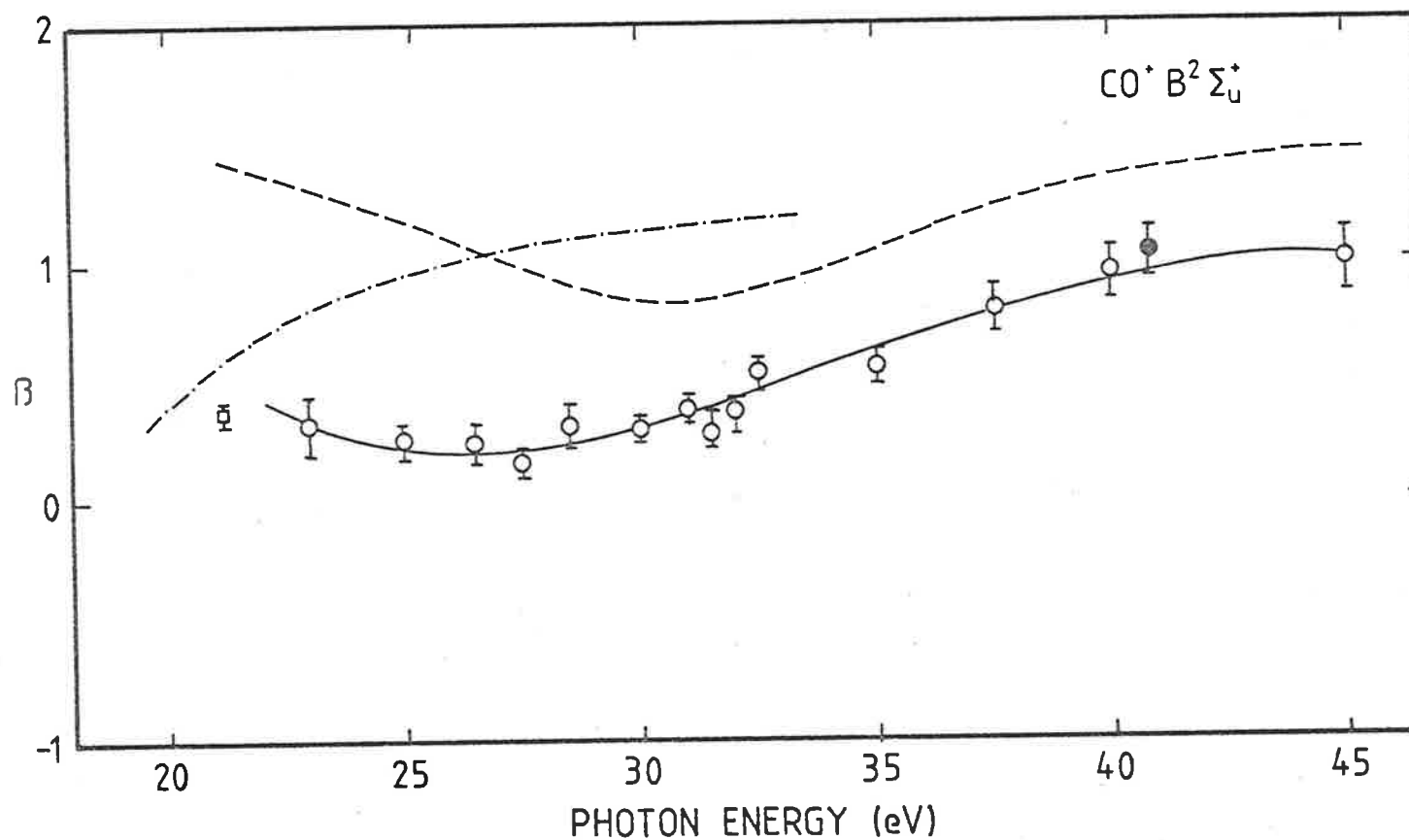


FIG 3.19 The value of β as a function of the photon energy for carbon monoxide where the ion is left in the $B^2\Sigma^+$ state (adapted from Marr *et al.* (1979a))

Experimental results: ● present result; ○, and the solid line, Marr *et al.*, (1979a);
□ Hancock and Samson (1976).

Theoretical results: - · - · - Hirota, (1976); - - - - Wallace *et al.* (1979).

Consider firstly the atoms. The prime reason for measuring the angular distribution of the outer p subshells of the inert gases using 58.4 nm radiation was to test the system. To a certain extent, this was a secondary test. The primary test had been the β value of helium photoelectrons and none of the measurements already discussed were made until the correct value of $\beta = 2$ could be obtained reliably. However, this value is only "correct" within certain error bars and there is always the possibility that the result might be luck and that when other gases are used, the answers will be incorrect. However, the comparison between the present results and other measurements was sufficient to convince us of the correct operation of the equipment. In particular, it was satisfying to obtain good agreement with Dehmer *et al* (1975) who also used the $\beta = 2$ helium test as an indication of the validity of their experimental procedure.

In general, the remaining atomic results, namely those from 30.4 nm radiation, agree well with Dehmer *et al* (1975) with the one exception of photoelectrons leaving xenon ion in the $^2P_{1/2}$ state. However, we know of no reason to doubt our value.

A comparison of the present results with those from synchrotron radiation, in general shows good agreement.

The comparison between the experimental picture and theory is largely as expected with the Hartree-Fock calculations providing a good approximation in the region where β rises from threshold up to its first maximum. Then, as the value decreases towards the position of the Cooper minimum, correlation effects become important and the RPAE and RRPA calculations provide a better fit. The exception, of course,

is neon which has no Cooper minimum and all theories provide a reasonable fit to the data. One point concerning the Hartree-Fock calculations is that an inspection Figures 3.3, 3.4 and 3.6 for argon, krypton and xenon shows that the velocity form provides a closer fit to the data than the length form. No reason is known for this and it in fact runs contrary to the indication given by Starace (1971) that the length results are more reliable in the Hartree-Fock approximation.

For both krypton and xenon, separate $\beta(^2P_{1/2}, ^2P_{3/2})$ values were obtained and these show the effects of spin-orbit coupling. There is a reasonable agreement with the theory for krypton, but for xenon, there is only agreement before the β maximum. Beyond that point, towards the position of the Cooper minimum, the data suggests that the theory is still incomplete.

Thus the results obtained from the inert gases provided confidence in the equipment and hence in the results that were obtained for the molecules. The molecular β values, with one exception, agree well with the trend in the data obtained from synchrotron radiation. The present data is able to provide an extra point in each of the β versus wavelength curves, and in most cases, the error bars on the present data are smaller than for the synchrotron radiation.

In general, there is poor agreement with the resonance radiation measurements of Katsumata *et al* (1979). The reason for this is not known. The data of Katsumata *et al* (1979) was only available some time after the present data had been taken and analysed. The differences were sufficient to prompt us into re-analysing the data, but no errors were found.

For photoelectrons corresponding to the ground state of CO^+ , there is a discontinuity between the present data point and the trend of the synchrotron radiation data. We believe our point to be accurate. Since there is no reason for believing there to be a gross error in the synchrotron data, this anomaly may be indicative of structure. This seems difficult to believe at such a high photoelectron energy, but it is interesting to note that the data of McCoy *et al* (1978) for photoelectrons corresponding to the ground state of O_2^+ also shows a truant data point (see Figure 3.16). No reason is known to explain these.

As regards the theoretical results shown, the multiple scattering method of Wallace *et al* (1979) seems to provide the most consistent fit to the data. However, in a few cases the fit is poor and in nearly every case, the data shows more structure than the theory. There is no doubt that molecules pose a very difficult problem for angular distribution theory. The reasons for this have already been covered in Chapter One.

Finally, it is of interest to classify the present molecular data according to the system of Chang (1978). He has shown that for diatomic molecules the photoionization process can be "classified according to (the) degree of parity favouredness". In fact it is shown that transitions of the type $\Sigma^\pm \rightarrow \Sigma^\pm$ are parity favoured, while $\Sigma^\pm \rightarrow \Sigma^\mp$ are parity unfavoured. Other transitions, such as $\Sigma \rightarrow \pi$, will be an incoherent sum of the two. It follows then that since β has the single value of -1 for a parity unfavoured

transition, it is to be expected that the β value for $\Sigma^+ \rightarrow \Sigma^+$ transitions will be greater than for $\Sigma \rightarrow \pi$ by an amount dependent on the amount of parity unfavoured component.

Chang (1978) was able to show that this indeed was the case for photoelectrons produced by 58.4 nm radiation. Table 3.5 shows the present data at 30.4 nm divided according to $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma \rightarrow \pi$ transitions. As can be seen there is no gross difference between the β values implying that at this energy, the parity favoured component predominates. Incidentally, to date there have been no measurements of a $\Sigma^+ \rightarrow \Sigma^+$ parity unfavoured transition.

TRANSITION TYPE		$\beta(30.4 \text{ nm})$
$\Sigma^{\pm} \rightarrow \Sigma^{\pm}$	$\text{N}_2 \text{ x}^1 \Sigma_g^+ \rightarrow \text{x}^2 \Sigma_g^+$	$.89 \pm .07$
	$\text{N}_2 \text{ x}^1 \Sigma_g^+ \rightarrow \text{B}^2 \Sigma_u^+$	$1.58 \pm .12$
	$\text{CO x}^1 \Sigma^+ \rightarrow \text{x}^2 \Sigma^+$	$1.24 \pm .05$
	$\text{CO x}^1 \Sigma_g^+ \rightarrow \text{B}^2 \Sigma^+$	$1.02 \pm .1$
$\Sigma \rightarrow \Pi$	$\text{N}_2 \text{ x}^1 \Sigma_g^+ \rightarrow \text{A}^2 \Pi_u$	$1.22 \pm .08$
	$\text{CO x}^1 \Sigma^+ \rightarrow \text{A}^2 \Pi$	$1.23 \pm .05$
	$\text{O}_2 \text{ x}^2 \Sigma_g^- \rightarrow \text{x}^2 \Pi_g$	$1.14 \pm .05$

TABLE 3.5

Measured values of β for 30.4 nm radiation classified according to $\Sigma^{\pm} \rightarrow \Sigma^{\pm}$ or $\Sigma \rightarrow \Pi$ transition type.

CHAPTER FOUR

FUTURE WORK

The work presented in this thesis has been the first stage of a program to measure the angular distribution of photoelectrons from gases. The aim of this chapter is to outline the direction of the next stage in this research.

The work so far, has been performed using helium resonance radiation at 58.4 nm and 30.4 nm. The next step is to extend the work to other wavelengths. One method for obtaining extra wavelengths is to use other gases in the resonance source (Samson, 1967) or to exploit lines other than the *raie ultime* as has been done by Mintz and Kuppermann (1978). But it would be preferable to have a continuum source since it would then be possible to finely scan across any interesting structure in the β versus wavelength curve.

At present, the only continuum source that has been used extensively to investigate angular distributions has been synchrotron radiation. This has been confined to just a few research groups. It was started by Marr's group with the 300 MeV electron synchrotron at Glasgow University. The same group then moved to the 5 GeV synchrotron at Daresbury and recently have used the 2.5 GeV electron synchrotron at the Physikalisch Institute, University of Bonn. This group has been responsible for a large body of wavelength dependent measurements, of which a significant number of examples have been shown in this thesis. The synchrotron at Stanford has also been used for angular distribution measurements (White *et al*, 1979) and recently Baudais and Taylor (1980) have published the design of an instrument to measure angular distributions

using the 240 MeV Wisconsin synchrotron.

But the general use of synchrotron radiation as a continuum source suffers from two problems. Firstly, synchrotrons are not readily available to the majority of experimenters. Secondly, a synchrotron represents a large and expensive investment, and the measurement of photoelectron angular distributions is only one of a number of research programs that could benefit from the use of this radiation. Therefore, one wonders if the number of measurements using synchrotron radiation will abate once the basic wavelength dependent measurements have been completed and it becomes necessary to concentrate on time consuming high accuracy studies.

It would seem therefore, that there is a good argument for investigating the suitability of laboratory sources which are known to be capable of supplying a continuum. One such source is a lamp which provides the Hopfield continuum of helium (Samson, 1967). An emission spectrum of this source can be seen in Figure 4.1. It was produced in this laboratory using a condensed discharge in helium. A spark rate of about 3 kHz and a peak current of 2 amps was used. The helium pressure in the lamp was 24 torr, requiring two stages of differential pumping between the lamp and the one metre normal incidence monochromator used to disperse the radiation.

As can be seen from the spectrum, the helium Hopfield continuum is limited in wavelength range to approximately 60 nm to 96 nm. However, it is a region which provides access to a wide range of auto-ionizing structure (Gardner, 1970; Blake, 1966). The advantage of using a variable wavelength source to study such structure, can be seen in the following example. A measurement by Carlson (1971) of the

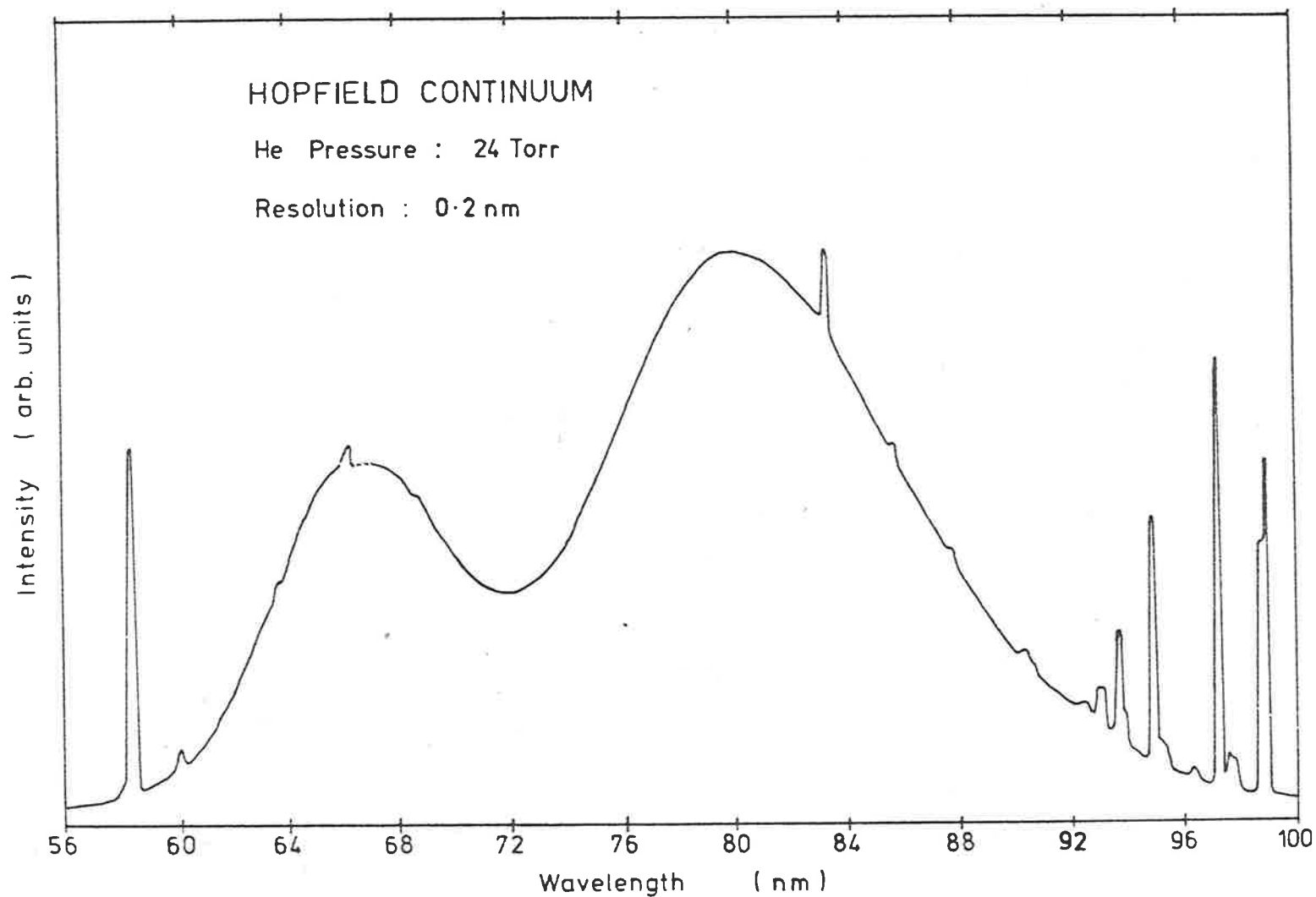


FIG. 4.1 Hopfield continuum in helium dispersed by a 1m normal incidence monochromator.

angular distribution of photoelectrons corresponding to the ground state of O_2^+ produced by 16.85 eV photons, showed β to have vibrational dependence. In particular it was found that β for the photoelectron peaks $v = 0$ to 3 was different to the β for $v = 4+$. This difference has been attributed to the $v = 4+$ peaks being produced through autoionization while the $v = 0$ to 3 peaks are produced by direct ionization. Using synchrotron radiation, Holmes and Marr (1979) were able to measure β for a range of energies about the 16.85 eV point for these two sets of vibrational peaks. They were able to show that the feature reported by Carlson (1971) was actually about 1.5 eV wide. The results of both Holmes and Marr (1979) and Carlson (1971) can be seen in Figure 4.2.

The possibility of furthering this type of study by using the helium Hopfield continuum is considered to be the direction of future work. However, the use of this continuum source raises a number of problems and these will now be considered.

The primary problem encountered when using the helium Hopfield continuum is low signal strength. At present, the continuum radiation is dispersed by a one-metre normal incidence monochromator. The emergent radiation is being used to measure photoelectron branching ratios using a spherical retarding grid analyser. This analyser has a large 36° field of view, but even then, the time taken to record the vibration structure for the ground state of O_2^+ to an accuracy of about 5% is of the order of a day. If we equate that to the plane retarding grid analyser used in the present work, the data collection time for measuring the angular distributions would be of the order of weeks. This

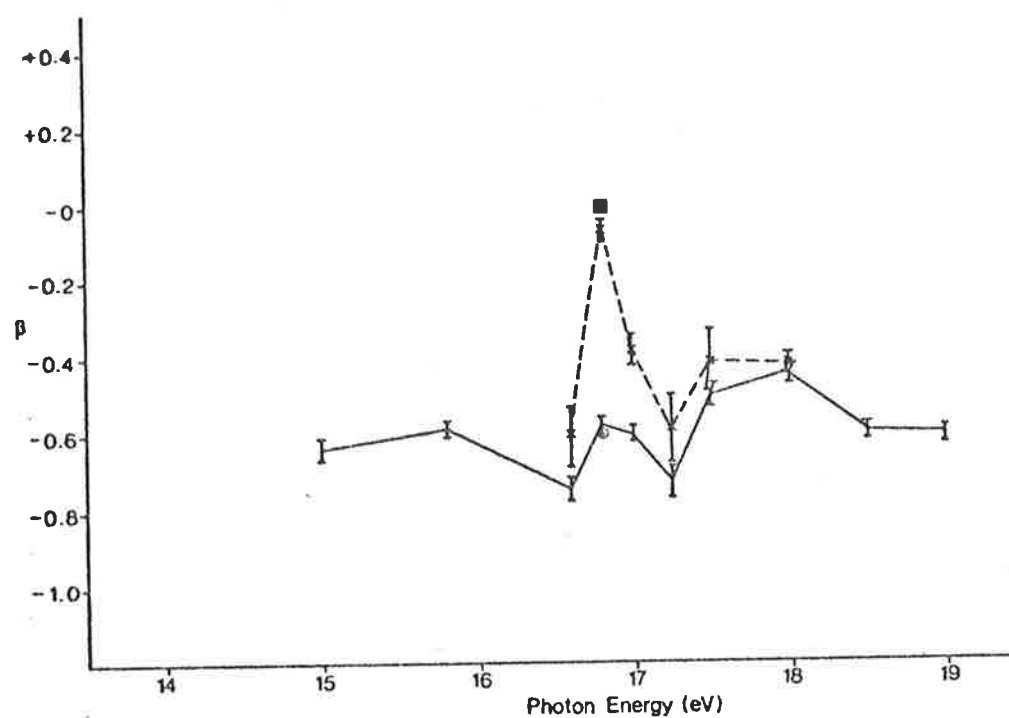


FIG. 4.2 The asymmetry parameter as a function of photon energy for photoelectrons corresponding to the ground state of molecular oxygen (from Holmes and Marr, 1979). Solid line for $\nu = 0-3$; dashed line for $\nu = 4+$. [Experimental points : $\bullet$ x Holmes and Marr, 1979; $\odot$ ■ Carlson, 1971.]

is clearly unreasonable, and means that the choice of analyser must be looked at carefully. A dispersive analyser cannot be used because its entrance angle is even smaller than the present analyser implying even longer data accumulation times.

An analyser that can be considered is the spherical retarding grid design. An example of such an analyser is shown in Figure 4.3. This is in fact the analyser mentioned above that is at present being used to measure partial photoionization cross sections. However, if a similar instrument was constructed to measure angular distributions, it is unlikely that the 36° full angle field of view could be tolerated, as this would blur out angle information. This will be checked by adapting the computer program discussed in Section 2.7.1 to look at the effect of the size of the field of view on the measurement of β .

If, as is probable, a much smaller angular field of view is required to enable sufficient angle resolution, we return to the problem of signal strength. It may be possible to increase the photoelectron count by increasing the intensity of the light source. This would require a much larger power supply than is presently being used. The design of such a supply is under investigation in this laboratory.

However, with the equipment presently available it would seem that a poor count rate may have to be tolerated. One way of reducing the total data accumulation time is suggested by the spectrum shown in Figure 4.3. In this count versus voltage curve, the curve is horizontal at both the top and bottom of the step. It would therefore only be necessary to count the number of electrons at one voltage before the step and one after the step, rather than scanning across the complete step. If this is done, experience suggests that the amount of time

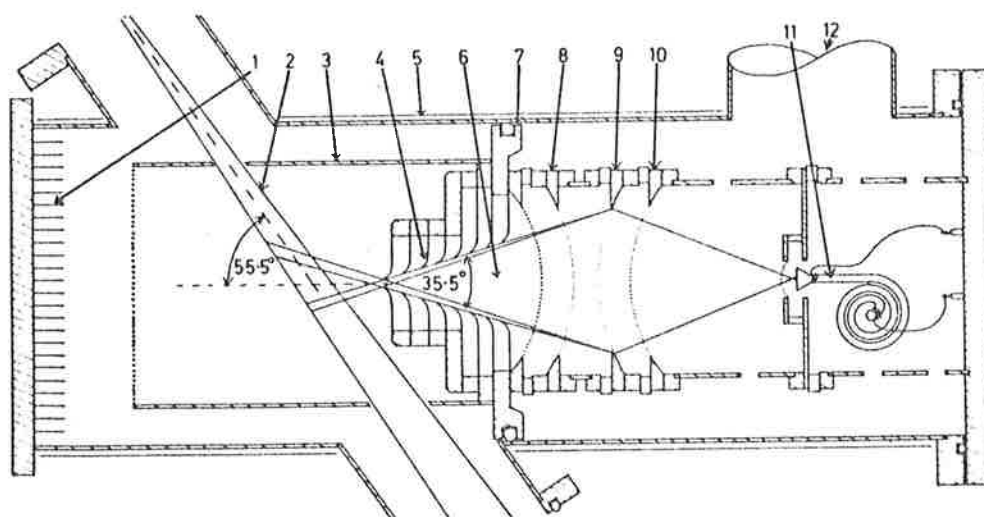
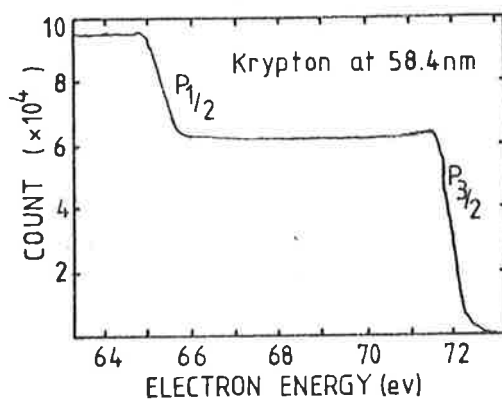


FIG. 4.3 Cross Section of spherical grid retarding analyser and photoelectron spectrum for krypton photoionized by 58.4 nm radiation. Shown are : (1) Electron & light trap, (2) Light beam, (3) Interaction chamber, (4) Electron baffle, (5) Magnetic shielding, (6) Field free region, (7) Gas partition flange, (8) Retarding grid, (9) Accelerating grid, (10) Focussing grid, (11) Channel electron multiplier, (12) Pumping port.
(taken from Lindemans et al, 1979)

needed for data collection is reduced by a factor of ten.

However, this is only a limited solution. If the photoelectrons being measured are from excited ionic molecular states, then in a number of cases, the scattered background from less energetic electrons will produce a slope in the curve at the top and bottom of the step. This situation was encountered with the present plane retarding grid analyser and as has been shown, implies that a full scan must be made.

Another possible method to reduce the amount of time needed for data collection would be to use more than one analyser. The simplest arrangement would be to have two fixed analyses. This is the minimum number required to make an absolute measurement of β .

However, two fixed analysers could not provide the information about the quality of the data that would be available if these analysers could be moved. Then the electron count can be measured at a number of angles to check the equipment. This involves plotting the corrected count against the square of the cosine of the angle as has been explained in Section 2.10. A further advantage of using a moveable system would be the ability to measure the relative sensitivities of the two analysers by using each to measure the photoelectron intensity at the same angle.

Therefore, it is proposed that the equipment to be built will consist of twin analysers positioned at a fixed angular separation on a single rotatable arm. The plane of rotation would be orientated to contain the light beam.

There are two monochromators available to disperse the continuum. One is a one-metre near normal incidence monochromator and the other a half-metre Seya Namioka style instrument. If the analysers are used on the one-metre monochromator, the orientation of the rotation

plane about the beam is not critical. This is because radiation from such monochromators has no appreciable polarization (Samson, 1967). On the other hand, if it is used on the half metre Seya-Namioka type instrument which provides partially polarized radiation (Samson, 1978), then the plane of rotation must be at an angle of 45° to the axis of polarization of the light.

In the present work, the measurement of the β value for photoelectrons from helium was found to be a valuable check on the equipment. It is therefore proposed to provide a resonance source capable of providing a 30.4 nm radiation light beam co-axial with the monochromator beam. This would allow the new instrument to be checked.

One final point that must be made concerns the electron energies in the wavelength region of interest. A large number of atomic and molecular photoionization transitions will yield electrons of energy typically less than 5 eV. This is a difficult region for angular distribution measurements since stray electric fields can easily distort the measurement. Therefore, great care will need to be taken to shield the interaction region. It is initially proposed to enclose the region in an earthed electrically conductive cage.

Therefore in summary, it is proposed to use a dual spherical retarding grid analyser to measure β through autoionizing resonances. It is proposed that the measurements will initially involve photoelectrons from diatomic molecules such as O_2 , N_2 , CO, and NO. The occurrence of autoionizing structure in the photoelectron spectra of these gases has already been extensively studied in this laboratory (see for example, Gardner, 1970).

It is expected that wherever such structure occurs in the spectra, that it will be reflected in the value of β . Therefore the spectroscopic work that has been done will be used as a guide to the most promising regions of study.

CHAPTER FIVE

DESIGN OF AN EUV SPECTROPHOTOMETER

5.1 INTRODUCTION

This chapter details work carried out in the design of a new form of rocket-borne EUV spectrophotometer. The instrument is based on the principle of using photoelectrons produced from a metal surface to provide information on both the intensity and wavelength of the incident radiation. The emitted photoelectrons were analysed with an electrostatic cylindrical mirror analyser.

The instrument was designed with the intention of measuring the two EUV airglow lines 58.4 nm and 30.4 nm. These occur from the resonance scattering of solar 58.4 nm and 30.4 nm radiation off atmospheric atomic and ionized helium respectively.

The instrument was flown as part of a payload on a Super Chief rocket on 23rd July 1974. However, vehicle failure resulted in complete loss of the payload and at that point, the project was terminated. Therefore, since no actual measurement was made of the airglow, this chapter is primarily concerned with the design, construction and testing of the instrument. Section 5.2 discussing the phenomenon of the airglow will thus be very brief, being concerned mainly with a description of the spatial distribution of the glow and its expected intensity.

Section 5.3 describes two of the possible measurement techniques that can be used for measuring EUV airglow. These are the

use of a photocathode, which is the method of interest in this work, and the use of thin film metal filters.

The design of the instrument is covered in Section 5.4. It discusses the type of photocathode used and the design of the cylindrical mirror analyser. As well, the special problems of using channel electron multipliers in rocket work are outlined.

Section 5.5 describes the instrument testing and calibration while Section 5.6, entitled "Concluding Remarks" outlines the status of the program at the time of the rocket flight.

5.2 EUV RESONANCE RADIATION FROM HELIUM

Up until 1972, there had been a number of rocket-borne measurements of 58.4 nm and 30.4 nm airglow during both the day and night (Donahue and Kumer, 1971; Paresce *et al*, 1973; Kumar *et al*, 1973; Ogawa and Tohmatsu, 1971; Young *et al*, 1968, 1971). Meier and Weller (1972) amalgamated these measurements in an attempt to construct a model of the distribution of both neutral and ionized helium about the earth. For the 58.4 nm measurements, it was found that the measured variation with altitude and solar zenith angle was in a good agreement with an atomic helium model consisting of an optically thick spherically symmetric geocorona. There were however discrepancies between the various experimenters as to the absolute intensity. Nor did the model explain a residual intensity in the antisolar direction and it was suggested by Meier and Weller (1972) that this was due to the scattering of 58.4 nm radiation off interplanetary or interstellar helium. Later work did indeed prove this to be the case as will be shown further on.

In the same article, Meier and Weller (1972) were able to account for the experimental measurements of 30.4 nm radiation as the scattering of solar 30.4 nm radiation off plasmaspheric He^+ . The plasmasphere is a region of relatively high ion density (10^3 to 10^4 ions per cm^3) which is contained along the closed lines of geomagnetic force (Banks and Kockarts, 1973(a)). It is shown in Figure 5.1. As can be seen, the region is dipole shaped due to losses from the open field lines at the poles; this outward flow is called the polar wind (Banks and Kockarts, 1973(b)).

The helium ions are optically thin to 30.4 nm radiation and therefore the intensity of scattered 30.4 nm radiation detected is proportional to the column density of helium ions along the line of sight. This fact led Johnson *et al*, (1971) to suggest the use of 30.4 nm scattered radiation as a means of viewing the magnetosphere. However, the occurrence of single scattering complicates the calculation of the helium ion number density since a knowledge of the solar flux and linewidth of 30.4 nm radiation incident on the plasmasphere is required.

After 1972, major advances were able to be made in the measurement of these radiations when detectors were carried aboard satellites. The first such measurement of scattered 30.4 nm radiation was from the satellite STP 72-1 (Weller and Meier, 1974a). The satellite was in a near polar orbit at an altitude of about 750 km. The spin axis of the satellite was aligned perpendicular to the orbital plane allowing the instrument to view a large section of the sky as the satellite rotated (see Figure 5.2). However, the line of sight of the instrument was inclined at 25° to the spin plane to avoid direct

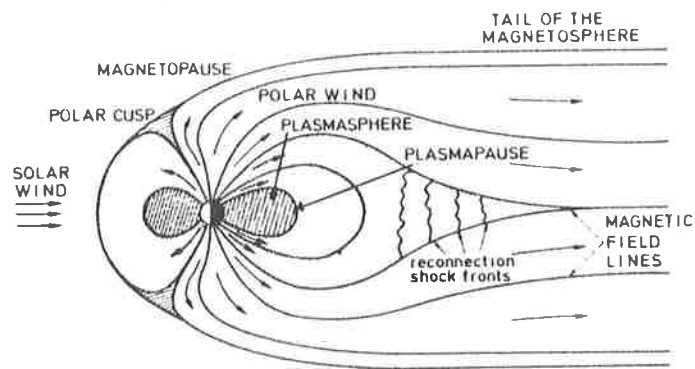


FIG 5.1 The different regions of the magnetosphere (from Banks and Kockarts, 1973(b)).

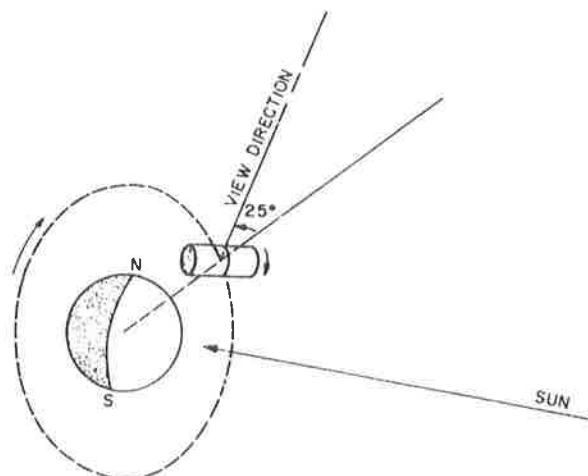


FIG 5.2 Orbit of satellite STP 72-1 and view direction of EUV photometer (Weller and Meier, 1974a)

viewing of the sun. Thus the view direction of the instrument could only come to within 25° of either the zenith or nadir direction.

An example of the 30.4 nm radiation detected in this near-zenith direction is shown in Figure 5.3. It is plotted as a function of the magnetic latitude. Also shown is the solar zenith angle which is the angle between the local zenith and the sun. Therefore the data at a solar zenith angle of 180 degrees has been taken on the night side of the earth.

As can be seen, the radiation terminates very sharply at about $\pm 55^\circ$ magnetic latitude thereby clearly showing that the 30.4 nm radiation is scattered from helium ions in the plasmasphere (Weller and Meier, 1974a). Also shown in Figure 5.3 are the results of two model calculations for two different heights of the plasmopause designated by the values of $L_c = 3$ and $L_c = 4.5$. The parameter L_c is the McIlwain L parameter for the boundary; the L parameter defines the size of the dipole shell at the equator in units of earth radii. The plasmaspheric model used assumes a constant helium ion density along a given L shell but does allow for an equatorial trough. This decrease in the helium ion density near the equator is a feature that is known from satellite ion measurements (Chandra *et al*, 1970).

Referring to Figure 5.3 it is apparent that both the $L_c = 3$ and the $L_c = 4.5$ models fit the dayside data well, but the fit to the nightside data is not as good. Weller and Meier (1974a) interpret this as implying the need for refinement in the model.

The dip in the model calculations in the anti-solar direction is due to viewing in the region where the plasmasphere is shadowed by

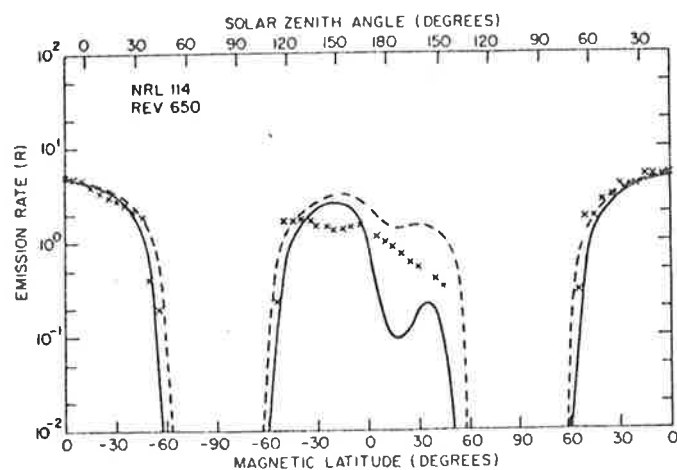


FIG 5.3 The emission rate for He^+ 30.4 nm radiation at 25° to the zenith. The measured data is shown by crosses, the solid line is a theoretical calculation for $L_c = 3.0$ and the dashed line is a theoretical calculation for $L_c = 4.25$ (from Weller and Meier, 1974(a)).

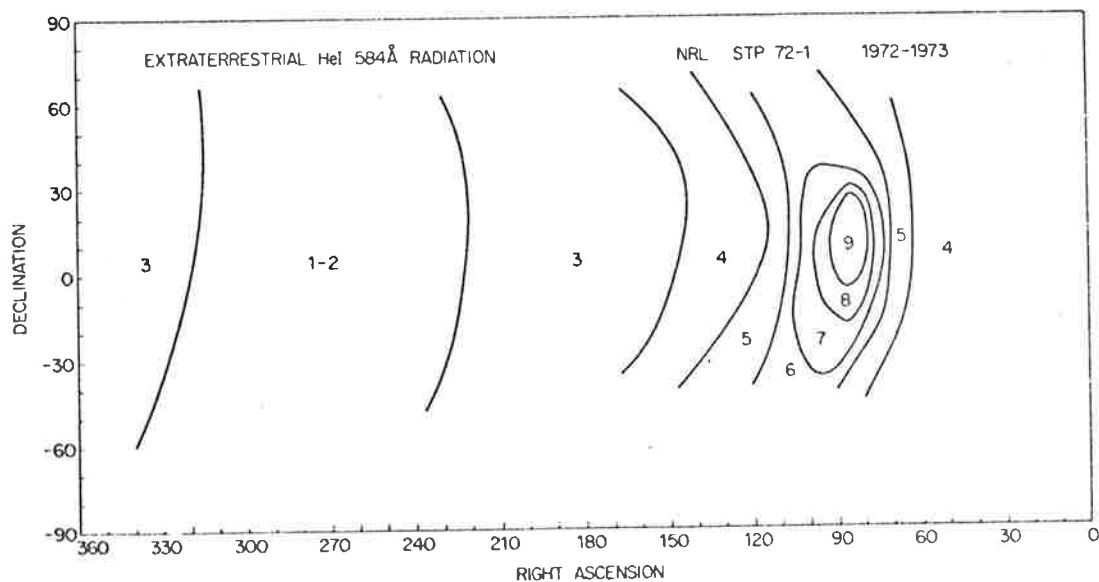


FIG 5.4 The observed extraterrestrial 58.4 nm radiation. The isophotes are in rayleighs. (from Weller and Meier, 1974(b)).

the earth. The fact that there is still substantial radiation measured in the anti-solar direction is due to the large size of the plasmasphere which extends to 3 to 4 earth radii. The angle of view of the detectors was such that they viewed sunlit regions above the earth's shadow (Meier, 1974).

The photometers on board the satellite STP 72-1 were also able to measure 58.4 nm radiation. From these measurements Meier and Weller (1974) were able to plot the latitudinal variation of atomic helium. Also, seasonal variations were examined (Anderson *et al*, 1979). However a more interesting possibility was the opportunity to investigate more fully the occurrence of the extraterrestrial source of 58.4 nm radiation mentioned earlier.

The possibility of an extraterrestrial source had already been investigated by rocket-borne experiments but these suffered from the problems of short data acquisition times, atmospheric attenuation of the radiation and the difficulty of differentiating between extraterrestrial and geocoronal helium glow. For the satellite photometers, it was found that when viewing deep into the earth's shadow, that the zenith intensity was typically a factor of ten greater than the nadir intensity (Weller and Meier, 1974b). Calculations showed that at the 750 km altitude of the satellite, this difference could not be explained by geocoronal scattering. Furthermore, it was possible to identify a maximum emission of about 9 rayleighs* at a position right ascension 85° and declination + 5°, and a broad minimum centred at right ascension 265° and declination 0°. This is shown in Figure 5.4.

* 1 rayleigh = $10^6/4\pi$ photons / cm² / sec / steradian.

Thus the above results not only showed the existence of 58.4 nm radiation scattered off extraterrestrial helium but also identified this helium as being part of the interplanetary wind. This flow of interstellar gas entering the solar system, was first proposed to explain the observations of extraterrestrial H-Lyman alpha (Bertaux and Blamont, 1971; Thomas and Krassa, 1971). The helium component is able to penetrate quite deeply into the solar system and is gravitationally focussed by the sun to produce a build up of helium in the down wind direction. This accounts for the maximum observed in the 58.4 nm scattered radiation.

From the measurements aboard the STP 72-1 satellite and further measurements from the OSO 8 satellite, Weller and Meier (1979) were able to place bounds on the velocity and temperature of this wind. This is shown by the shaded region in Figure 5.5.

As mentioned previously, attempts to measure the scattering of 58.4 nm radiation from extraterrestrial helium with rocket-borne experiments are hampered by the need to differentiate between the extraterrestrial and the geocorona helium nightglows. However, a recent series of rocket flights were able to separate the two by using a gas absorption cell in place of the more usually used wide bandpass photometers (Freeman *et al*, 1976(a), (b)). The technique is based on the 9-27 km/sec velocity of the interstellar wind (Weller and Meier, 1979) being greater than the 2 km/sec thermal velocity of geocoronal helium (Freeman *et al*, 1976b). Because of the speed of the wind, the scattered radiation is doppler shifted and passes through the absorption

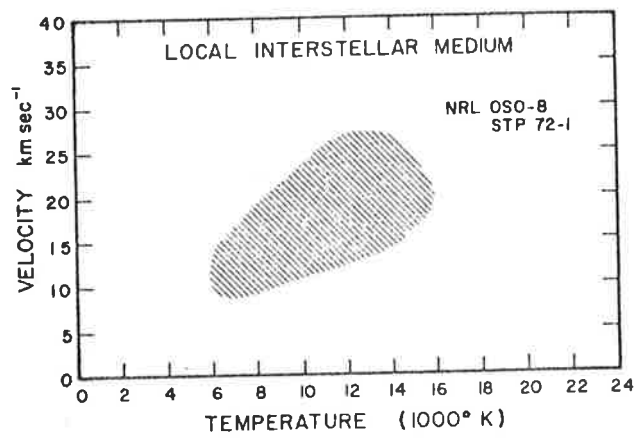


FIG 5.5 Range of values of the velocity and temperature of the local interstellar medium (Weller and Meier, 1979).

cell to be detected, while the geocoronal glow is absorbed (Crifo *et al*, 1979). In this way, Freeman *et al*, (1976b) were able to place an upper limit on the geocoronal night flux of $.09 \pm .74$ R.

In the above, a very brief description has been given of the occurrence of 58.4 nm and 30.4 nm airglow. Table 5.1 gives a summary of the maximum emission rates that have been observed. However, these are only intended as a guide to typical values as the measurement is very dependent on the solar zenith angle, angle of view and even the season.

5.3 MEASUREMENT TECHNIQUES

A spectrophotometer has two basic parts; the first to select a particular wavelength band and the second to detect the radiation and produce an output proportion to the intensity. However, when an instrument is to be flown on a rocket, a number of constraints are imposed on both the instrument choice and design.

Firstly, the space available for a payload is generally restricted and the instrument should be as compact as possible. Secondly, the payload is subjected to a large number of forces during launching and the instrument must be capable of withstanding these severe vibrations. Finally, there is the short viewing time of 5 to 10 minutes that is available during a flight. This requires that the sensitivity of the instrument be as high as possible.

Within these criteria, two techniques for measuring the helium airglow are to be described. These are the photoemission from a

Dayglow		Nightglow
58.4 nm	max ~ 550 R (Anderson <i>et al</i> , 1979)	Geocoronal : ~ 9 ± 2 R (Weller and Meier, 1974) Extraterrestrial : ~ $09 \pm .74$ R (Freeman <i>et al</i> , 1976(b))
30.4 nm	~ 5 R (Weller and Meier, 1974a)	~ 2 R (Weller and Meier, 1974)

TABLE 5.1 Maximum emission rates for scattering of solar 58.4 nm and 30.4 nm radiation of atomic and ionized helium respectively,

metal surface (Section 5.3.1) and the use of thin film metal filters (5.3.2). Of these, the metal filters have seen the most extensive use due to their high sensitivity and compact construction. However, their bandpass is of the order of 10 nm, while the photocathode technique although having a lower sensitivity, has the potential for providing a much narrower bandpass.

5.3.1 PHOTOELECTRIC EUV DETECTORS

The photoelectric effect offers a very simple technique for measuring intensities in the extreme ultraviolet. Radiation incident on a photocathode ejects a number of photoelectrons proportional to the intensity of the incident radiation provided its wavelength is below a certain critical value. This critical wavelength for most photocathode materials is in the range of 120 nm to 140 nm and they have a useful photoelectric yield extending to about 20 nm. This makes them ideal detectors for the extreme ultraviolet as by measuring the number of photoelectrons ejected and knowing the quantum yield of the material, a measure of the intensity of the incident radiation is obtained.

The emitted electrons can also be analysed for information about the wavelength of the incident radiation. Essentially, the energy of the photoelectron is the difference between the photon energy and the work function of the metal. However, due to collision processes as the electron escapes, the result is a range of energies up to a maximum energy equal to this difference. Therefore if the work function of the metal is known, then measurement of this maximum energy allows calculation of the wavelength. Or alternatively, if there are, say, two separated wavelengths of radiation producing the photoemission, then by

energy analysing the electrons, the contribution to the measured photoemission due to each wavelength can be ascertained. As such a photocathode/electron energy analyser combination can be used as an EUV spectrophotometer.

To energy analyse the electrons, there are two basic techniques; the retarding grid analyser which is a high pass energy filter, and the dispersive instrument which is a bandpass energy filter. Figure 5.6 shows an idealised metal electron spectrum due to monochromatic radiation and the resulting spectrum obtained from each of the two types of analysers.

The retarding grid analyser is the simplest and the photo-electrons emitted by the photocathode can be monitored as a current. A retarding potential can be applied to a grid in front of the photocathode. Under these conditions, only those electrons whose energy component normal to the surface of the photocathode is greater than the retarding potential can escape.

The resulting spectrum is shown in Figure 5.6. If all the electrons are emitted normal to the surface, the spectrum is a sloping line of constant gradient. However, in reality, the spectrum obtained is curved. This is due to the fact that the analyser only measures the component of energy normal to the grid which augments the retarding curve at low energies and depletes it at high energies. The difficulty arises then that for different wavelengths, there is very little difference in the curves at low energy. To dissect a curve that is a composite of two wavelengths, it is necessary to analyse the high energy tail which of course is the region of poorest statistics.

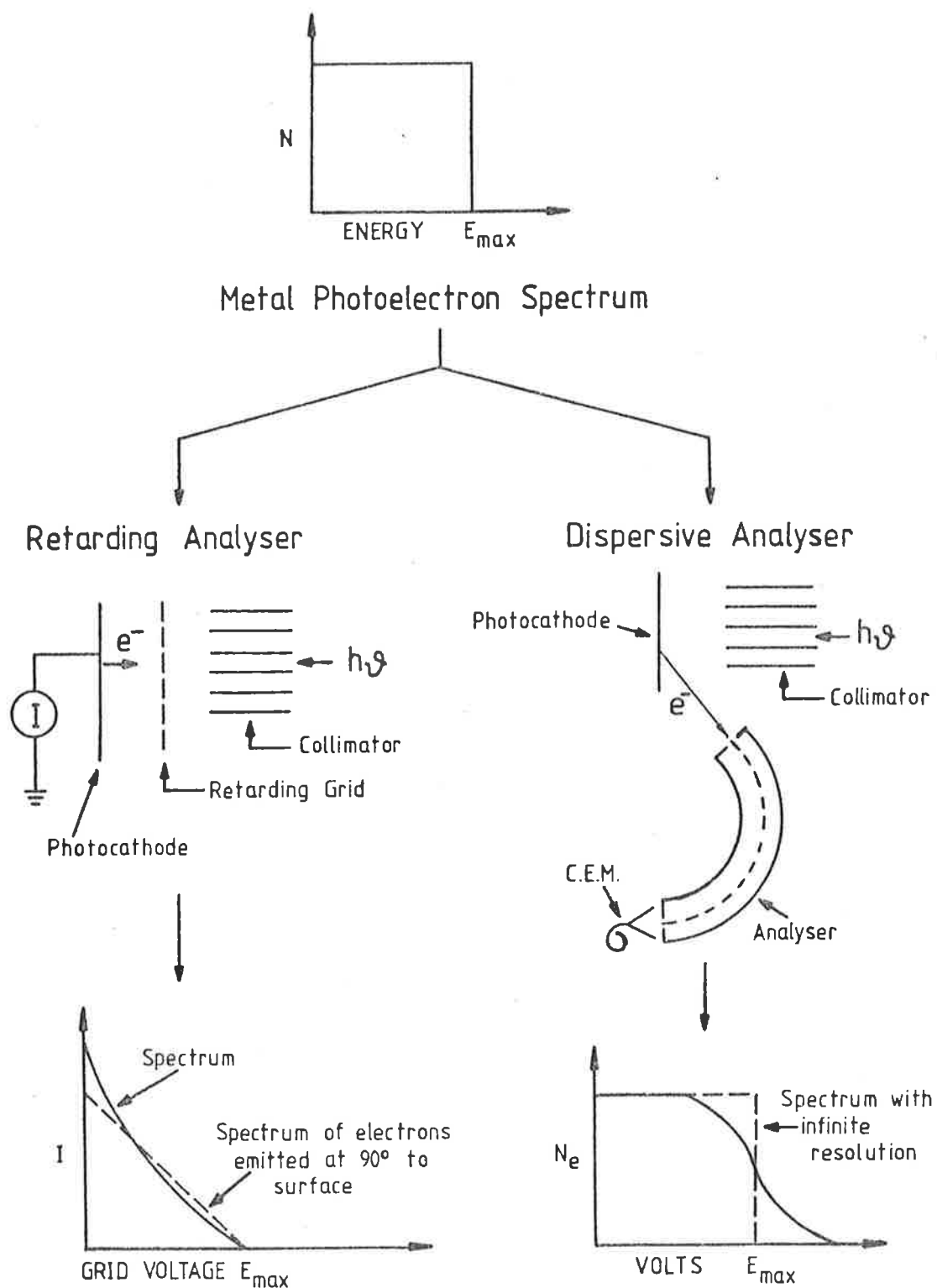


FIG. 5.6 The effect of analysing an idealised metal photoelectron spectrum with two different types of electron energy analyser.

An advantage of the retarding grid analyser is its simplicity. The signal produced is directly proportional to the area of the photocathode but the sensitivity is limited by the need to measure current. The sensitivity could be improved by detecting the electrons with a CEM or channel plate. But a difficulty in the design then is that if there is a line of sight direction from the photocathode to the CEM, any scattered radiation from the cathode will enter the detector and cause a catastrophic amount of background. This was discovered in the present work when an instrument built along these lines was tested. It was eventually discarded.

Figure 5.6 also shows the use of a dispersive analyser. Since it is an energy bandpass analyser, the resulting spectrum is similar to that emitted from the surface. This is also due of course to the simple observation that the small entrance aperture of the analyser necessary for proper focussing, also only permits electrons from a small range of directions to enter. However, this severely limits the sensitivity since only a small area of the photocathode can be viewed, although this will depend to a great extent on the type of analyser used.

One great advantage in using this form of energy analyser is that it separates photons and electrons and allows a CEM to be used.

There have been few examples of rocket-borne spectrophotometers based on the above techniques. Hinteregger *et al*, (1959) used a planar photocathode and measured the emitted current to investigate the solar EUV. A later instrument used a Be - Cu electron multiplier (Heroux and Hinteregger, 1962).

Another instrument is that of Donahue and Kumer (1971). This is of some interest in this work since it was used to measure helium

dayglow. It is shown diagrammatically in Figure 5.7. Photons enter the instrument through the collimator aperture, travelling past the electron multiplier to strike the target which is a nickel photocathode. The energy analysis is achieved with the cylindrical "retarding potential screen". Its action is as follows. As the voltage on this grid becomes negative, electrons emitted from the nickel photocathode are focussed on to the electron multiplier and the detected signal increases. However, as the grid becomes more negative the field begins to pinch off the electrons thereby reducing the signal until no electrons are able to penetrate the field. The resulting spectrum is shown in Figure 5.7.

The instrument was first flown in 1966 but suffered very badly from a large structured background. This was explained as due to "photoelectrons produced on the face of the multiplier housing that succeeded in passing through the collimator tubes". A ninety volt positive bias on the front of the collimator was designed to prevent this, however it was considered that its effect was lessened by atmospheric current drawn to the vehicle. This had the effect of lowering the bias voltage due to a current limiting resistor inserted between the collimator and the bias voltage supply.

In general, the use of a photocathode to provide both wavelength discrimination and intensity measurement has seen little application. This is largely due to the fact that a metal photoelectron spectrum is very different from the idealised step function used in the discussion above. In particular it has a certain amount of structure and the actual spectrum obtained depends on the surface contamination. Both of these effects are shown in Figure 5.8.

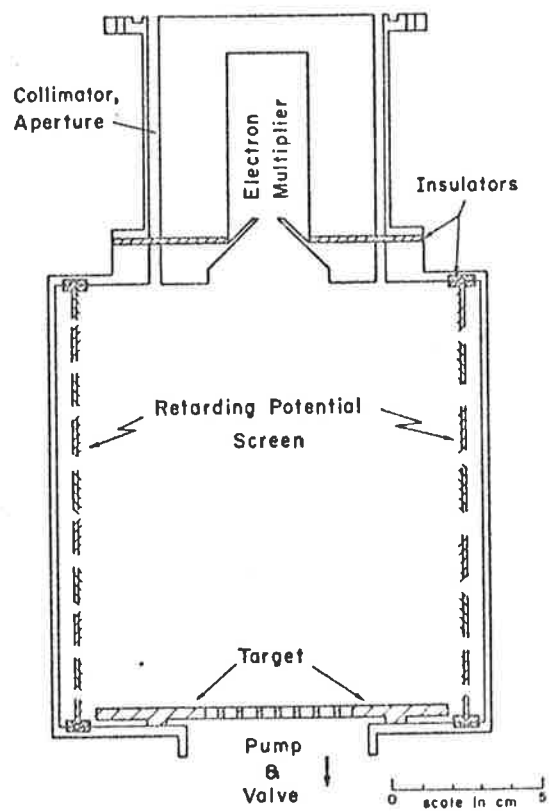
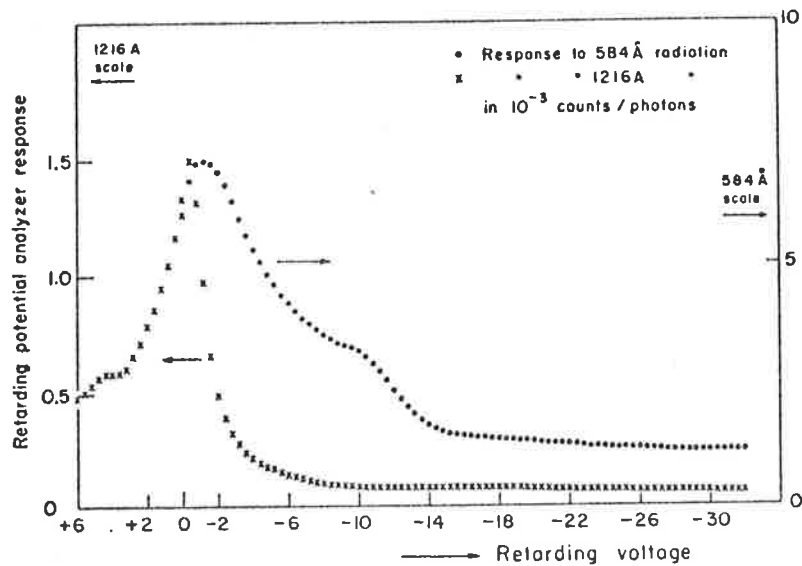


FIG 5.7 The retarding potential photometer of Donahue and Kumer (1971) and a typical spectrum (diagram taken from Donahue and Kumer, 1971).

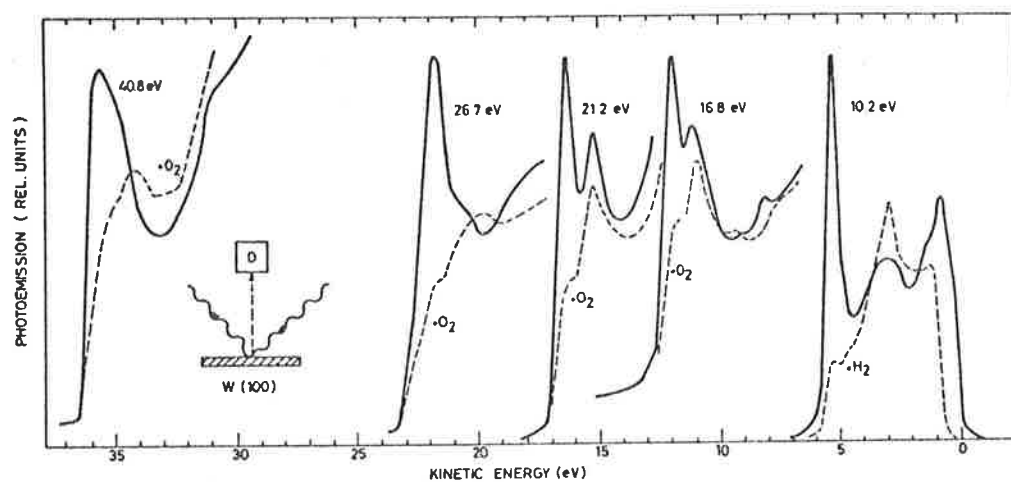


FIG 5.8 The spectra of photoelectrons emitted normal to the (100) surface of tungsten (from Feuerbacher and Willis, 1976).

The solid curves are for a clean surface, the dashed curves after a saturation covering of O_2 or H_2 as indicated. The curves have been normalised to the high energy peak and except for the 10.2 eV curve, only the high energy portion of the curve is shown.

It can be seen that the peak at the high kinetic end of the curve is different for a clean sample as against one with absorbed gas. For the reason for this, the reader is referred to Feuerbacher and Willis (1976) since it is not of concern here. In fact the field of solid state physics concerned with the photoemission from metals was found to be of little use in this work. This is due to the majority of measurements being done on metals of controlled or known surface contamination in ultra-high vacuum and generally for a particular surface orientation. None of these apply when a photocathode is used as discussed here.

Nevertheless, one fact that is apparent from the curves in Figure 5.8 is that the high kinetic energy end of the curve does follow the wavelength, at least up to 30.4 nm. Therefore, the action of the photocathode in providing wavelength discrimination can be clearly seen.

5.3.2 METAL FILTERS

The majority of the measurements of helium resonance radiation have used unbacked metal filters (Bowyer *et al*, 1968; Ogawa and Tohmatsu, 1971; Paresce *et al*, 1973, 1974; Riegler and Garmire, 1974; Young *et al*, 1971; Bowyer *et al*, 1970). These are metallic films of about 100 nm thickness that have a transmission window in the EUV (Hunter *et al*, 1965; Samson, 1967). The three most commonly used in the detection of 58.4 nm and 30.4 nm radiation are aluminium, carbon and tin and the transmittance of each of these as a function of wavelength is shown in Figure 5.9(a)).

The only one of these that actually isolates one of the two lines of interest is tin. However, a commonly used arrangement is to have two detectors, one with a carbon film, the other with aluminium.

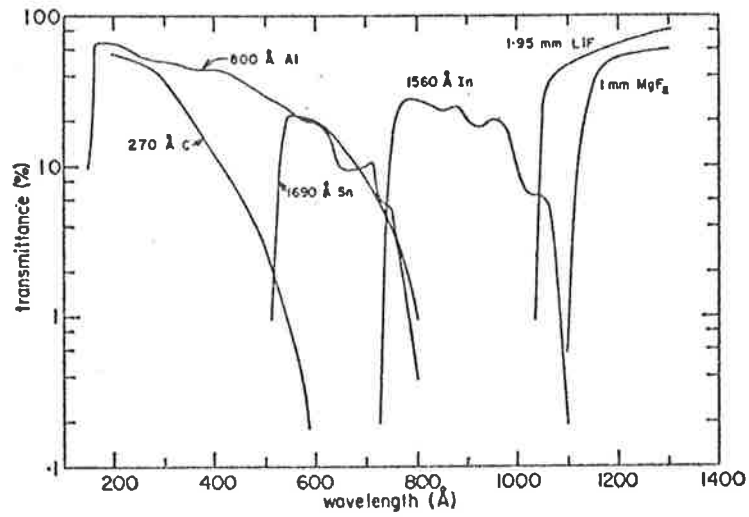


FIG 5.9(a) Transmission of some metallic filters (from Bowyer *et al*, 1970).

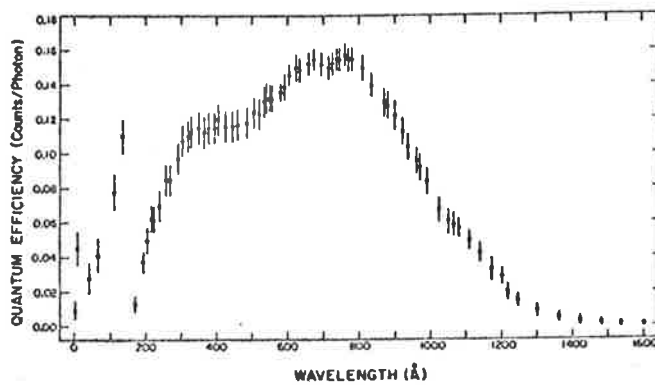


FIG 5.9(b) Quantum efficiency of a channel electron multiplier (from Mack *et al*, 1976).

From the signals of the two detectors, the relative contributions of 58.4 nm and 30.4 nm radiation can be determined.

The detectors used are channel electron multipliers. Their use as electron detectors has already been described in Section 2.3.3. Their mode of operation as photo detectors is essentially the same except that it is a photoelectron produced by the incident photon on the entrance of the cone of the CEM that starts the avalanche process. The electronics and electrical connections are also the same as for electron detection except that in this case the entrance cone of the CEM can be earthed. The quantum efficiency of a typical CEM as a function of wavelength is shown in Figure 5.9(b)).

The method of construction of the filters is very critical if one is to achieve a filter that has both a low pinhole area and is able to withstand the rigors of launch. This has been extensively covered by Hunter (1973), and the following brief discussion on the method of construction is based both upon that review and to a lesser extent, on the experience of the author.

The steps in the construction of the filter are as follows. Firstly, a parting agent is deposited on to a glass or quartz substrate, then the metal filter is evaporated on top of it. The substrate is then lowered into the solvent in which the parting agent is soluble, thus freeing the metal filter. Finally, the filter is picked up and glued to a piece of nickel electroform mesh that has previously been fastened to a frame.

The quality of the film produced depends strongly on the techniques used to execute the above sequence of events. For example,

both the substrate and the layer of parting agent must be as smooth as possible since any irregularities here will also appear in the metal film and either result in pinholes or create weaknesses where pinholes can form. This will also apply to any dust or lint which becomes trapped between the substrate and the parting agent or between the parting agent and the metal film. Elaborate cleaning procedures and methods for stripping away any collected dust on the parting agent just before metal evaporation are outlined by Hunter (1973).

There are a large number of parting agents that can be used and Hunter (1973) catalogues the properties of fourteen of them. Of prime importance is that there is no chemical activity between the metal film and the dissolving parting agent.

A further problem that causes pinholes is irregularities in the electroform mesh. These may take the form of broken wires or blobs of metal. These are points of stress and under vibration, can lead to tearing of the film.

It is virtually impossible to construct a pinhole free filter. However, the pinhole density tolerated depends on the use to which the film will be put. In a solar spectrograph where the metal filter is used to remove the visible portion of the sun's radiation, a comparatively small number of pinholes could be sufficient to cause substantial fogging of the film. However, when used with CEM's to detect 58.4 nm and 30.4 nm radiation, this is not a problem and the background that is encountered is 121.6 nm H-Lyman alpha radiation.

A disadvantage of metal filters is that the range of wavelengths they transmit extends over ten or more nanometres. Therefore

their use relies on the assumption that the wavelength to be measured is the only one in the passband. This may not be the case and in fact, it has recently been shown that for a measurement of the 58.4 nm dayglow emission, there are a number of lines of almost comparable intensity within the passband of an aluminium filter. (Gentieu *et al*, 1979). This measurement was made at 250 km and thus affects any rocket-borne measurement. However, for the STP 72-II satellite 750 km, Anderson *et al*, (1979) stated that these extra emissions which are due to OII were not a problem provided measurements were only taken when the instrument was pointed away from the earth.

Apart from this limitation due to the wide bandpass, metal filters have seen significant use in rocket-borne measurements of EUV radiation. They are light and compact, and when combined with a CEM, provide an instrument of reasonably high sensitivity.

5.4 A PHOTOELECTRIC EUV DETECTOR

At the time this project was started, namely in 1972, the majority of measurements of helium airglow had been with thin metal filters. The one exception was the retarding grid analyser of Donahue and Kumer (1971) described previously.

It was felt that the use of a photocathode as the analysing element deserved further investigation. There were two main reasons for this. Firstly, of the measurements that had been made, there were discrepancies between the absolute magnitudes of the radiation detected. Therefore, it seemed desirable to design a new instrument to measure the helium airglow. Secondly, there was the possibility of errors with the metal filter measurements due to other wavelengths in the passband of the filter. The better wavelength discrimination of the photocathode

method would help to analyse this problem.

An investigation of possible designs, revealed that a fault with open instruments of the type of Donahue and Kumer (1971) is that while the electrons have an easy path to the detector, so do any extraneous ions, electrons or even scattered light that may enter the instrument. Therefore, the instrument to be described in Section 5.4.1 used a cylindrical mirror analyser not only to energy analyse the electrons, but also as a means of separating those electrons from the assorted backgrounds discussed above.

The photocathode that was used is discussed separately in Sections 5.4.2 and 5.4.3, is concerned with the channel electron multiplier. A description of the operation and use of a CEM has already been given in Section 2.3.3 and the discussion here aims to extend that description to cover the use of a CEM in rocket-borne instrumentation.

5.4.1 THE SPECTROMETER

A diagram of the instrument is given in Figure 5.10. Incident radiation passes through the collimator and two grids on to the cone shaped photocathode. Those photoelectrons emitted into a certain range of angles enter the first aperture and pass into the dispersive analyser. This is a cylindrical mirror analyser with axial focussing. An analysis of this form of analyser has been given by Zashkvara *et al* (1966) and the instrument parameters are shown in Figure 5.11.

The analyser consists of two concentric cylinders. The inner one is at earth potential, the outer has a varying negative voltage applied to it, with the resulting field between the two cylinders being used to energy analyse the electrons. The electrons enter and leave the

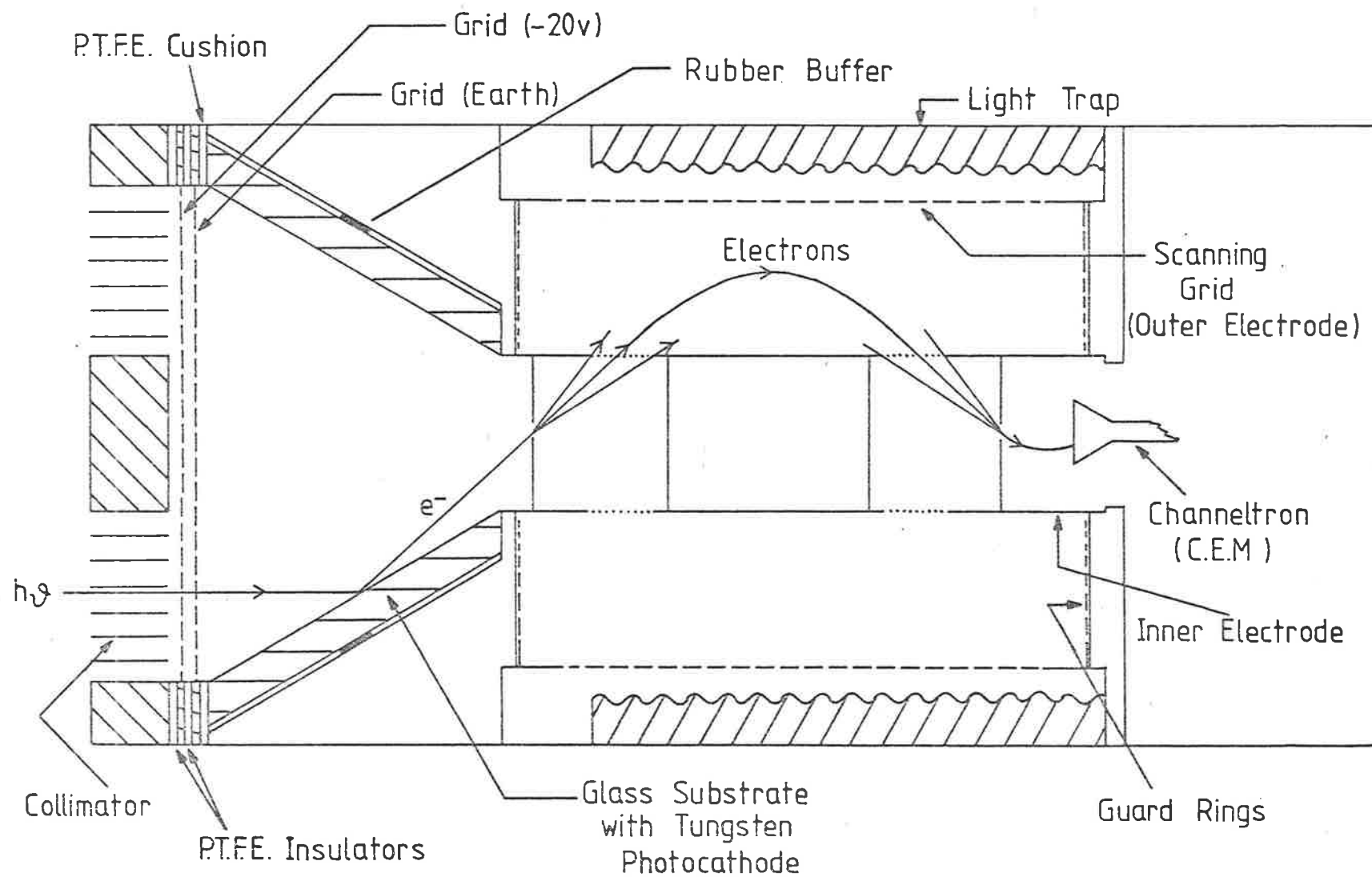
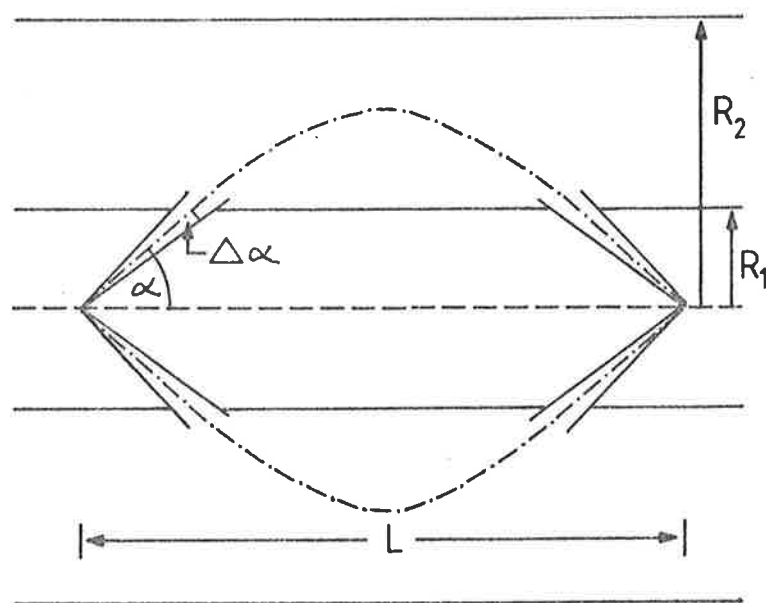


FIG 5.10 Diagram of the EUV Spectrophotometer.



Design Parameters for Cylindrical Mirror with Axial Focussing (Zashkvara *et al*, 1966)

$$\alpha = 42^{\circ} 20'$$

$$L = 6.12 R_1$$

$$V = .763E \ln (R_2/R_1), \text{ where } E \text{ is the electron energy.}$$

Instrument parameters.

$$R_1 = 1.3 \text{ cms}$$

$$R_2 = 3.8 \text{ cms}$$

$$\Delta\alpha = 10^{\circ}$$

$$L = 7.8 \text{ cms}$$

FIG 5.11 Details of the design of the cylindrical mirror analyser with axial focussing.

region through slots cut in the inner cylinder. The slots are bevelled in the appropriate direction to minimise scattering off the edges. For a particular energy electron, it will pass through both slots and out through the second aperture when the voltage on the outer cylinder is (Steckelmacher, 1973),

$$V = .763 E \ln (R_2/R_1)$$

where V is the applied voltage, E the electron energy and R_1 , R_2 the radii of the inner and outer cylinders respectively.

The slots are covered with a fine mesh to maintain a uniform field without excessively affecting the electron throughput. The mesh is wrapped around the entire length of the cylinder. This was done partly for ease of construction but also to provide a slightly roughened surface to inhibit the scattering of electrons that fell short of the second slot. An alternative electrode was tried that had a hollow central region (Figure 5.12) and a rod at a positive potential to remove these electrons. However, it was found to offer little advantage, and the simpler more rugged design shown in Figure 5.10 was used.

The outer electrode is a mesh grid and beyond it is a deeply grooved aluminium cylinder to act as a light trap. This combination was to prevent any scattered light that may have entered the analyser from producing spurious photoelectrons in the region between the cylinders.

A collimator constructed from aluminium honeycomb is situated at the front of the instrument. The angular response is shown in Figure 5.13. This was measured by rotating the collimator about a collimated beam of 121.6 nm radiation and using a lithium fluoride/

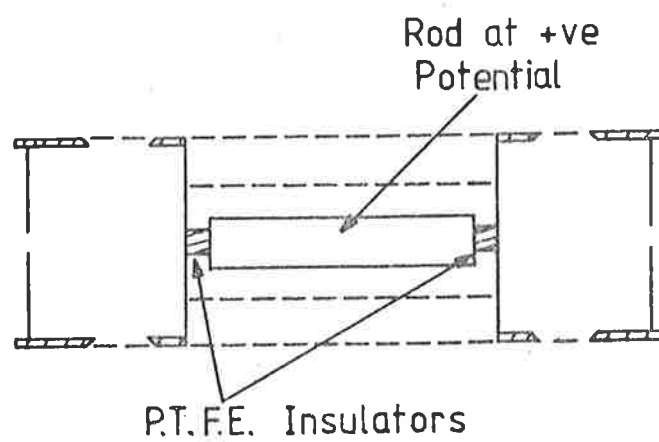


FIG. 5.12 Alternative design for central electrode.

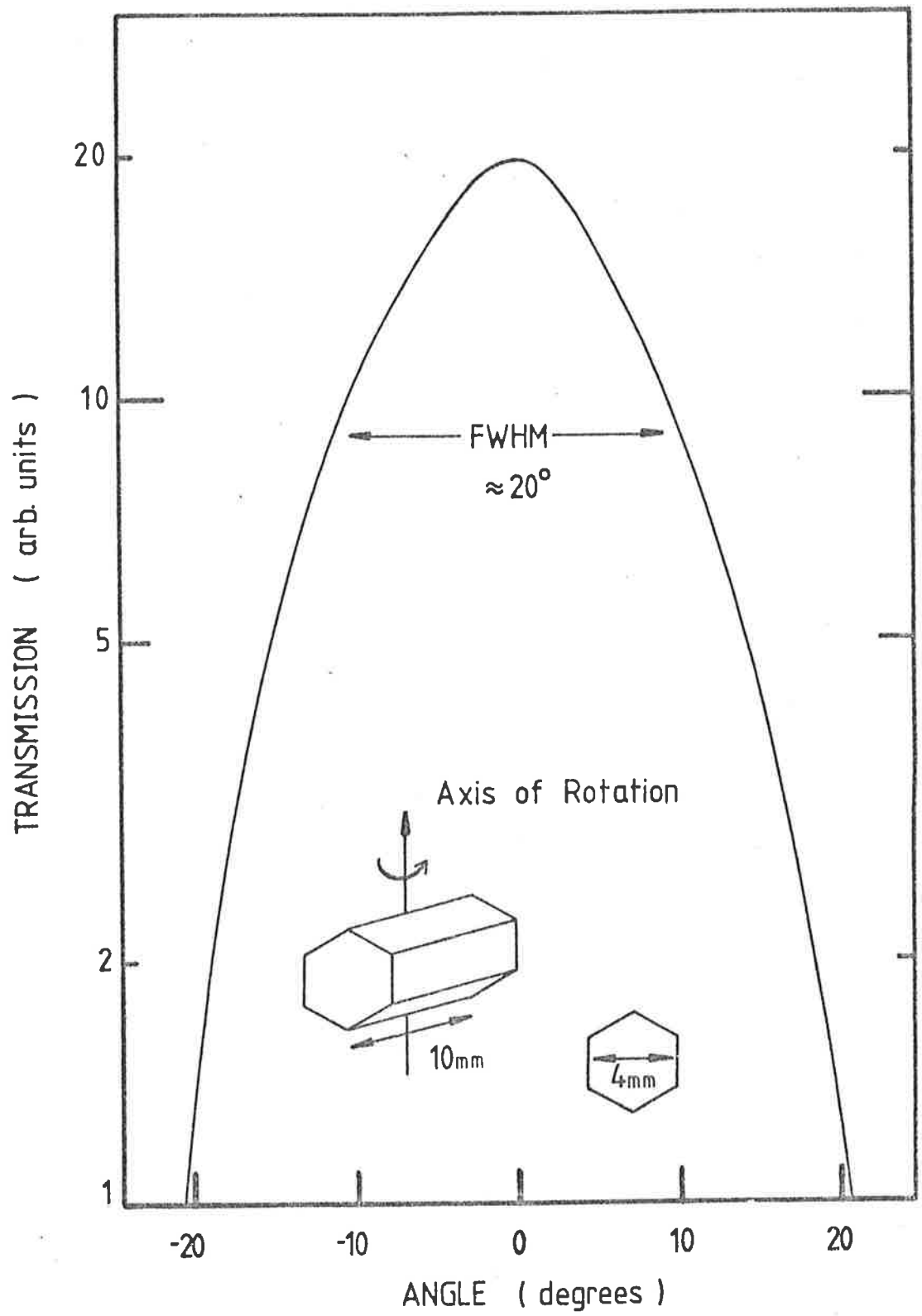


FIG. 5.13 Angular response of the collimator.

nitric oxide ion chamber (Carver and Mitchell, 1964) as a detector.

There are two grids between the collimator and the cone photocathode. The one nearest the collimator is at a negative potential to prevent atmospheric photoelectrons from entering the analyser. An example of their energy profile is shown in Figure 5.14 (Bibbo, 1979) and it is evident that the majority of the electrons are of low energy. Consequently, a potential of -45 volts was chosen for the grid. This voltage is isolated from the photocathode by the second grid which is at earth potential.

To reduce end effects in the field between the two electrodes guard rings were added. These can be seen in Figure 5.10. They are in the form of a set of concentric annuli which were designed so that the voltage difference between any two adjacent rings was constant. The voltages on the rings were provided by partitioning the voltage difference between the inner and outer electrodes. This was achieved with a voltage divider constructed from matched one megohm resistors.

In summary, there are a number of advantages in using the cylindrical analyser. It is relatively simple to construct and has a ruggedness well suited to rocket work. Also, the cylindrical symmetry permits a reasonable photocathode area, although the small angular acceptance of the analyser is a limiting factor.

5.4.2 THE PHOTOCATHODE

A photocathode was required which had both high yield and good reproducibility. Metzger (1965) has shown that the alkali halides have a high yield in the EUV but most are deliquescent and require care in handling (Bowyer *et al*, 1970). Cairns and Samson (1966) have measured

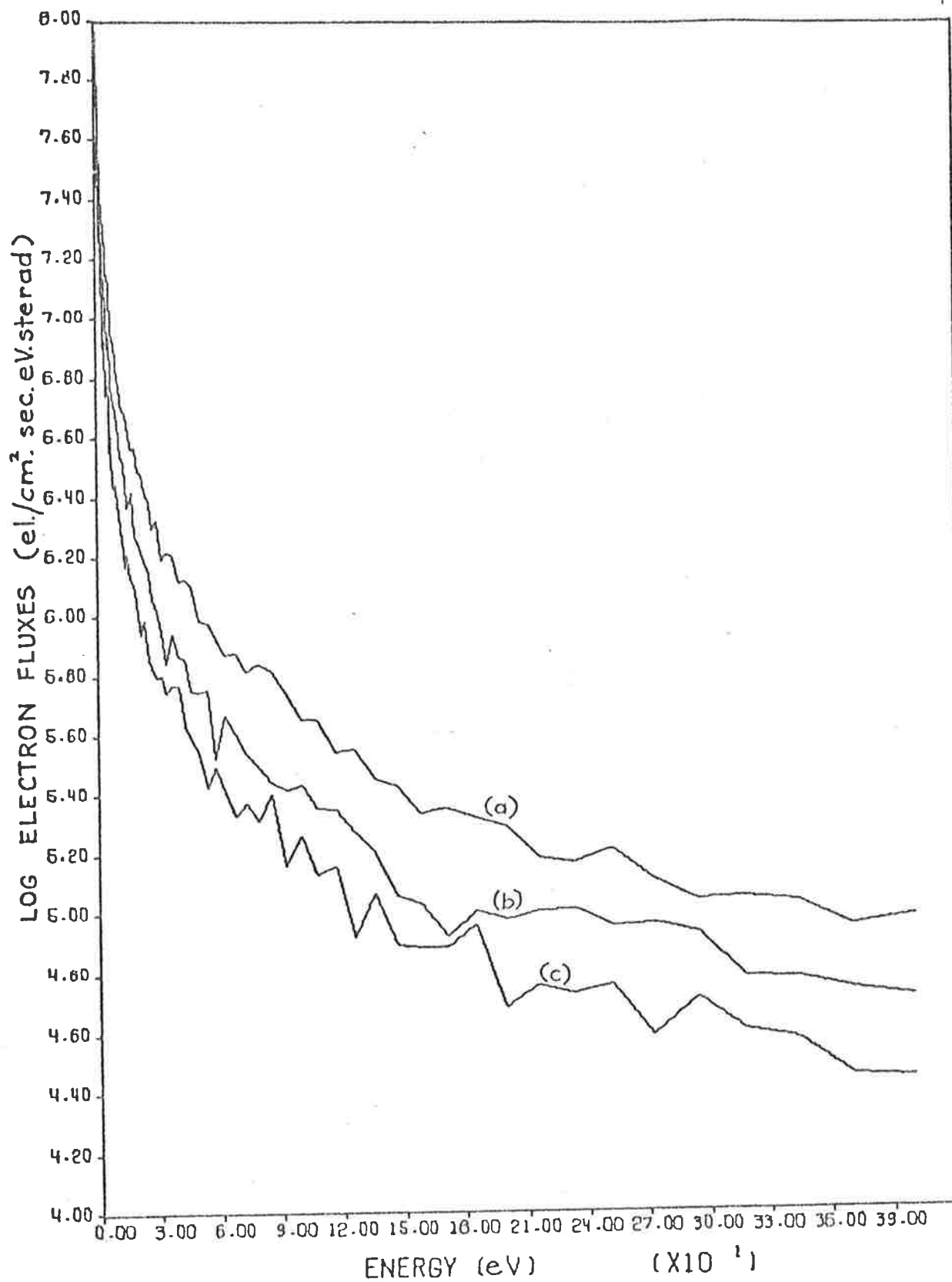


FIG. 5.14 Photoelectron energy spectra at an altitude of: (a) 178 km (b) 142 km (c) 110 km. (From Bibbo, 1979.)

the yields of a number of metals and while these are not as high as the alkali halides, they show good reproducibility of yield and are to a certain extent tolerant of different surface conditions. This is important in an instrument that will suffer a number of changes of environment before it is flown.

Although a number of metals have similar yields in the EUV, gold and tungsten were chosen because they have had wide use as photocathodes and their properties are described extensively in the literature.

The conical shape of the photocathode presented several problems. Neither gold nor tungsten lent itself to shaping into a solid photocathode and it was decided to deposit the metal on to a glass cone. The cone was formed by cutting a section from a pyrex funnel which had a half angle of 30 degrees, providing a source of photoelectrons closely matching that for which the analyser was designed. The cone and the field of view of the analyser are illustrated in Figure 5.15. The field of view extended slightly beyond the cone but this was effectively masked by the grids and the collimator. The metal was sputtered on to a thickness of 100 nm which is large compared with the 10 nm or so escape depth of photoelectrons formed by EUV radiation.

It was not felt necessary to apply any special handling techniques to the photocathode. In fact, the absorbed gases and oxides formed are partly responsible for the high photo-electric yield which is typically 15% (Walker *et al*, 1955). Wheaton (1964) has shown that the photoelectric yield can be affected by contamination from the vacuum system, but if then cleaned, subsequent exposure to the atmosphere had

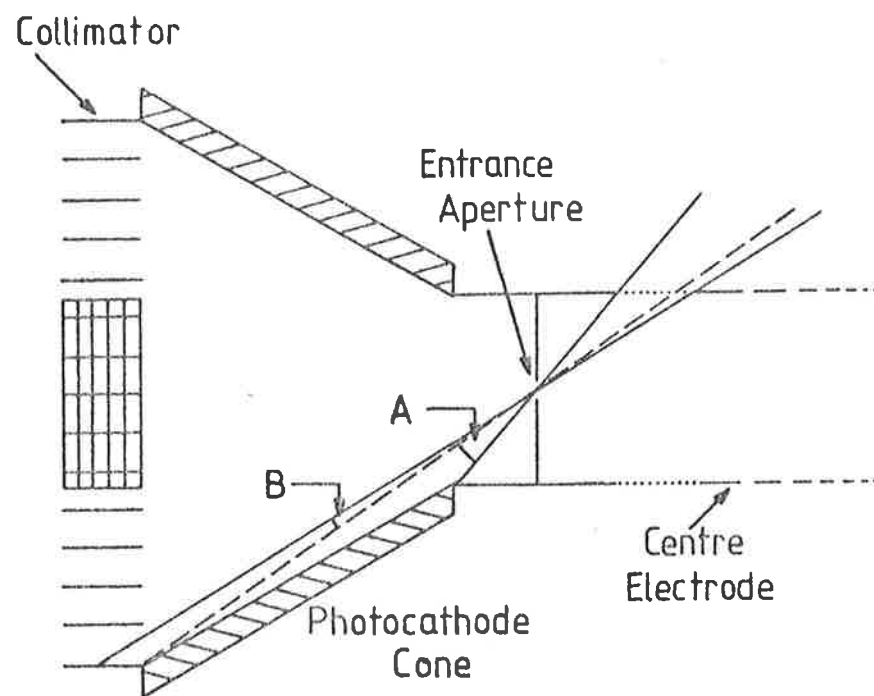


FIG 5.15 Diagram illustrating field of view of the analyser which is angle $(A+B)$. Angle (A) is the entrance angle for electrons from the photocathode. Angle (B) is the excess field of view of the analyser.

little effect. For this reason, the only maintenance applied to the photocathodes was a gentle cleaning with methyl alcohol.

Both gold and tungsten photocathodes were constructed, but no appreciable difference was found between them. Eventually tungsten was chosen as it seemed to survive the rigors of the laboratory environment somewhat better than the softer gold.

The cone was mounted in a PVC block. Three rubber buffers fitted into the side of the block to allow for slight differences in the sizes of different glass cones. The narrow end of the cone rests on a stop at the end of the PVC block. The wide end is clamped in place with a metal annulus with a cushion of PTFE between them. The annulus also forms part of the earth grid and three phosphor bronze springs extend from it on to the cone to earth it. This arrangement seemed to securely clamp the cone and it survived vibration, handling and travelling without shifting.

The photoelectric yield of tungsten between 30 nm and 130 nm is shown in Figure 5.16. The yield is defined as the number of photoelectrons emitted per incident photon. From this, the approximate yields are .15 at 58.4 nm, .08 at 30.4 nm and .02 at 121.6 nm. However, these yields were measured at normal incidence while for the spectrometer, radiation strikes the surface of the cone at 60 degrees to the normal. The effect of this angle on the yield is as follows. If we define the photoelectric yield as the number of photoelectrons emitted per absorbed photon, rather than incident photon as before, then this yield monotonically increases for increasing angle (Heroux *et al*, 1965) as illustrated in Figure 5.17. However, at the same time the reflectivity is increasing as shown in Figure 5.18, and correspondingly

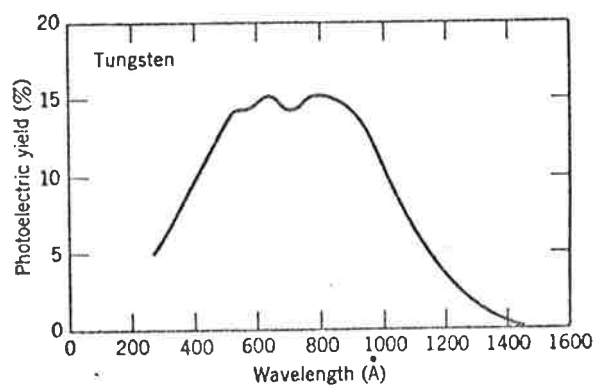


FIG. 5.16 Photoelectric yield of tungsten for normal incident radiation (from Samson, 1967).

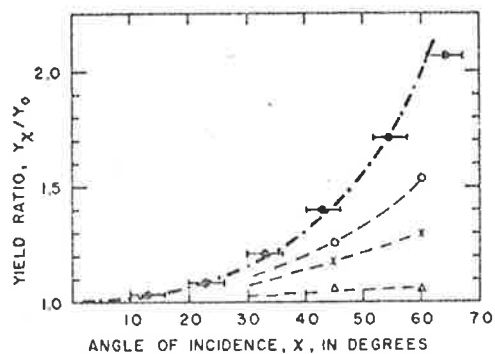


FIG. 5.17 The ratio of the photoelectric yield at an angle χ to the yield at normal incidence, as a function of the angle χ : Δ , 121.6 nm; $\times$, 104.8 nm; $\circ$, 58.4 nm; $\bullet$, 30.4 nm. (from Heroux *et al* 1965).

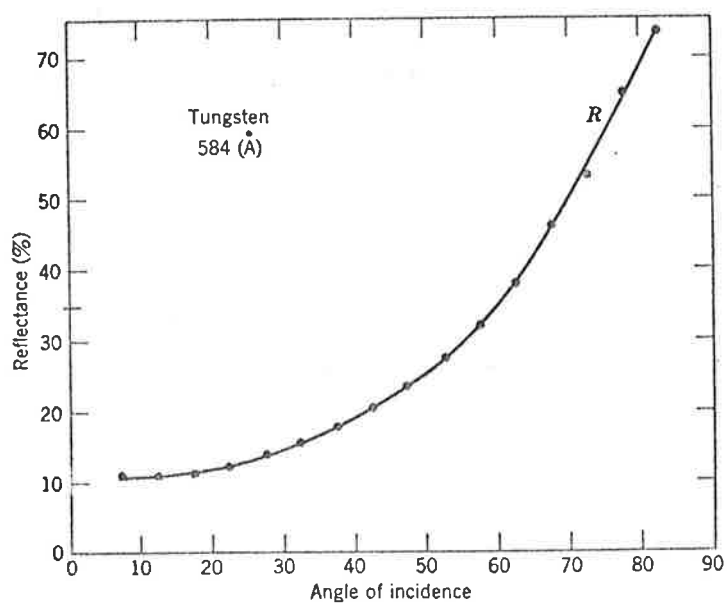


FIG. 5.18 Reflectance of tungsten as a function of the angle of incidence for 58.4 nm radiation (from Samson, 1967).

the amount of radiation absorbed is decreasing. The two effects of increasing yield and increasing reflectivity offset one another so that at the 60° angle of incidence of radiation on the photocathode, the yield in electrons per incident photon is essentially the same as for normal incidence. However, the reflectivity at 60° is such that only 65% of the radiation is absorbed. Nevertheless, an important property of the cone is that for part of its area, it is possible to have multiple reflections. Referring to Figure 5.19, ray B is reflected off the lower face on to the upper face which it strikes at 90 degrees. From there it is reflected back the way it came. All rays between A and C undergo this triple reflection which increases the amount of absorbed radiation to about 95%. This discussion refers to rays that are parallel to the axis of the cone, but it is obvious that rays from other directions will produce multiple reflections as well.

5.4.3 ELECTRON DETECTOR

The electron detector used was a channel electron multiplier. This has already been described in Section 2. Its suitability for rocket payloads arises from its small size, simplicity of use and ease of rugged mounting.

There are a number of considerations to be met in the use of a CEM in space research which do not normally arise in the laboratory situation. Firstly, there is time dependent gain degradation. This can be caused by prolonged exposure to ultra high vacuum (Bennett and Thorpe, 1970; Prince and Cross, 1971) or a large accumulated count. Frank *et al* (1969) note gain degradation after an accumulated 10^{10} counts. However, for the short duration of a rocket flight, gain degradation need not be considered (Sharber *et al*, 1968) but it is important in satellites.

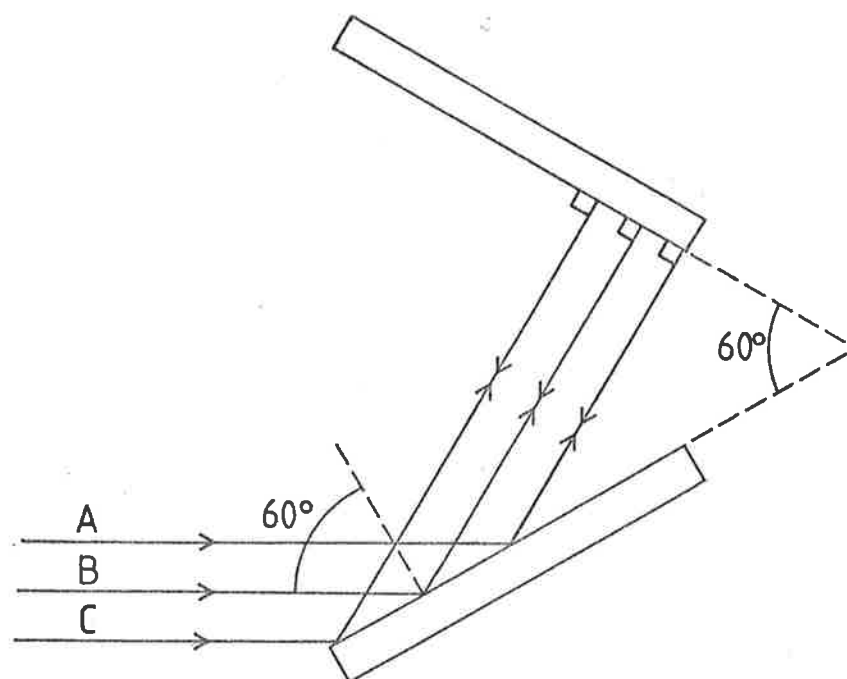


FIG 5.19 Diagram showing the occurrence of multiple reflections for radiation incident on the cone photocathode.

Photograph of the interior of the EUV Spectrophotometer. Clearly visible are the cone shaped photocathode, the PVC support block, the inner and outer cylindrical electrodes of the analyser and one set of guard rings.



A second problem, more applicable to sounding rockets is the rate of outgassing of the CEM. The maximum ambient pressure with the high voltage applied is stated by the manufacturers to be 5×10^{-4} torr. Although this is reached at an altitude of 100 km, this may not be the case in the region around the CEM. Outgassing material or even residual gas inside the CEM spiral could cause the local pressure to be higher than this. The solution is to pump the payload prior to launch (Rimothy, 1973) and seal it with a vacuum tight door. Once the door is ejected at the proper altitude a short delay is allowed to elapse before the high voltage is turned on.

Adequate mounting for the CEM is very important when it is used in a rocket environment. Although being made of glass means it is somewhat delicate, nevertheless, if it is supported adequately, its low mass ensures it will suffer little damage under acceleration and vibration. In addition, care must be given to the high voltage end to isolate it sufficiently from any possible source of charge leakage.

To this end, the CEM was mounted in a hollowed block of PTFE. Silastic 732 RTV adhesive was used to fasten both the CEM and the electronic components into their respective compartments. Epoxy resin was applied to points where wires connected to the CEM. After construction, all components were washed in methyl alcohol to ensure cleanliness and reduce the chance of surface current leakage. CEM's mounted in this way performed satisfactorily in the laboratory and were undamaged after pre-flight vibration testing.

5.5 INSTRUMENT TESTING AND CALIBRATION

The following sections contain a discussion of the techniques used to test and calibrate the instrument. The instrument was tested in

two parts. Firstly, the electron energy analyser was tested on its own by measuring the photoelectrons produced from argon by 58.4 nm radiation. Then the photocathode was fitted and the combination tested and calibrated. This procedure is described in Section 5.5.3.

This is preceded though by a description of the EUV source used and the method used to calibrate the light monitor. These are described in sections 5.5.1 and 5.5.2 respectively.

5.5.1 EUV LIGHT SOURCE

The light source used was a water cooled capillary discharge lamp. A capillary of about 5 mm bore and 80 mm long was fitted between two electrodes, one of which is also the flange that attaches the lamp to the rest of the equipment. The other electrode is connected to the high voltage (see Figure 5.20).

Due to the large amount of heat produced, the capillary is constructed of pyrex with an integral water jacket. The high voltage electrode is air cooled whilst the other electrode (the flange) which is at earth potential, is water cooled.

An A.C. voltage at a frequency of 50 Hz is supplied from a 15 KV transformer through a series resistance. The voltage was adjusted with a variable transformer attached to the primary of the EHT transformer. A maximum current of 40 ma was available.

The lamp was used with a half-metre Seya-Namioka monochromator. Helium was generally used in the lamp, producing 58.4 nm radiation. To obtain other wavelengths, neon was also used. It has two resonance lines at 73.6 nm and 74.4 nm.

Since the spectrometer was to be used in the detection of both 58.4 nm and 30.4 nm airglow, it would have been useful to also

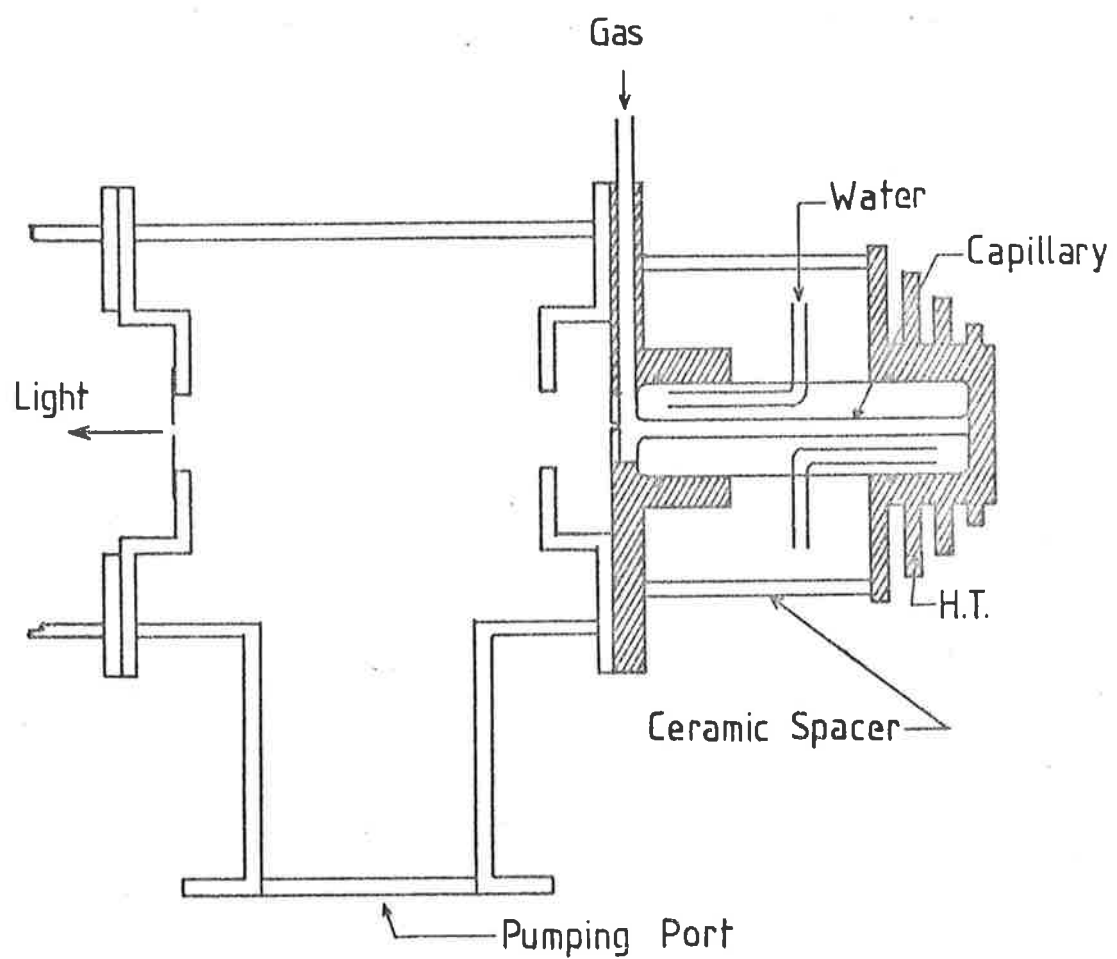


FIG. 5.20 Capillary discharge lamp with a single stage of differential pumping.

have a source capable of producing 30.4 nm. Although such a source has been described in Section 2.4, the work on the spectrometer precedes the angular distribution work by a few years and the source was not available at that time. Repeated attempts were made to coax 30.4 nm radiation from the capillary discharge but without success.

5.5.2 LIGHT SOURCE CALIBRATION

To calibrate the spectrometer, it is first necessary to calibrate the light source which implies calibration of a secondary standard to be used as a radiation detector.

A common monitoring technique is to use a phosphor that absorbs the extreme ultraviolet and re-radiates the energy in the visible spectrum to be monitored by a photomultiplier. A widely used phosphor is sodium salicylate. It fluoresces under radiation from 350 nm to 11.6 nm (Samson and Haddad, 1974; Watanabe and Inn, 1953; Samson, 1964; Knapp and Smith, 1964) and emits a spectrum centred about 443 nm (Allison *et al*, 1964) which is well matched to the sensitivity of S-type photomultiplier cathodes. It has a relatively constant yield from 11.6 nm to 125 nm (Samson, 1964; Samson and Haddad, 1974). From 125 nm onwards, the yield increases up to a wavelength of 150 nm where it is then constant to 160 nm.

The sodium salicylate was deposited on to a fine mesh by dissolving the salicylate in methyl alcohol and using an atomiser to produce a fine mist that was drifted on to the mesh with a stream of warm air. The mesh was positioned so that it intersected the light beam from the monochromator and the fluorescence from the sodium salicylate passed along a perspex light pipe to be detected by a photo-

multiplier. This can be seen in the left of Figure 2.21.

Absolute calibration of the monitor can be done by having the radiation photoionize an inert gas (Samson, 1964). For these it is possible to assume 100% yield and by measuring the photoelectron or ion current when the beam is completely absorbed, the beam intensity in photons per second can be computed. If this technique had been used, the salicylate could have been directly calibrated at 58.4 nm. However, the method could not be used as the differential pumping which is necessary between the absorption chamber and the monochromator was not available. Instead, the salicylate was calibrated at 121.6 nm using the photoionization of nitric oxide. At this wavelength it is possible to use a lithium fluoride window to isolate the chamber from the monochromator since the short wavelength cut-off of lithium fluoride is 105 nm. The experimental arrangement is shown in Figure 5.21. Radiation from the monochromator passes through the lithium fluoride window and through the chamber between two parallel plates. At the end of the chamber, it strikes a sodium salicylate coated glass plate whose fluorescence is detected by a photomultiplier.

With the chamber initially evacuated, nitric oxide is gradually admitted. The nitric oxide is ionized and the ion current collected and monitored on one of the plates. The reason for monitoring the ions rather than the photoelectrons is to avoid errors due to photoelectrons produced from the beam striking parts of the chamber.

As the gas is admitted, the ion current and the back photomultiplier are monitored. By graphically plotting these two quantities (Figure 5.22) it is possible to estimate the point at which total absorption has just taken place. This point is the knee in the curve shown in Figure 5.22. If we assume at this point that the total current

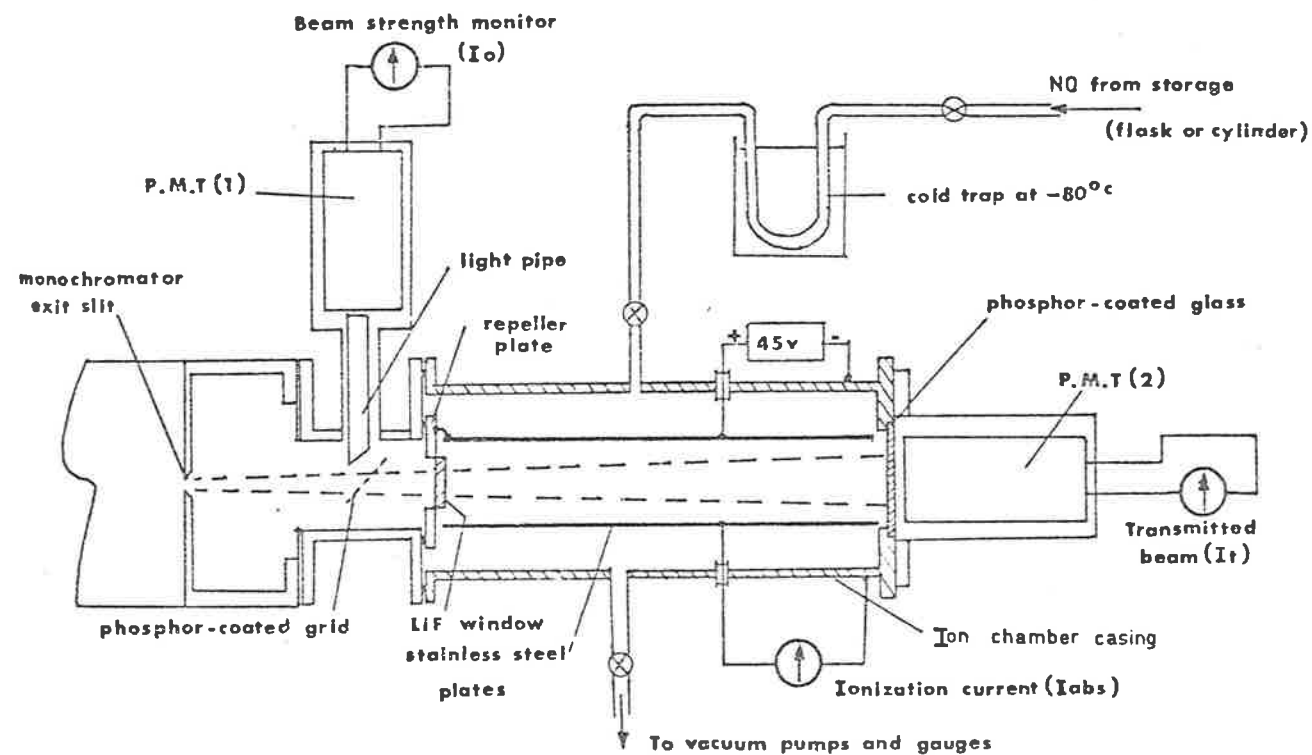


FIG. 2.21 Calibration of the beam monitor (photomultiplier No.1) using a standard ion chamber (taken from O'Connor, 1973).

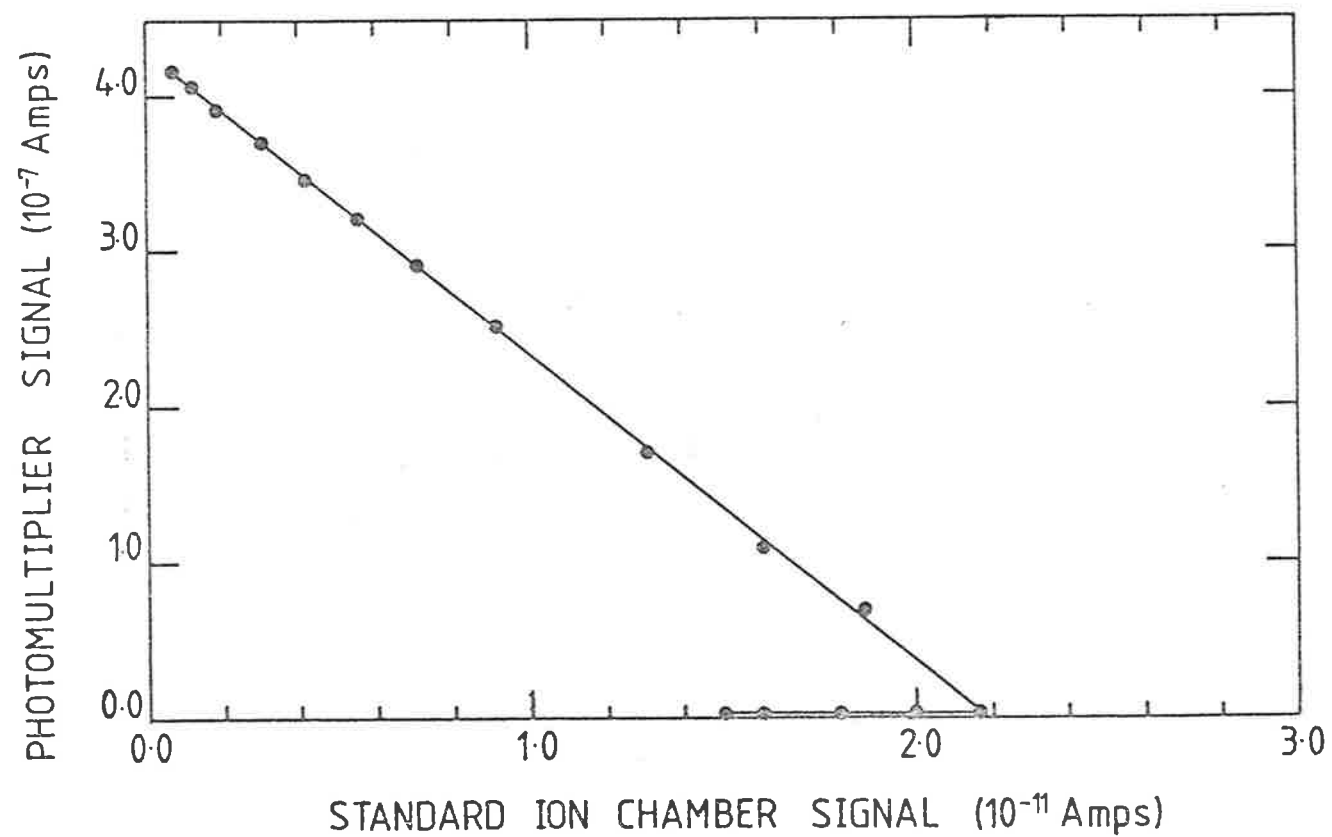


FIG. 5.22 A graph of the standard ion chamber current versus the rear photomultiplier signal as the pressure of nitric oxide is increased. The knee in the curve is the point of total absorption.

is being collected, then this can be related to the flux by taking the ionization efficiency of nitric oxide to be 81% (Watanabe *et al*, 1967). The final measurement necessary was of the transmission of the lithium fluoride window at H-Lyman-alpha. This was done by measuring the intensity with and without the window using a lithium fluoride/nitric oxide ion chamber (Carver and Mitchell, 1964).

For a fresh sample of sodium salicylate, the quantum efficiency is the same at 121.6 nm as at 58.4 nm (Samson, 1964) and the calibration is complete. However, caution must be exercised in this extrapolation. For an aged sample, the efficiency decreases at shorter wavelengths (Samson, 1964; Knapp *et al*, 1964). Samson (1964) has shown that for a several days old sample, the quantum yield is relatively constant between 40 nm and 90 nm, but at 121.6 nm it is some 12% higher. Thus for the calibration, as fresh a sample as possible was used, but some uncertainty in extrapolating the calibration from 121.6 nm to 58.4 nm is unavoidable.

5.5.3 INSTRUMENT EVALUATION

The first stage of instrument evaluation involved testing the electron analyser as a separate unit. To do this it was necessary to construct a special end cap in place of the PVC cone holder. This can be seen in Figure 5.23. The end cap was constructed of perspex and had its inner edges bevelled so as not to interfere with the field of view of the analyser. It was also coated with colloidal graphite to minimise electron scattering and provide an equipotential earth surface.

The electron source used was photoelectrons from argon produced by 58.4 nm radiation. The experimental arrangement is shown

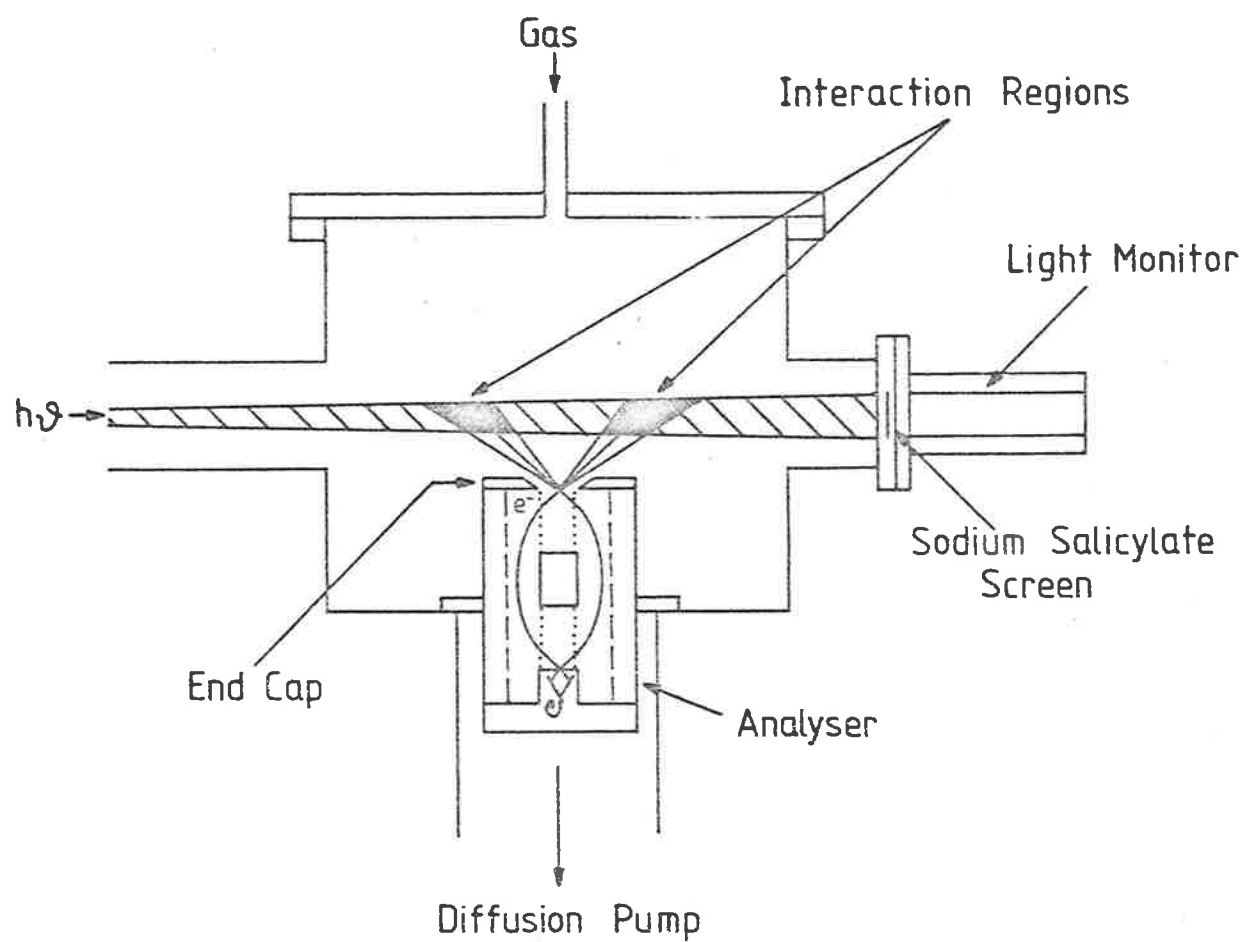


FIG 5.23 The use of photoelectrons from the photoionization of argon by 58.4 nm radiation to test the cylindrical mirror analyser.

in Figure 5.23. The radiation passed through the vacuum chamber and was monitored by a sodium salicylate screen and a photomultiplier.

Argon was leaked into the chamber up to a pressure of 6×10^{-4} torr. The photoelectron spectrum obtained is shown in Figure 5.24. As can be seen, the individual peaks of the doublet are only just visible and the FWHM resolution was calculated to be about 7%.

Having established the correct operation of the electron analyser, the photocathode was fitted and testing of the complete instrument started. Figure 5.25 shows the experimental set-up adopted with the light beam from the monochromator monitored by a sodium salicylate covered mesh and photomultiplier. This monitor had been calibrated as described in Section 5.5.2.

The instrument was positioned in the vacuum chamber so that the whole of the beam fell on the photocathode. A negative voltage ramp was applied to the scanning grid and the accumulated counts at each voltage step fed into a multichannel store.

The spectrum obtained from 58.4 nm radiation is shown in Figure 5.26(a). It is apparent that the spectrum has considerable structure unlike the simple step function assumed in the discussion in Section 5.3.1. This feature makes the interpretation of the data more difficult. However, just before the high voltage slope, there is a section about one volt wide where the electron count does not vary rapidly. This section was considered to be a straight line for the purposes of the calibration and it is this plus the slope and the background level that are the three important features of the spectrum.

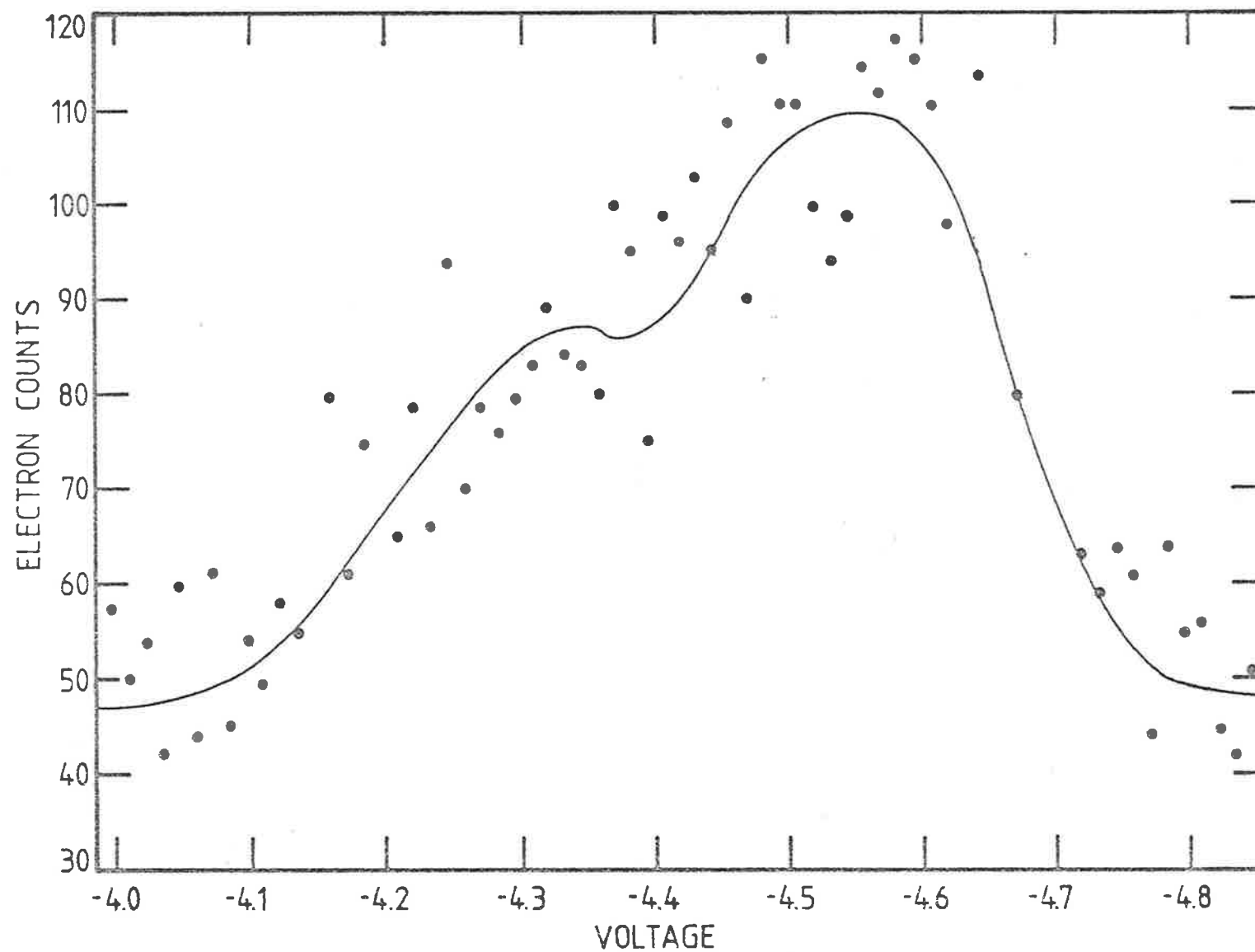


FIG 5.24 Photoelectron spectrum of argon from 58.4 nm radiation, obtained with the cylindrical mirror analyser.

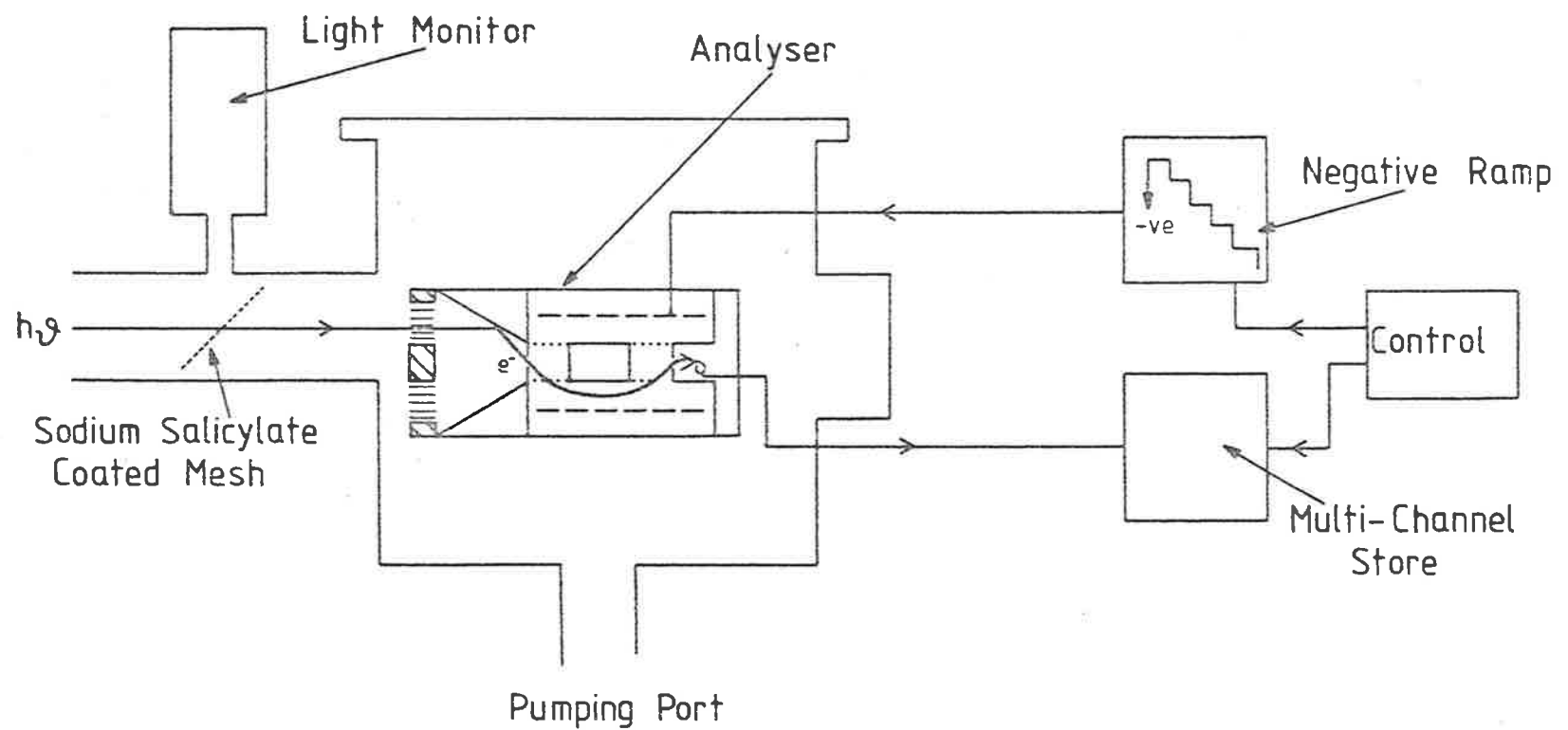


FIG 5.25 Set up for testing and calibration of the EUV Spectrophotometer.

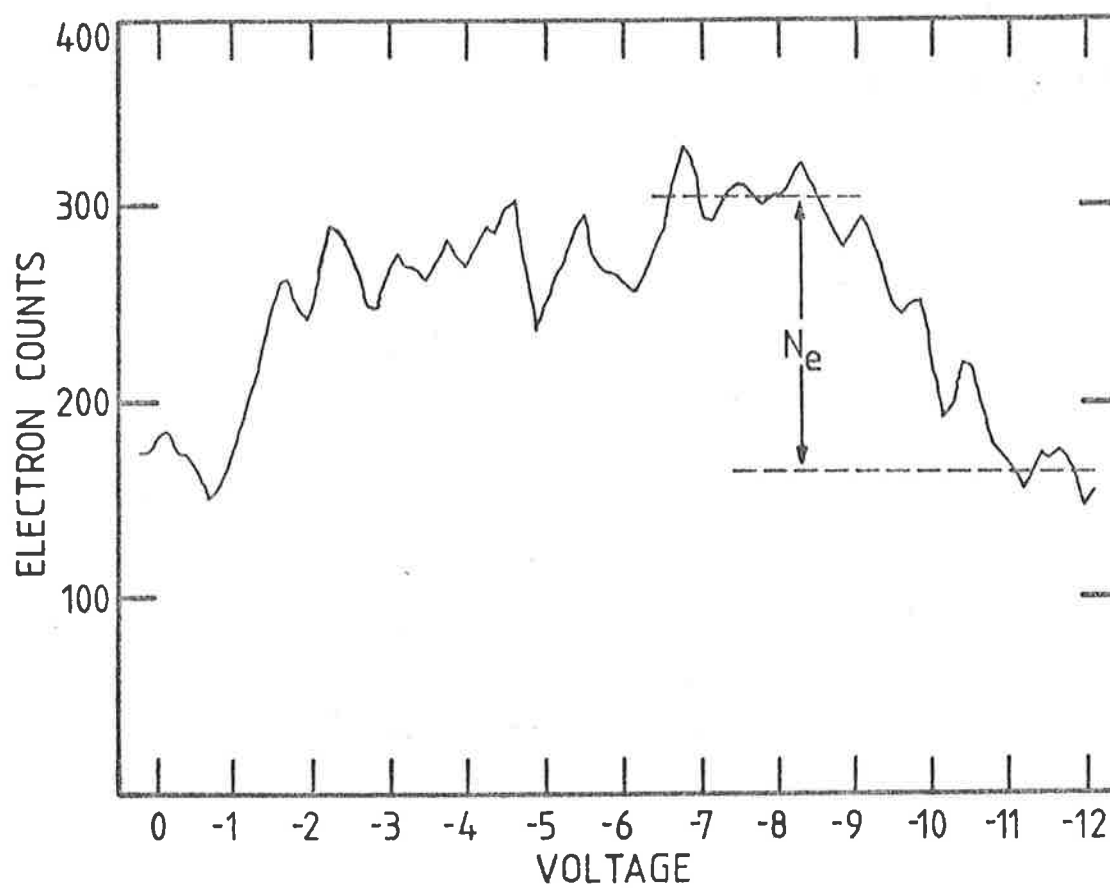


FIG. 5.26(a) Spectrum obtained with 58.4 nm radiation. N_e is taken to be the step height.

Similar features can also be seen in Figure 5.26(b) which shows the spectrum obtained with 73.6 nm radiation.

From the height in the step of the 58.4 nm spectrum, the number of electron counts per second corresponding to the 58.4 nm intensity as measured on the photomultiplier was known. Since the salicylate/photomultiplier combination had already been calibrated, the yield of the instrument in counts per photon could be calculated. This was found to be 10^{-8} counts per photon.

It is now necessary to convert this to counts per rayleigh. By definition, the rayleigh is given by

$$1 \text{ R} = \frac{10^6}{4\pi} \text{ photons/cm}^2/\text{sec/steradian}.$$

This definition refers to an extended source. The cm^2 term refers to the area of the source viewed by the detector and the steradian refers to the solid angle subtended by the detector at the source. If this area and solid angle are designated A and Ω as shown in Figure 5.27, then each rayleigh corresponds to $10^6 A\Omega/4\pi$ photons per second entering the detector. However, it is more convenient to consider the signal in terms of the area of the detector (A') and the solid angle (Ω') for the field of view of the detector. It is simple to show that,

$$A\Omega = A' \Omega'$$

and therefore, if we define E as the efficiency in counts per photon for the detector, the sensitivity of the detector is given by,

$$\text{Sensitivity} = E A' \Omega' \times 10^6/4\pi \text{ counts per rayleigh}.$$

In the present instrument,

$$A' = 42 \text{ sq cms}$$

$$\Omega' = 2\pi(1 - \cos(10^\circ)) = .1^c$$

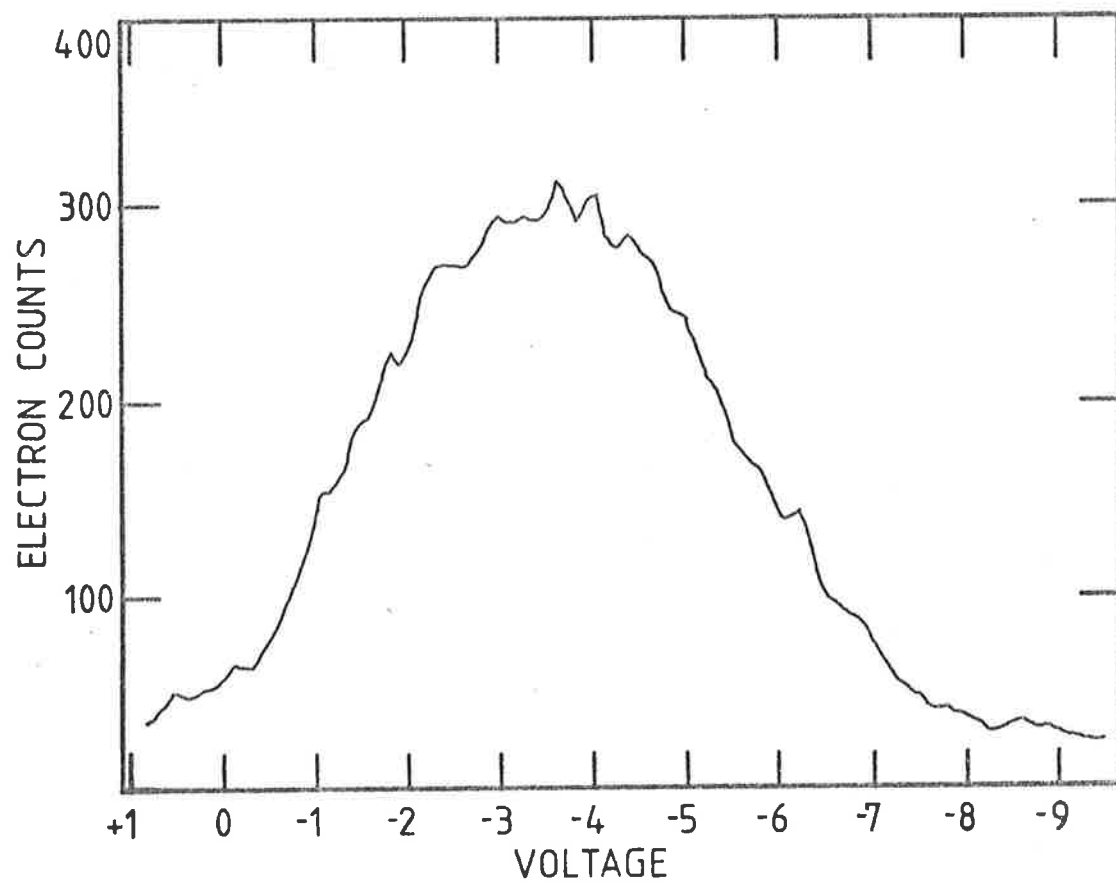


FIG. 5.26(b) Spectrum obtained with 73.6 nm radiation.

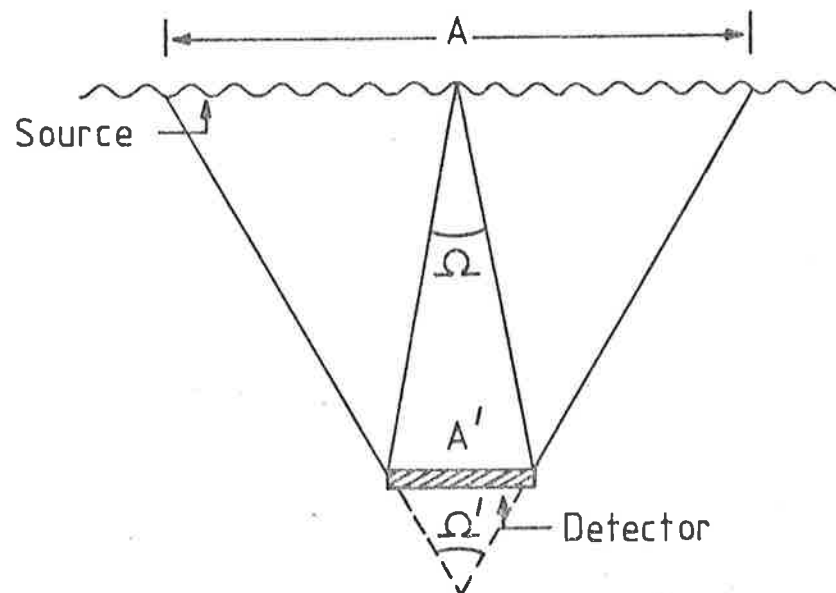


FIG. 5.27 Illustration of Notation used in the definition of a rayleigh.

and therefore the sensitivity is .003 counts/R.

The estimation of the sensitivity can at most be considered only an estimate. It is based on only a very small part of the photocathode being illuminated and since the sensitivity would be expected to vary across the photocathode, a more accurate calibration would require an extended beam. Also no measurement was made of the sensitivity for off-axis illumination. It was assumed above that it would simply follow the transmission curve of the collimator (Figure 5.13). However, this may not be the case since for off-axis radiation there can be complicated multiple reflections.

There was one unexpected result that was encountered with the instrument. This was associated with the grids between the photocathode and the collimator. The grid closest to the collimator was designed to have a negative potential of -45 volts to repel any atmospheric electrons and it was found that the potential applied to the grid affected the spectrum obtained. This was despite an earthed grid between the retarding grid and the photocathode. However, field leakage through this earthed grid is not surprising as the grid wires had a 2 mm spacing.

Figure 5.28 shows two spectra obtained with 58.4 nm radiation. One spectrum is with the -45 volts bias applied, the other without. As can be seen, the bias significantly enhances the yield. Figure 5.29 shows the count rate at one point in the spectrum as a function of the grid voltage. The count increases until a voltage of about 15 volts and then levels off.

These extra electrons are obviously not from the collimator as they could not penetrate past the negative grid. Nor was such a large

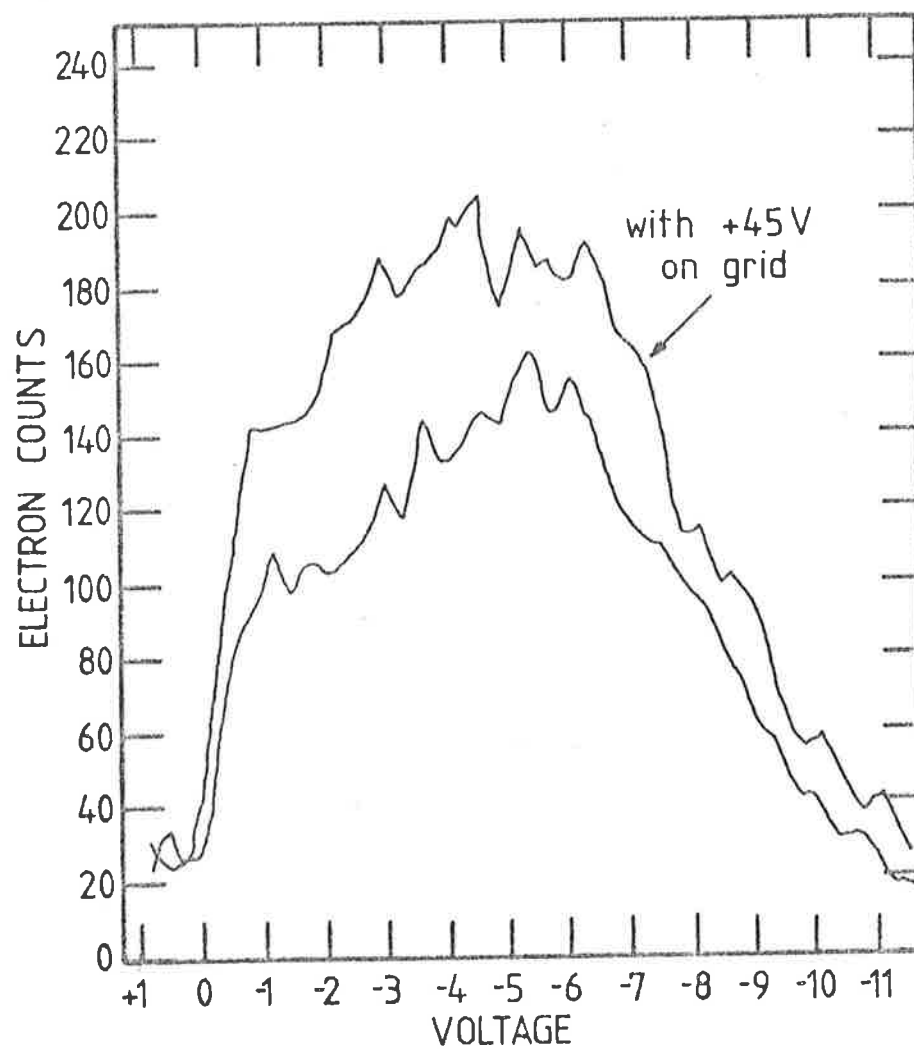


FIG 5.28 Spectrum obtained from 58.4 nm radiation. One spectrum is for +45V on the grid, the other for the grid earthed.

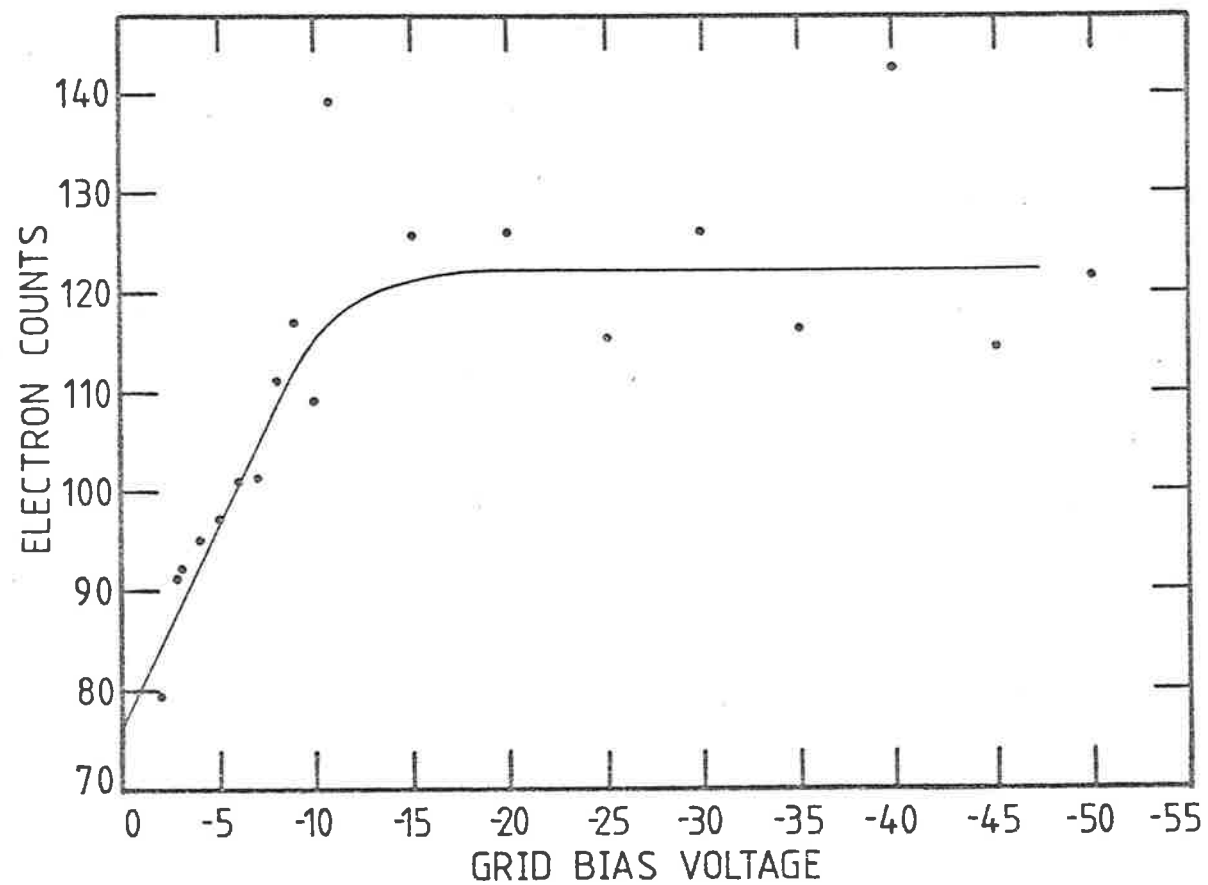


FIG. 5.29 Electron count at one point in the spectrum as a function of the bias voltage on the electron repeller grid.

increase thought likely to be due to any photoelectrons from the grids themselves since there is no line of sight path from the grids into the cylindrical analyser. The conclusion then was that they were photoelectrons from the tungsten photocathode.

One possible mechanism for this enhancement can be seen if it is recalled that in Section 5.4.2. it was mentioned that the glass cone used had a slightly larger apex angle than the analyser was designed for. This meant that the field of view of the analyser extended beyond the photocathode but this was effectively masked by the grid supports and the collimator edge. However, it is believed that the field of the negative grid which penetrates through the earth grid is sufficient to repel a turn electrons into this extra field of view. This was supported by the fact that the increase in sensitivity was strongest at the outer edge of the photocathode.

The effect was found to increase the sensitivity by about 20% to give about .004 counts/R. Obviously it was an effect that warranted further investigation since any method that can enhance the sensitivity is of interest. However, it was discovered very late in the instrument development and there was insufficient time to investigate it further.

5.6 CONCLUDING REMARKS

The spectrophotometer was flown as part of a flyalong payload on an NRL Superchief II rocket. It was launched from Wallops Island on Tuesday, 23rd July 1974 at 2308 hours local time. Due to the complete failure of the flight, no details will be given of the electronics or mechanical integration, since such details are peculiar to the particular rocket and not of general interest. It is sufficient to say that the intensity of 58.4 nm radiation was to be measured by counting the

number of electrons at the top and bottom of the high voltage step. For 30.4 nm radiation, the position of the step was calculated and a similar pair of voltages used.

It may seem strange that an attempt was made to measure nightglow. The measured sensitivity of .004 counts per rayleigh would imply a maximum count rate of .04 c/sec for 58.4 nm and .008 c/sec for 30.4 nm radiation. However, this was not realised at the time of flight. An error in the calculation had placed the sensitivity some two orders of magnitude higher than the above value. The reason this error was not realised can be seen by considering the following order of magnitude calculation: for a point at the centre of the photocathode, its field of view into the cylindrical analyser is about .0017 radians. If we assume then that the electrons are emitted isotropically, then approximately .03% of the electrons produced enter the analyser. If we assume the photoelectric yield to be .1 electrons per photon, and that about 70% of the radiation is absorbed, then this results in a yield of about 2×10^{-5} electrons per photon. However, this is for the total number of electrons emitted, while the analyser only accepts those electrons within a fixed energy bandwidth.

If we assume that the resolution is about 5%, and that the number of electrons emitted up to the cut-off is constant, then the yield is 10^{-6} electrons per photon. Comparing this to the measured yield of 10^{-8} electrons per photon, it is obvious that there is a discrepancy. The above calculation does not include the efficiency of the analyser, but it is unlikely to account for the difference.

Unfortunately, the discrepancy must remain unresolved. During the flight, the early failure of the EHT powering the CEM prevented any

data being collected and vehicle failure later in the flight resulted in complete loss of the payload.

It is possible to think of a large number of "errors" in both the order of magnitude calculation and the measured calibration and it is difficult to decide which is closer to the truth. If we examine the only comparable instrument, namely the analyser of Donahue and Kumer (1971) shown in Section 5.3.1, it has a sensitivity at 58.4 nm of 4 counts per rayleigh. It seems difficult to believe that the present instrument had a sensitivity three orders of magnitude smaller than this. This comparison then throws doubt on the measured sensitivity. One place where there is no doubt errors are involved is in the use of the standard ion chamber at 121.6 nm to calibrate the salicylate at 58.4 nm. However, this would probably only account for a factor of two error which could be in either direction.

A further possibility is a fault in the analyser. It might have occurred that electrons from the photocathode just did not enter the analyser. This may have been due to stray fields effectively reducing the size of the entrance hole. A possibility would have been to provide a positive potential to the entrance hole of the analyser. But this would have altered the energy distribution of the electrons.

However, since the instrument is not available for further testing a discussion of this type becomes pointless. All that can be concluded is that the measured sensitivity is too low and that the order of magnitude calculation provides an upper limit.

The project was begun in 1972, and abandoned in 1974 after the failure of the rocket flight. At the time it was started, there

were few measurements of the helium airglow and then considerable discrepancies between the measurements (Meier and Weller, 1972). However, since that time a large number of measurements have been made and in fact, the majority of the information given in Section 5.2 is based on that more recent data.

The majority of the measurements have used thin film filters. These filters have also been used in the very difficult area of EUV astronomy by using a large grazing incidence focussing collector to increase the sensitivity (Henry *et al*, 1975). Also, diffraction gratings are now being used to measure airglow. In general, lack of sensitivity prevents rotating the grating to scan the wavelength and instead, channel electron multipliers are fixed to monitor particular wavelengths (Broadfoot *et al*, 1977). Nevertheless, the sensitivity is still less than for metal filters.

Thus, the photocathode based instrument is now somewhat obsolete. It does not have the sensitivity of the metal filters nor the wavelength resolution of a diffraction grating.

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