CHAPTER II

PHOTOELECTRON SPECTROMETER

II.1 INTRODUCTION

The necessity of studying the high resolution photo-electron spectra of gases as a function of the incident energy has been pointed out in the first chapter. The essential requirements for such a kind of work are a line emission/continuum light source, a vacuum ultraviolet monochromator and a high resolution, high sensitivity electron spectrometer. The experimental set-up used in the present work included a line source, a monochromator, an electron spectrometer and the necessary data acquisition system. The electron spectrometer consisted of the ionizing region, the electron energy analyzer and the electron detector. The block diagram of the photo-electron spectrometer assembly has been shown in Fig II.1. The details of the various parts and the operation and performance of the system is presented in the following sections.
Fig II.1 BLOCK DIAGRAM OF THE PHOTOELECTRON SPECTROMETER ASSEMBLY

A. LIGHT SOURCE
B. DIFFERENTIAL PUMPING STAGE
C. ROOTS PUMP + ROTARY PUMP
D. MONOCHROMATOR
E. BEAM SPLITTER
F. PHOTOMULTIPLIER
G. PICO AMMETER

H. CHART RECORDER
I. ELECTRON SPECTROMETER
J. DIFFUSION + ROTARY PUMP SYSTEM
K. DIFFERENTIAL PUMPING LINE
L. DIFFUSION + ROTARY PUMP SYSTEM
M. DATA ACQUISITION SYSTEM
II.2 Electron Energy Analyzer

The electron energy analyzer is used to obtain the kinetic energy distribution of the photoejected electrons and is the most important part of the photoelectron spectrometer. In general, the energy distribution of charged particles is obtained by the proper use of an electric or a magnetic field. Usually, for low energy particles, the electric/field analyzer is preferred to the magnetic field type because of its simplicity and direct analysis of the energy, rather than the momentum. In photoelectron spectroscopy for studying the valence electrons, it is convenient to use the electric field analyzers since the energy of the electrons is in general less than 40 eV, and in most of the cases in the range of 0 to 10 eV.

The electric field analyzers are classified into two main groups - the retarding potential analyzers and the deflecting field analyzers. In the retarding potential type, all the electrons above a certain threshold are collected and counted as a function of the threshold voltage, and as a result one obtains an integral spectrum. In the deflecting field analyzers, particles of various energies are spatially separated and focused on to different points in space and the number of particles at a particular point is counted as a function of the deflecting voltage, thus getting the differential spectrum. The deflecting field analyzers, therefore, have an advantage over the retarding potential
analyzers in providing the differential energy spectrum directly.

The deflecting field analyzers used commonly are parallel plate, cylindrical, spherical, and cylindrical mirror analyzers. A comparative analysis of these are given by Hafner et al (1968) and Heddle (1971). The various deflecting field analyzers have also been reviewed by Afanasev and Yavor (1975). A discussion of these analyzers are also available from Wannenberg et al (1974) and Roy and Carrette (1977) where they have reviewed all the traditional types of electron energy analyzers and the criteria for their selection.

II.2.1 Choice of the Analyzer

Though there are various versions of electron energy analyzers available, the specific requirement of the experiment, and limitations of instrumentation precludes most of them from being used. The basic requirement of the analyzer in measuring the relative vibrational intensities is that the photoelectron spectra obtained should be independent of the angular distribution of the emitted photoelectrons. The angular distribution of the electrons in turn depends on the state of polarization of the ionizing radiation and the asymmetry parameter $\beta$ of the molecule. When a monochromator is used along with the light source, the resulting photon beam is partially polarized because of the reflection at the concave
The differential cross section for electric dipole transition with partially polarized light, leaving the residual ion in the $j = \frac{1}{2}$ state is

$$\frac{d\sigma}{d\Omega} = \frac{c^2}{4\pi} \left[ (1 - \frac{1}{2} \beta) + \frac{3}{5} \frac{\beta}{\epsilon} \left( \eta \cos^2 \alpha + \cos^2 \gamma \right) \right]$$

as given by Samson (1969 a, '70), where the degree of polarization is defined by $\eta = I_x/I_y$, $I_x$ is the irradiance of the radiant energy vibrating along the x-axis, and $I_y$ is the irradiance vibrating along the y-axis, $\beta$ is the asymmetry parameter of the molecule and $\alpha$ and $\gamma$ are the angles between the direction of electron emission and x and z axes respectively.

In the above expression, it is assumed that the photon beam is along the y-direction and that either the x or z axis is oriented along the direction of maximum polarization. It has been shown (Samson and Gardner, 1977 b) that for a cylindrical mirror analyzer with complete azimuthal symmetry, the intensity distribution of the photoelectron spectra is independent of the state of polarization of the ionizing radiation. It is also shown that (ibid), with such a geometry of the analyzer and with electrons analyzed at 54° 44' to the direction of the photon beam, the photoelectron spectrum is also independent of the asymmetry parameter $\beta$ of the molecule. This particular angle has conveniently been named as magic angle.

The only other analyzer which can give results independent of the angular distribution of electrons directly is the
spherical retarding potential analyzer covering all $4\pi$ solid angle.

Apart from giving an integral spectrum its usefulness is limited because of the difficulties in detecting and measuring the analyzed electron intensity. This drawback becomes more pronounced when the incident photon intensity reaching the ionization region drops substantially when a vacuum ultraviolet monochromator is used along with the light source. Thus for accurate measurement of vibrational intensities the choice is for the high resolution, high luminosity cylindrical mirror analyzer.

The focusing properties of the cylindrical mirror analyzer have been discussed in detail by Zashkvara et al (1966), Sar - El (1967) and Aksela et al (1970). It has been shown that a wide range of focusing conditions can be obtained by suitable choice of the angle $\theta$ and of the deflecting potential applied to the outer cylinder. Aksela (1971) has compared in detail the energy distribution of electrons transmitted through a CMA at the location of both the minimum trace width and the image of the second order focus. When the effect of a large divergence in entrance angles is greater than the effect due to the size of the slit widths, Aksela found that the base width of the energy distribution was smaller at the minimum trace width location; however, FWHM was significantly smaller at the second order focus. Furthermore,
the distribution at the minimum trace width exhibited two sharp peaks. These double peaks could produce serious complications in spectrum analysis. When the effect due to the size of the source and exit slit is not negligible, the double peaks are smoothed out and the FWHM for both distributions are comparable.

Risley (1972) has presented design parameters for various geometrical arrangements of the CMA. From the curves for various parameters given by Risley it is seen that for second order focusing at $\theta = 55^\circ$, the sum $d$ of the perpendicular distances of source and image from the surface of the inner cylinder should be about fifty times the radius of the inner cylinder. Even when $d = 2 r$, i.e., for axial focusing the second order focusing is possible for $42^\circ$ only. Hence with the CMA operating at $55^\circ$ angle only first order focusing is possible. Aksela (1970) has shown that the figure of merit which is the product of the resolving power and the entrance solid angle is better for a CMA with axial focusing than that with surface focusing when the source is not larger than the entrance aperture. In the case of an extended source, Heddle (1971) has redefined the figure of merit as luminosity or etendue which is the product of the entrance area and the solid angle and has also compared this figure of merit for three dispersive electron spectrometers in terms of the resolving power and a dimension. He has shown that the CMA with surface focusing has the largest etendue for a given resolution and dimension. For a CMA with a given radius
and resolution of about 100, the etendue for surface focusing type is about four times that of the axial focusing type. Moreover in the axial focusing CMA, the electron detector has to be very critically positioned to collect the electrons. Also, the definite size of the detector might affect the energy resolution. Thus it was decided to use a CMA with surface of focusing property even though second order effect is greater in this type compared to that in the axial focusing type.

II.2.2 Cylindrical Mirror Analyzer - Design Aspects

In a cylindrical mirror analyzer with surface focusing, the distance between the entrance and exit slits is expressed as

\[
\frac{L}{r_1} = \frac{\sqrt{\pi k}}{4} \cos \theta \exp \left(-k \frac{r_2^2}{r_1^2}\right) \frac{2eV}{\sqrt{k} \sin \theta} \text{ II.2}
\]

where \( L \) is the distance between the slits, \( \theta \) is the angle at which the electrons enter the analyzer and \( k \) is the analyzer constant given by

\[
k = \frac{2}{V} \ln \frac{r_2}{r_1} \text{ II.3}
\]

In the above expression, \( E \) is the electron energy in eV, \( V \) is the deflecting voltage applied to the outer cylinder, and \( r_2 \) and \( r_1 \), are the radii of the outer and inner cylinder respectively. The various parameters were fixed in the following way. The values of \( \frac{L}{r_1} \) were plotted as a function of \( \theta \) for various values of \( k \). For each value of \( k, \frac{L}{r_1} \) has a maximum at a particular value of \( \theta \). From these, the curve for which \( \frac{L}{r_1} \) was
maximum at $54^0 44'$ was chosen. This curve corresponded to $k = 1.03$, at $\theta = 54^0 44'$ giving $\frac{L}{r_i} = 3.232$. The luminosity or etendue of the analyzer as given by Heddle (1971) is

$$\xi \approx \frac{50 \, r_i^2}{f^2}$$

where $\rho = \frac{E}{\Delta E}$ is the resolution.

From this it follows that the larger the radius $r_i$, the more the etendue. Hence a large radius of 2" was fixed for the inner cylinder. With this radius the distance between the slits was $L = 6.264"$. The radius of the outer cylinder was selected to be 5". This is sufficiently larger than $r_m = 4.2"$ where $r_m$ is the maximum radial distance the electrons can achieve from the axis of the analyzer when they enter the analyzer at $55^0 \pm 3^0$. The slit width of the analyzer as given by Heddle (1971) is

$$s = \frac{1.5 \, L}{\rho}$$

where $s$ is the slit width for the two slits. This is valid when $\alpha < 2(3f)^{-1/2}$ where $\alpha$ is the angular spread of the electrons. It was decided to restrict the angular spread to $\pm 3^0$, i.e., $\alpha = 6^0$, and the resolution was chosen to be 100. With these values of $\alpha$ and $\rho$ the condition $\alpha < 2(3f)^{-1/2}$ was satisfied. Hence the slit width calculated was 2.4 mm.

A slit width of 2 mm was fixed in the present G2A. The corresponding resolution turned out to be $\rho \approx 120$. The corresponding luminosity was

$$\xi = \frac{50 \, r_i^2}{f^2} \approx 0.1 \text{ sterad.cm}^2.$$
Table II.1

Design Parameters of the Analyzer

Radius of inner cylinder \( r_1 = 2" \)
Radius of outer cylinder \( r_2 = 5" \)
Distance between the slits \( L = 6.264" \)
Analyzer constant \( k = 1.03 \)
Slit width \( s = 2 \text{ mm} \)
Luminosity (etendue) \( E = 0.1 \text{ sterad.cm}^2 \)
Resolution \( \rho = 120 \)
II.2.3 Analyzer Details

The cylindrical mirror analyzer was constructed with the parameters given in the previous section. The details of the analyzer are given in Fig II.2. The photoionization region is enclosed within the innermost electrode D of the analyzer and the photoelectrons could be accelerated or retarded by holding this electrode at a proper potential with respect to the inner cylinder before they entered the analyzing region enclosed within the outer cylinder A and inner cylinder B. Since the electrons travelled at an angle of 55° to the analyzer axis before they entered the analyzing region, the electrode D and the collimator C had to have the special geometry as shown in the diagram. The width of the slits on C and D are such that the angular divergence of the electrons is ± 3°.

The photon beam before entering the ionization region was made into a narrow pencil by a number of circular baffles E. These baffles were mounted on a machinable glass ceramic (MACOR) flange fixed to the end of the inner cylinder. To keep the source region (ionization region) free from any electric field, the baffles were kept at the same potential as D. The cylinder D was separated from C by MACOR flanges. C was machined in such a way so as to push-fit in B and was at the same potential as B. A collimator F was provided at the detector side also. This prevented the electrons from coming
Fig. H.2. ELECTRON SPECTROMETER

A OUTER CYLINDER  B INNER CYLINDER  C COLLIMATOR  D ACCELERATING RETARDING ELECTRODE  E LIGHT BAFFLES  F COLLIMATOR  G CHANNELTRON HOUSING  H CHANNELTRON
to the detector directly from the source region. It also prevented the electric field due to the voltage applied to the channeltron face from penetrating into the analyzing region. The photon beam after passing through the source region was blocked by the solid cone on F with a semivertical angle of 45°. This prevented the reflection of the photon beam into the source region. A small cylinder sufficiently screened from the source region and held at a few volts positive potential was fixed around the cone. This was to collect the metal electrons produced in that region. It was found that this did not have much effect and was subsequently removed. The inner cylinder was held in position and insulated from the outer cylinder by MACOR spacers at the ends. These spacers had large openings so as to facilitate rapid evacuation.

All the metal parts of the analyzer were made out of stainless steel 304. The outer cylinder was made from a sheet and hence had nonuniformity of about 2% in the diameter. Both the entrance and exit slits were about 5 inches away from the ends. This prevented the end field effects from affecting the resolution. The entrance and exit slits were cut almost through 360°, except for 3 small bridges on each slit spaced symmetrically around the surface to hold the cylinder together. The pieces C, D, and F were machined from single rods. Again slits were cut through almost 360° leaving three small bridges on each one. The light baffles were made from
thick sheets and mounted together with the help of three stainless steel screws. These baffles had apertures of 3 mm diameter and were kept 1 cm from each other.

II.3 Beam Splitter, Vacuum System and other details

The electron spectrometer was mounted in an 18" long 14" diameter stainless steel chamber which was evacuated by a 4 inch oil diffusion pump with an unbaffled speed of 500 lit/sec. This chamber was connected to the monochromator through a coupler which incorporated a beam splitter also. This coupler was provided with ports for detecting the reflected light from the beam splitter by a photomultiplier, for introducing the gas sample into the ionization region, and for the capacitance monometer connection. The beam splitter was made of thin wire mesh with about 80% transmission and was mounted at 45° to the direction of the photon beam. The reflected light from the beam splitter fell on the sodium salicylate coated face of a perspex light pipe. The ultraviolet radiation was converted into visible light by the sodium salicylate and the visible light was transmitted through the light pipe to a photomultiplier. The PMT output was monitored using a picoammeter and a chart recorder. The whole analyzer was mounted onto the flange of the vacuum chamber with proper electrical insulation. This flange had an opening 4 inches in diameter, and an electron detector with a
separate mounting was introduced through this opening. Additional pumping of the gas leaking into the analyzing and detection regions through the narrow slits of the analyzer was achieved by a second 4" oil diffusion pump connected through a T-shaped line attached to the rear flange of the main chamber. This helped in maintaining the analyzing region and the detector at sufficiently low pressure even when the source region was at a high pressure of the order of $10^{-2}$ torr. The free end of the T-line was closed by a blanking plate to which the channeltron housing was mounted. This flange had a number of high voltage ceramic-metal seals also for the necessary electrical connections. The preamplifier and the amplifier were also mounted directly on this flange.

The pressure in the source region was monitored using an MKS Baratron Capacitance Manometer (head 310 MH-10) and the pressure in the main chamber was measured by an ionization gauge (gauge head-Veeco and unit - Veeco- RG 830).

It was found that the analyzer performance was greatly hampered by the earth's magnetic field. To reduce the effect of this field the whole experimental system was positioned in such a way that the axis of the analyzer was normal to the magnetic plane and the whole analyzer was covered by a number of mu-metal cylinders. These mu-metal cylinders were about 16" long and were made of 1/32" thick perfection annealed alloy.
conetic alloy. They were separated by thin aluminum foil in between. This mu-metal shield assembly was fitted inside the main chamber and was supported by the outer cylinder of the analyzer. The outer cylinder was insulated from this shield by a thin mica sheet.

II.4 Electron Detector

The electron detector used was a channeltron (Mullard B419 BL). The characteristics of the channeltron are given in the counting Table II.2. The channeltron was used in the mode, so that for each electron detected, it gave a saturated pulse at the output. These pulses went through a preamplifier and amplifier before getting stored in a computer controlled multichannel analyzer. The channeltron face was held at +100V so that it could attract the electrons onto it, and energize them sufficiently to produce secondary electrons. The end of the channeltron was kept at +3 KV potential.

The channeltron was housed as shown in Fig II.3. Because of its asymmetric shape, special attention had to be given to mount it properly. Two teflon flanges to fit around its cone and neck and a third one with a slot to fit its helical position were made, each in two symmetric pieces. The channeltron was fixed in these pieces with proper spacers in between along with the thin stainless steel flange A. This set up was mounted on the cylindrical support E which in turn was fixed onto the
Table II.2

Characteristics of Mullard CEM-B419BL

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Operating Voltage</td>
<td>3.5 KV</td>
</tr>
<tr>
<td>Nominal Resistance</td>
<td>$5 \times 10^9$ ohm</td>
</tr>
<tr>
<td>Gain</td>
<td>$1.1 \times 10^8$ @ 2.5 KV</td>
</tr>
<tr>
<td>Noise ( @ 2.5 KV)</td>
<td>2.0 p.p.s</td>
</tr>
<tr>
<td>Pulse Height Distribution Resolution (@ $10^8$ gain and 1000 p.p.s)</td>
<td>0.6</td>
</tr>
<tr>
<td>Minimum effective cone diameter</td>
<td>9 mm</td>
</tr>
</tbody>
</table>

Note: The noise was found to be one order of magnitude less than the one given above.
A. Stainless Steel Flange
B, C, D. Teflon Flanges
E. Cylindrical Support
F. Stainless Steel Flange
G. High voltage Ceramic Metal Seals
H. Channeltron

Fig 1 3 CHANNELTRON HOUSING.
flange F. A few high voltage ceramic-metal seals were fixed on F for electrical connections. The cylindrical support E was provided with large holes on it for evacuation.

The voltage (+3 KV) given to the rear end of the channeltron was well shielded by the channeltron housing which was grounded. This was needed to prevent the electrons from coming to the rear end instead of the face and also to reduce the leakage of the field lines into the analyzing region. But it was found that there was some loss of resolution when the electrons were analysed at low energies, due to the field from the channeltron face. So it was found necessary to reduce the face voltage to 20-30 V to achieve better resolution. But this in turn, reduced the total count rate.

II.5 VUV Monochromator

An asymmetric type normal incidence 1 meter monochromator (Jobin-Yvon, France) was used to monochromatise the radiation coming to the electron spectrometer. The special holographic concave grating (Jobin-Yvon, France) used had a ruling of 1200 lines per mm and could be conveniently used in the spectral range from 300 to 1500 Å in the first order. The various photon energies could be selected by rotating the grating. The best beam width obtained was 0.1 Å. The monochromator was provided with a 4" oil diffusion pump and could be evacuated to a base pressure of ~ 10⁻⁶ torr.
II.6 Light Source

The light source used was a microwave discharge lamp giving neutral emission lines characteristic of the gases used. Most of the work presented in this thesis was done using HeI 584 Å, NeI 736 Å, and 744 Å lines. Certain ArI and HI lines were also used. The gas from the cylinder was allowed to flow through a 1 cm diameter, 20 cm long quartz tube. The gas flow was controlled with a fine metering needle valve (Granville-Philips). The quartz tube was fixed on a metal flange with an 'O' ring seal. This flange was mounted on the differential pumping arrangement connected to the entrance slit side of the monochromator. The differential pumping arrangement included a roots pump backed by a rotary pump and a movable slit of width 1 mm and height 1 cm. The roots pump had a speed of 40 litres/sec and could give an ultimate vacuum of $10^{-3}$ torr. The slit could be moved for proper alignment. The diffusion pump of the monochromator acted as a second stage of the differential pumping.

The light source was powered by a 2450 MHz Kiva supply (Ophthos Instruments, MD) with a maximum output power of 100 watts. For certain experiments, modulation of the microwave power was needed. For that, another microwave generator, MR III (K.K.Ewig Shokai, Japan) was used. This had
a maximum output power of 200 watts, and could accept modulating pulses through an external circuit. As far as possible, the Kiva supply was used because of its smooth functioning. The microwave power was coupled to the discharge through an Evenson cavity which could easily be clamped around the discharge tube. The cavity and the discharge region were cooled by passing compressed air through the part provided in the cavity. The tuning of the cavity had to be done by the two tuning stubs provided and also by slight adjustment of the pressure in the discharge tube. The intensity of the radiation was found to be dependent on the pressure in the discharge tube and there was an optimum pressure at which the intensity was maximum. This optimum pressure varied from one gas to another. This effect could be due to the self absorption of the radiation.

The microwave discharge provided quite intense radiation. The main advantages in using this source were in its steady functioning, almost constant intensity and ease of operation.

II.7 Data Acquisition System

The data acquisition system included a preamplifier, an amplifier, a comparator, a 256 multichannel analyzer operated in the time mode and a staircase generator. The multichannel analyzer and the staircase generator were controlled by a microcomputer. The data display and recording were done by a cathode ray tube and a teleprinter respectively. All the data
Fig. 2.4 BLOCK DIAGRAM OF THE DATA ACQUISITION SYSTEM
collection system was built in our own laboratory. The block diagram of the set up is shown in the Fig II.4.

The preamplifier was a high input impedance voltage pulse amplifier. The amplifier was AC coupled, linear wide band type with a gain of about 25. The comparator made the pulses TTL compatible.

The MCA included the pulse counter, oscillator or timer, the master programmer and storage, and the digital to analog (D/A) converters for the staircase and display. The pulses from the comparator go into the pulse counter and the number of counts for a definite time \( t \) is stored in the memory. The timer is used to fix the data collection time \( t \) per each channel. This time \( t \) is dictated by the master programmer which receives commands in the beginning of the experiment through the teleprinter. After each time interval \( t \), the channel number is advanced and is counted by the channel number counter. This channel number goes into the memory as well as a D/A converter. The output of this D/A converter is proportional to the channel number and hence it produces the corresponding step of the staircase. This D/A converter has a range of 0 to 5 V only corresponding to the 256 channels of the MCA and has to be further amplified by a Level Shifter Amplifier. This Level Shifter Amplifier has provision to fix the initial voltage \( V_0 \) in the range of \(+30\) to \(-30\) volts and the stepsize \( \Delta V \). The
step size can be controlled continuously or in discrete values in the range from 2mV to 200 mV. From the memory, the channel number and the corresponding number of pulses stored in each channel go through two different D/A converters, the output of them being connected to the cathode ray tube display. The data at the end of each run is printed out or punched out on paper tapes by the teleprinter.

To start the data collection, first of all the initial voltage $V_0$ and the step size $\Delta V$ are fixed manually. Commands are given through the teleprinter to select the data collection time $t$ per each channel as well as the number of scans required. The time $t$ can be set in any of the 0.1, 1, 10, 100, 200, 300 and 400 sec. intervals. The mode of operation, i.e., addition or subtraction of the data can also be fixed by the external command. Once the necessary commands are given, the system collects data automatically and displays it simultaneously until all the commands are fulfilled. The data collection can be stopped or restarted in between if needed. After each collection the data are printed out or punched out on the paper tapes by separate commands.

At times, large number of spurious pulses were observed at the output end of the channeltron. It was found that these pulses were due to some sort of leakage at the high voltage seals when the atmosphere was very humid and the seals were unclean. To eliminate this a simple RC filter was used and this filter along with the load resistance and the coupling condenser were
enclosed in the spectrometer vacuum chamber itself. This completely eliminated the spurious pulses.

The output from the photomultiplier which monitored the intensity of the photon beam was fed into a picoammeter (ECIL). The picoammeter output voltage is given to a strip chart recorder (OMNISCRIBE). In the course of an experiment any change in the photon intensity was noted down from the chart recorder and the necessary corrections were made in the data.

II.8 Operation of the Spectrometer

When the electron source region of the photoelectron spectrometer was held at the same potential as the inner cylinder of the analyzer, the energy of the electrons entering the analyzing region was not modified in anyway. While analyzing the electrons in this way, it was found that the collecting efficiency of the analyzer was very small for electrons of energy from zero to about 1 eV. This was mainly due to the stray electric and magnetic fields remaining in the system. This collecting efficiency problem was partly overcome by a preacceleration of the electrons before they entered the analyzing region. Thus in general the analyzer was operated in two different ways. The first one by keeping the source region at the same potential as the inner cylinder (usually both are kept at the ground potential) and the second one was by having a preacceleration. To distinguish these modes
the first one is named the grounded mode and the second one the accelerating mode.

Apart from having a large collecting efficiency for near zero energy electrons, the accelerating mode had a definite advantage over the grounded mode. In this mode all the electrons could be analyzed at a fixed energy, thereby maintaining the same resolution throughout the spectrum. Hence all the experiments were done in the accelerating mode by giving the staircase voltage to the source region and keeping the inner cylinder at the ground potential and outer cylinder at a fixed negative voltage. The constant negative voltage given to the outer cylinder was derived from a nickal-cadmium cell through a high resistance potentiometer.

II.9 Performance of the Spectrometer

The performance of the photoelectron spectrometer was studied with respect to the resolution, the collecting efficiency, the energy calibration and the shape of the peaks. It was found that all these characteristics were greatly affected by the earth's magnetic field and the small amount of the stray fields in the analyzer and also the electron scattering due to the parent molecules or atoms. The stray fields include the magnetic field due to any remnant magnetism present in the spectrometer material, the electric field due
to the contact potentials and the small amount of field leaking into the analyzer from any high voltage points like the channeltron inside the spectrometer. The effects of the various fields were studied in detail and are being described below.

II.0.1 **Effect of the Earth's Magnetic Field**

Initially, in the spectrometer, no magnetic field shielding or field compensation was used and the argon photoelectron spectrum with He 584 Å radiation was studied with the spectrometer in the grounded mode. But for a very weak hump nothing was discernible in the spectrum. After the introduction of three layers of $\mu$-metal shield the hump became very pronounced and the two peaks $\frac{1}{2}P_{1/2}$ and $\frac{3}{2}P_{3/2}$ could be barely distinguishable. The introduction of three more $\mu$-metal shields improved the spectrum to such an extent that about 80 meV resolution was obtained. A study of the molecular oxygen spectrum in the grounded mode at the same wavelength revealed that the collecting efficiency below about 1 eV was practically zero even with six layers of $\mu$-metal shielding. Thus it was decided to introduce three more layers of $\mu$-metal shielding. With this arrangement a final resolution of about 40 meV was obtained at an electron energy of about 5.5 eV in the grounded mode. In the same mode the collecting efficiency, especially below 1 eV was seen to improve drastically and the
It has been reported by Gardner and Samson (1973) that the presence of the magnetic field caused splitting of the peaks in the photoelectron spectra. They observed a splitting of the argon doublet into a pair of doublets separated by 360 meV in a 50 milli Gauss field with 584 Å radiation strongly polarized by a 1 m Seya-Namioka monochromator. In the present analyzer also the splitting of the peaks into two or more components was observed; but it never could be connected to the presence of the magnetic field. It was found that these splittings were only due to the contact potentials present due to impurities as discussed below.

II.9.2 Effect of Contact Potential

Whenever the spectrometer was exposed to humid atmosphere, corrosive or sticking gases or oil vapour the resolution degraded dramatically. The transmission of the analyzer reduced drastically and the analyzer constant was found to change and even presented multiple values resulting in more than one peak corresponding to each original peak. This problem was solved by extensive cleaning of the spectrometer parts followed by continuous evacuation of the system along with baking and plasma cleaning by making use of an RF discharge, the details of which will be given later in this section.
After obtaining a reasonably good performance of the analyzer, it was decided to see how exactly the 'poisonous' atmosphere affected the spectrometer. To see the effect of water vapour alone, the spectrometer was kept at about 25 torr pressure of water vapour for about 12 hours. The adverse effect of this on the performance of the spectrometer can be seen in Fig II.5, where the argon spectrum in the grounded mode of the analyzer at 584 Å is presented. In Fig II.5a is shown the spectrum before the exposure to water vapour and in Fig II.5b after the exposure. The overall intensity, the resolution, and the nature of the peaks are seriously affected by the exposure.

A similar study was done by exposing the spectrometer to the atmosphere. A similar effect is seen in the two spectra in Fig II.6, one before exposure and the other after exposure to the atmosphere for about 2 hours. The performance of the photoelectron spectrometer was badly affected when the system got exposed to oil vapour and the worst thing happened when introduction of nitric oxide gas into the system was followed by water vapour. This happened accidentally. Right after taking a nitric oxide spectrum, the spectrum of H₂O was tried. Initially the performance was satisfactory, but as time elapsed the resolution and the intensity went down and after about two days no spectrum could be obtained. Extensive cleaning starting from abrasive cleaning to introduction of RF discharge only could restore the original performance.
Fig 11.5 Effect of moisture on the spectrometer performance
EFFECT OF EXPOSURE TO ATMOSPHERE

Argon PES with 584 Å

FIG. II.6 Effect of exposure to atmosphere on the spectrometer performance
To reduce the effect of contact potential, the following procedures were adopted right from the beginning. As a first step, all the spectrometer parts were made from stainless steel 304. Moreover each part was machined and made in single pieces. Each piece was then degreased with trichloroethylene, followed by cleaning with detergent and distilled water. Other methods of cleaning using acid or alkali did not yield better results. After setting up the spectrometer the whole system was evacuated continuously for days together along with baking at about 100°C, using heater coils wrapped around the vacuum chamber. It was found that this baking time could be reduced drastically by using a plasma cleaning. The plasma was produced in argon at about 0.5 torr with the help of an RF supply. The accelerating/retarding electrode was used to introduce the RF power into the system. The effect of a typical plasma cleaning is shown in the Fig II.7. Even though the effect of this cleaning method was tremendous, this alone never gave satisfactory results. Always it had to be followed by further evacuation and baking. The main drawback was in the change in energy calibration after each discharge. After the plasma cleaning, it was necessary to wait for two or three days so that the analyzer constant k attained a steady value. Too much of discharge or discharge at very low pressures were found to degrade the performance on certain occasions. On most of the occasions it was found
Fig 1.7. EFFECT OF RF DISCHARGE ON THE SPECTROMETER PERFORMANCE.

(a) Before discharge  
(b) After 5 minutes of discharge  
(c) After 30 minutes of discharge
necessary to have an optimum use of the RF discharge for reducing the baking time.

It was also found that the R.F discharge affected the performance of the channeltron. Everytime after the discharge the number of dark current pulses were found to increase. It took a number of hours for the channeltron to heal and give the original dark current count rate. This adverse effect of the discharge on the channeltron was found to reduce by applying a negative potential of about 100 V to the channeltron face during the time of the discharge.

II.9.3 Effect of Draw-out Voltage

It was found that whenever the spectrometer was operated at very high resolution, the draw-out voltage applied to the channeltron face affected the performance. It was found that for a given resolution it was always necessary to find a draw-out voltage by trial which gave the maximum signal to noise ratio and the least distortion of the peaks.

II.9.4 Effect of Electron Scattering

The number of photoelectrons produced is proportional to the gas pressure in the ionization region. Thus it is good to have a high pressure to obtain large intensity for the peaks in the photoelectron spectrum. But this could not be the case, firstly because the channeltron has to be operated at less than
5 x 10^{-4} \text{ torr} \text{ pressure and secondly because of the scattering of the electrons by the parent molecules. It was found that the scattering of the photoelectrons by the parent molecules decreased the intensity of the electron peaks as well as the resolution of the instrument. So before obtaining the spectrum of any gas, it was necessary to find the maximum pressure at which there was very little effect due to scattering. The photoelectron spectra were taken at this pressure.}

\textbf{II.9.5 Collecting Efficiency Calibration}

The collecting efficiency of the analyzer is a function of the electron energy and also depends on the mode of operation of the analyzer. An exact calibration of the collecting efficiency of the analyzer is required to measure relative intensities of the various peaks in the photoelectron spectra accurately. The ideal way of calibrating for the collecting efficiency is to measure the intensity of a particular peak in an atomic photoelectron spectrum for a continuous range of photon energies. This requires the use of a continuum source like synchrotron radiation or a BRV light source. Another method is the inverted pass curve method described by Poole et al (1973) and modified by Gardner and Samson (1975b). In another paper (Gardner and Samson, 1976b), the relative vibrational intensities of strong vibrational peaks in the He(I) photoelectron spectra of N\textsubscript{2}, CO, CO\textsubscript{2} and O\textsubscript{2} were
FIG 8 Collecting efficiency of the electron energy analyzer

- SAMSON (1979)
- PRESENT WORK
- EXTRAPOLATED
measured with a CMA whose relative luminosity was calibrated to an accuracy of ± 5%. These data were used to calibrate the collecting efficiency of the present analyzer by comparing the vibrational intensities observed for the various peaks. The collecting efficiency curve obtained for a particular analyzing voltage in the accelerating mode is given in the Fig II.8. The curve shows that at electron energies greater than 2.4 eV, the collecting efficiency is independent of photon energy, while at low energies, a varying gain in the collecting efficiency is found. It was observed that the gain (ratio of collecting efficiency at energies less than 2.4 eV to the constant value at greater energies) at a particular electron energy, was for all practical purposes, independent of the constant energy at which photoelectrons were energy-analyzed. The curve obtained is compared with that given by Samson (1979). This curve has been normalized with respect to the present one at 3 eV.

II.9.6 Energy Calibration

The energy calibration is determined by the analyzer constant k defined earlier by eqn. II.3. In the present analyzer, as discussed earlier k was selected to be 1.03. The value of k was experimentally determined by taking the photoelectron spectra of the monatomic gases Ar, Kr and Xe. The value of k was found to be in the range 1.01 to 1.05 on various
occasions. This value of \( k \) was measured when the performance of the spectrometer was reasonably good, and the small fluctuation could be due to changes in the contact potentials present at the analyzer slits. Usually before and after the collection of a spectrum the Ar spectrum was taken and from the \( ^2P_{3/2} \) and \( ^2P_{3/2} \) separation, the value of \( k \) was determined. Occasionally there was a small change in the value of \( k \) after a long experimental run.

11.9.7 Resolution

The resolution obtained for the spectrometer was a function of the operating conditions and the cleanliness of the spectrometer. Usually before and after every data collection, the argon spectrum was taken from which the resolution was determined. The spectrum of argon obtained with 736 Å radiation and analyzed at 1.5V in the accelerating mode is shown in Fig II.9. The FWHM was about 10 meV which corresponded to a resolution of 150. The symmetric nature of the peaks without any distortion and the intensity ratio of the \( ^2P_{1/2} \) and \( ^2P_{3/2} \) states was quite satisfactory. Also, the photoelectron spectrum of molecular hydrogen at 736 Å was studied in the accelerating mode and is shown in fig II.10. The figure shows only a small portion of the photoelectron spectrum corresponding to \( v' = 6 \) vibrational level of the ground electronic state of
Argon PES with Na 736 Å Line

Fig. II.9  ARGON PES WITH Na 736 Å LINE
FIG II 10 Rotational levels in the H₂ PES
the molecular ion. The rotational states corresponding to $J = 1, 2, 3$ in $\nu' = 6$ vibrational state are clearly resolved with an energy resolutions of about 9 to 10 meV.