

Design and fabrication of an ultraviolet photoelectron spectrometer for the study of free molecules[†]

V JAYARAM and M S HEGDE*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

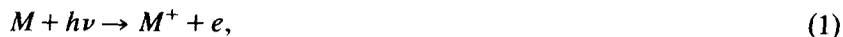
MS received 21 August 1986

Abstract. An ultraviolet photoelectron spectrometer for the study of free atoms and molecules has been designed and fabricated with indigenous components. The spectrometer consists of a 100 mA HeI discharge lamp, 180° hemispherical electron energy analyser (127 mm mean dia) and electron multiplier ratemeter electron detection systems. The resolution of the spectrometer is 90 meV and the intensity of N₂ (5σ) band is 10⁵ c/sec. The sample inlet and the collision chamber can be heated to 500 K so that solids of low vapour pressure can be studied. Typical spectra of molecules recorded with the instrument are shown.

Keywords. UV photoelectron spectroscopy; electron states of molecules; free molecules.

1. Introduction

Ultraviolet photoelectron spectroscopy (UVPES) is an invaluable spectroscopic method for the study of electron states of atoms and molecules. The method involves photoionization of atoms or molecules from HeI (21.22 eV) or HeII (40.8 eV) UV radiation, the ejected photoelectrons being energy analysed. The process is given by:



where $h\nu$ is the energy of the photon beam and M stands for atom or molecule. Kinetic energy of the photoelectrons is given by the energy balance equation:

$$h\nu = E_{KE} + E_{BE} \quad (2)$$

where E_{KE} is the kinetic energy of the photoelectrons to be measured experimentally and knowing the photon energy $h\nu$, the binding energy of the photoelectron, E_{BE} , can be obtained. Turner *et al* (1970) were the first to develop this method and since then, a large number of molecules have been studied employing UVPES as can be seen from the reviews (Heilborner and Maier 1977; Rao *et al* 1979).

It was considered most worthwhile to fabricate a UV photoelectron spectrometer for the study of free molecules. A prototype was fabricated earlier in this laboratory (Hegde and Basu 1978). In this article we describe the design and fabrication of a photoelectron spectrometer in sufficient detail so that the information can be profitably used for the fabrication of the instrument.

[†]Contribution No. 373 from the Solid State and Structural Chemistry Unit.

*To whom all correspondence should be addressed.

2. Design and fabrication

The basic components of the spectrometer are: (a) a HeI UV lamp; (b) electron energy analyser; (c) photon-molecule collision chamber; (d) electron detection system; and (e) differential vacuum systems. Design and fabrication of each of the above systems are given below:

(a) *He lamp*: HeI radiation is obtained from a capillary discharge tube. The transition due to 2^1P-1^1S with 21.22 eV (584 Å) energy is the most intense resonance line in the helium discharge lamp which can be used as the photon source. The half-width of this line is less than 0.01 eV and therefore it is essentially monochromatic for this purpose. The wavelength of this radiation being in the far UV region, no optical window can be used. Therefore, the radiation should be obtained through a windowless capillary discharge tube. The cross-sectional view of the helium lamp and its mounting in the spectrometer chamber is shown in figure 1. The lamp consists of two aluminium electrodes connected by 1.5 mm ID, 6 mm OD, 40 mm long fused quartz capillary tube. The aluminium electrodes can be watercooled and are insulated using teflon insulators. The lamp is connected to an aluminium connector having the provision to pump out the helium gas. A brass capillary of 1 mm ID, 6 mm OD and 35 mm length is mounted on the aluminium connector through which the HeI radiation can be collimated to the collision chamber. The aluminium connector is mounted on a 30 cm dia aluminium flange of the spectrometer chamber. Pure helium gas is let in through a precision needle valve and a discharge can be struck between the electrodes by applying 3 kV, after which the pressure of helium gas is reduced and up to 100 mA discharge current obtained at 500 V. The discharge current is controlled through a potentiometer. The pressure at which discharge is maintained is about 1 torr.

The lamp should be assembled such that there should be clearance of 1 mm throughout the length of the lamp (20 cm), so that the scattering of the HeI radiation by the walls of the capillary is reduced. In order to maintain 1 torr pressure in the discharge zone, a constriction is provided through a stainless steel piece of 1 mm ID before the helium pumping line. Helium gas needs to be pumped out to minimize self absorption of the resonance radiation and also to minimize flooding of helium gas in the collision as well as the spectrometer chambers. These details can be found in figure 1.

(b) *Electrostatic electron energy analyser*: For high resolution, a 180° hemispherical sector analyser is employed here. If r_1 is the radius of the outer surface of the inner sector and r_2 is the radius of the inner surface of the outer sector, the electrons of E_{KE} energy get collimated when voltage across the analyser, V_p , is applied such that the beam enters at zero potential at the slit and is collected at zero potential. For this, the outer hemisphere is connected to $-V_p/2$ and the inner to $+V_p/2$. The relation between the kinetic energy of the photoelectrons and V_p is given by the equation

$$E_{KE} = eV_p [(1/r_1) - (1/r_2)]. \quad (3)$$

The resolution of this analyser is given by

$$(\Delta E/E_{KE}) = (S/2r_0), \quad (4)$$

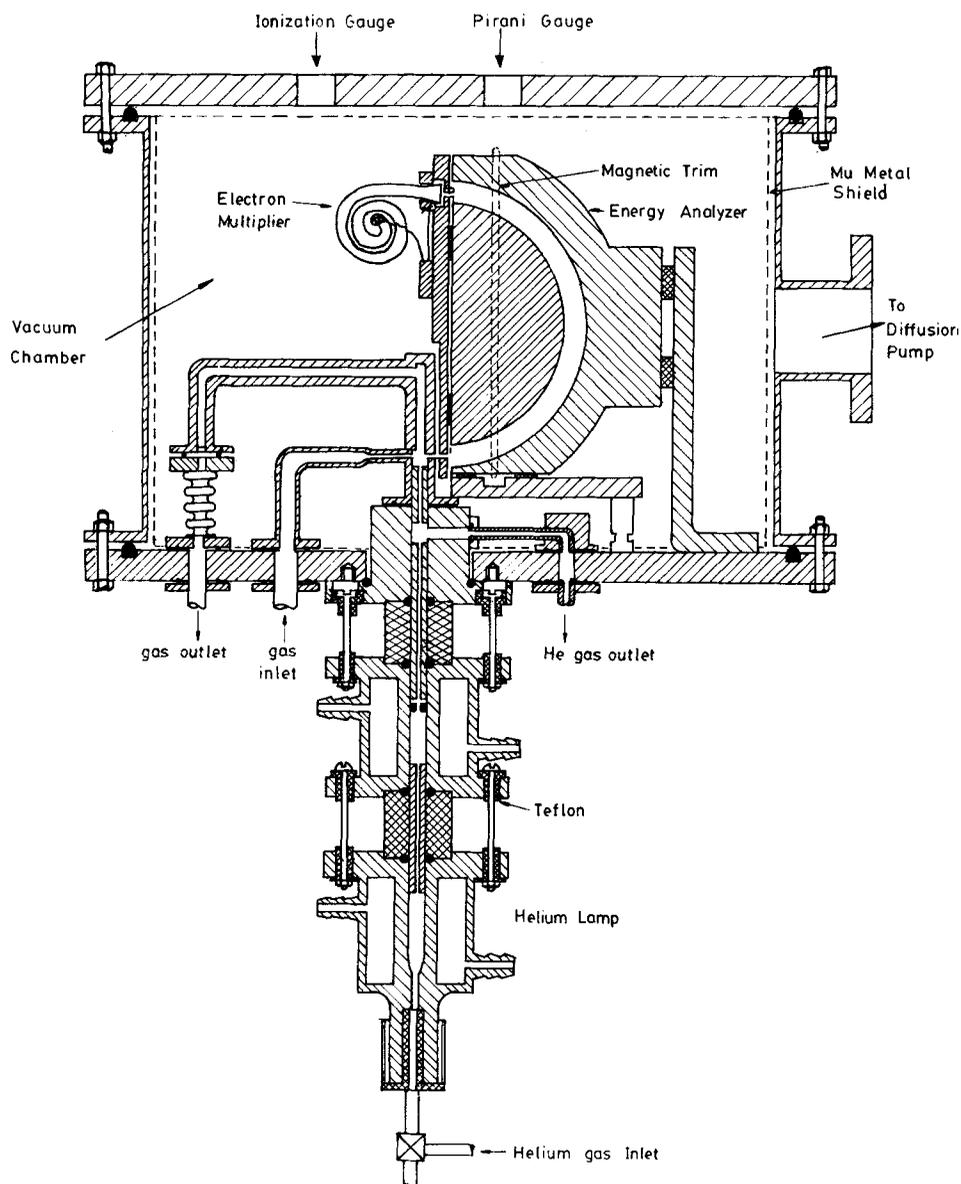


Figure 1. Cross-sectional view of the UV photoelectron spectrometer.

where $r_0 = (r_1 + r_2)/2$ and S is the slit width. The binding energy of the valence electrons in molecules vary from 7 to 20 eV, and thus, kinetic energy varies from 15.22 to 2.22 eV. Taking E_{KE} of about 10 eV and a convenient slit width of 1 mm dia, r_0 can be decided depending upon what resolution we need. Generally, ΔE of 70 to 100 meV is sufficient for most studies. Thus, when slit diameter $S_0 = 1$ mm, $\Delta E = 0.07$ eV and $E = 10$ eV, r_0 required is 71 mm for (4) to be satisfied. It is

convenient to have a sweeping voltage of 1–10 V, and thus, hemispherical sectors of r_1 and r_2 equal to 64 and 76 mm were chosen, which meet all the above criteria. Details on the electrostatic analyser can be found in Seviere (1972).

Analyser sectors were fabricated from extruded aluminium rods. The hemispherical sectors were machined on a HMT lathe using a radial cutter. The accuracy of the surface is within ± 0.025 mm. The inner as well as the outer hemispheres are mounted on an aluminium plate wherein 1 mm dia inlet and outlet slits are provided at 180° . The analyser pieces and the plate were coated with gold by the vacuum deposition method in a vacuum system having a planetary rotation facility at the Hind High Vacuum Co, Bangalore. The inner and the outer hemisphere and the plate are insulated with teflon washers. The hemispheres are aligned within ± 0.05 mm with reference to r_0 . The cross-sectional view of the analyser is shown in figure 1. Around the outer hemisphere, a magnetic trim coil of only one turn is provided to fine tune the signal. The mechanical mounting arrangement can be seen in figure 1.

(c) *Collision chamber*: A 4 mm diameter stainless steel tube collinear with the helium lamp acts as the collision chamber. A sample inlet tube with separate pumping facility is connected to the collision chamber. An orifice of 1.5 mm diameter acts as an outlet of photoelectrons from the collision chamber. The direction of photoelectrons taken from the collision chamber is perpendicular to the photon beam direction. The distance between the orifice and the electron inlet slit to the analyser is kept to a minimum of 3 mm so that the maximum solid angle is available to enable a higher number of photoelectrons to enter the inlet slit of the analyser. Also, the distance between the photon source and the electron outlet orifice is kept to a minimum so that the production of photoelectrons is maximum.

The mean free path, λ , of the photoelectrons is equal to $1/n\sigma$ where n is the number of molecules per cm^3 and σ is the photoionization cross-section (McDaniel 1964). For most molecules, σ is of the order of 10^{-16} cm^2 and taking the value of the number of molecules at 1 torr sample pressure, λ obtained is about 3.5 cm. This is about double the distance an electron has to travel before leaving the collision chamber. This means that photoelectrons ejected do not collide with the molecules before they leave the collision chamber. This is how the collision chamber dimension has been decided. If the vapour pressure is lower than 1 torr, the mean free path is even longer.

Sample inlet tubes can be heated to 500 K and thus, solids and liquids having lower vapour pressure can be studied in this instrument. The mounting of a gas inlet system and the collision chamber is also shown in figure 1.

(d) *Electron detection*: Since the number of photoelectrons obtained after the analyser stage is about 10^3 – 10^5 electrons/sec, an electron multiplier is used for amplification and detection. Channel electron multiplier made by Mullard (B419BL) is used in this instrument. This is the only component imported from U.K. which costs about £280. An electron entering the low potential end of the channel multiplier generates secondary electrons when about 2 kV is applied across the multiplier. These are accelerated and finally, an avalanche of electrons produce a charge pulse of $\sim 10^8$ electrons at a duration of 10 n sec. The amplitude of the resulting voltage pulse depends upon the value of the resistance and capacitance in the anode circuit of the amplifier. This small voltage pulse is fed to

the ratemeter for further amplification, pulse shaping, counter and finally to the recorder. Block diagram of the ratemeter is given in figure 2.

An AMPTEK A101 PAD charge sensitive preamplifier and discriminator is used for initial amplification and pulse shaping. This amplifier is capable of sensing a nominal threshold referred to the input of 0.16 picocoulomb charge. This is equivalent to 10^6 electrons. Input charge threshold can be varied by the addition of a variable resistance from 0.16 picocoulombs to 10 picocoulombs. Output pulse width can be varied from 220 n sec to 800 n sec. Output of the amplifier can be interfaced directly with CMOS or TTL. In this ratemeter, the output pulse is given to a decade counter. If the frequency of pulse is high, we can select divide by 10 or 100 so that the number of charge pulses can be counted accurately. Output of the counter is given to the monostable for a fixed pulse width of 30 microseconds of about 4 V. A voltage translator changes the output of the monostable to a fixed 12 V pulse. These incoming voltage pulses are converted to analogue voltage using a frequency to voltage converter. The DC output voltage is given to the buffer amplifier and to the y-axis of an x-y recorder. Some of these details are given in figure 2.

(e) *Differential vacuum system:* A three-stage differential vacuum system is required in this instrument. The main vacuum system consists of a 10 cm oil diffusion pump with a liquid nitrogen trap. The spectrometer chamber made of SS sheet with aluminium flanges of 30 cm diameter can be pumped to 10^{-6} torr. The helium gas is pumped by a separate pumping line with a 100 l/min rotary pump and the sample inlet-outlet system is pumped by a 10 cm dia oil diffusion pump. The diameters of the HeI photon source and the electron outlet orifice are adjusted such that during the experiment, helium discharge can be maintained at 1 torr, the collision chamber at 1 torr, and the spectrometer chamber better than 10^{-5} torr.

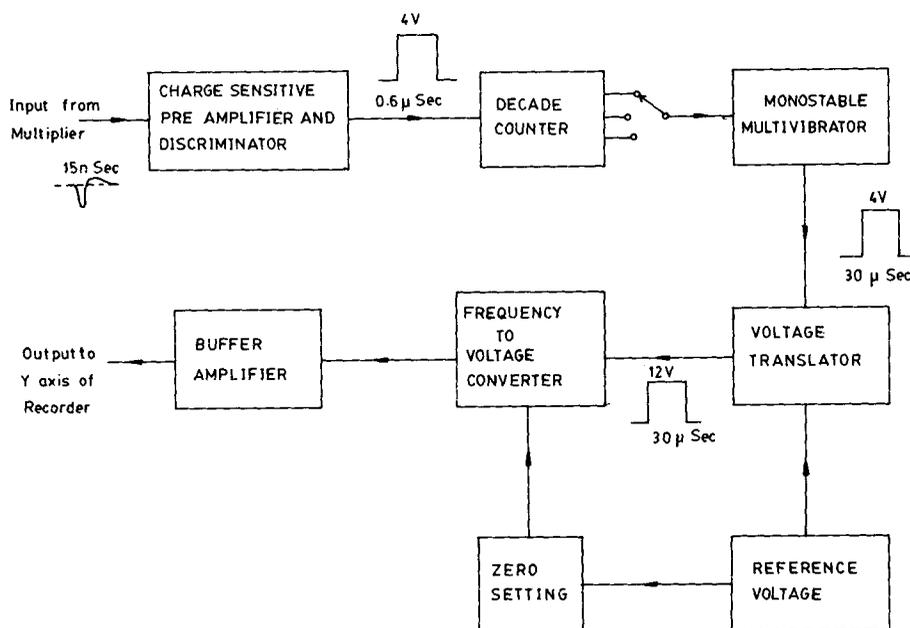


Figure 2. Block diagram of the ratemeter.

Hot cathode ionization and thermocouple vacuum gauges are used to measure the vacuum.

The spectrometer chamber is shielded from the earth's magnetic field by a 0.5 mm thick μ metal sheet. This is indicated in figure 1.

3. Operation of the UV photoelectron spectrometer

The system is first pumped to 10^{-6} torr. The helium vacuum line as well as the sample inlet vacuum line are also evacuated. The electrical connections to the helium lamp, analyser and the electron detection probe are made as shown in figure 3. In addition, connections to the heating line, the sample inlet and the magnetic trim provided around the outer hemisphere of the analyser have to be made. This is also shown in figure 3. The electrical connections are taken through a ceramic vacuum feed through made by ECIL, Hyderabad.

After initiating He discharge, the pressure is adjusted to get a 100 mA discharge current. The spectrum sweeping circuit, called analyser control, consists of a magnetic trim power supply and a programmable ramp generator. The ramp voltage applied across the hemispherical sector can be programmed such that

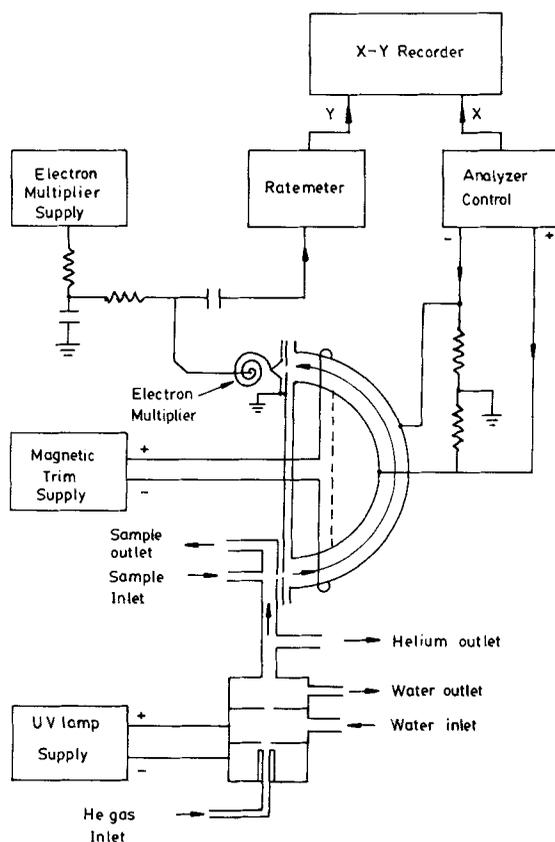


Figure 3. Electronic control in the spectrometer.

analyser voltage V_p can be varied in steps of 2, 5, 10 and 20 V and the scan time can be varied in steps of 50, 100, 300 and 500 sec. A start-reset switch is provided to start the scanning and reset the ramp at any point of recording.

The low frequency ramp is obtained using Intersil 8038 IC which operates under ± 15 V and other parts of the circuit are designed using OP Amps. The analyser control block diagram is shown in figure 4. Put on the ratemeter and apply about 1.9 – 2 KV to the multiplier. The background count in the ratemeter should be less than 10^2 c/sec when the helium lamp is on. If not, ground the body properly so that the background signal is reduced.

Helium is known to have two autoionization states with electronic configurations $1s^1 2s^1$ and $1s^0 2s^2$. In the discharge lamp, the population of these states is sufficiently large and they get autoionized to give electrons of kinetic energy 19.64 eV. Thus, at this kinetic energy (equivalent to $24.6 - 19.64 \equiv 4.96$ eV binding energy), an electron peak can be obtained with about 3×10^3 c/sec intensity. The scanning voltage to the analyser should be varied such that this peak is detected. Maximise this signal by varying helium pressure, magnetic trim supply and electron multiplier voltage. Then air can be leaked in through a fine leak valve. Look for N_2 and O_2 photoelectrons which are well documented (Turner *et al* 1970) and calibrate the spectrometer. Then the vapour or gas under study can be leaked in and photoelectron spectra can be taken. A photograph of the photoelectron spectrometer is given in figure 5.

4. Results and discussions

The photoelectron spectrum of N_2 gas taken in this spectrometer is shown in figure 6. 5σ , 1π and 4σ bands of N_2 molecule are well recorded. The vibrational fine structure of 1π band corresponding to N_2^+ is clearly resolved. The FWHM of each of the photolines is about 90 meV which is close to the expected value with the design parameters of slit width and the analyser sizes chosen here. The electron counts obtained are in the 10^4 to 10^5 range for the N_2 signal and this is a sufficiently good performance for recording photoelectron spectra of molecules.

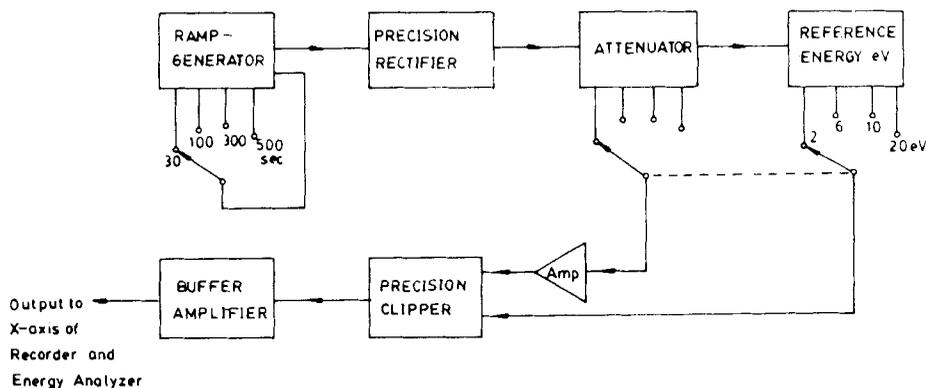


Figure 4. Block diagram of the analyser control.

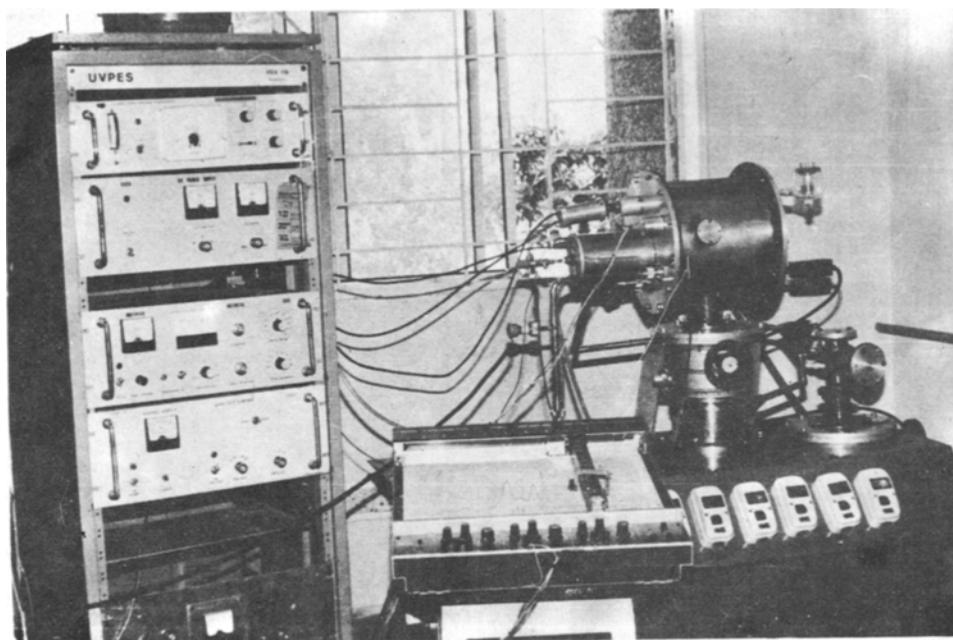


Figure 5. Photograph of the UV photoelectron spectrometer.

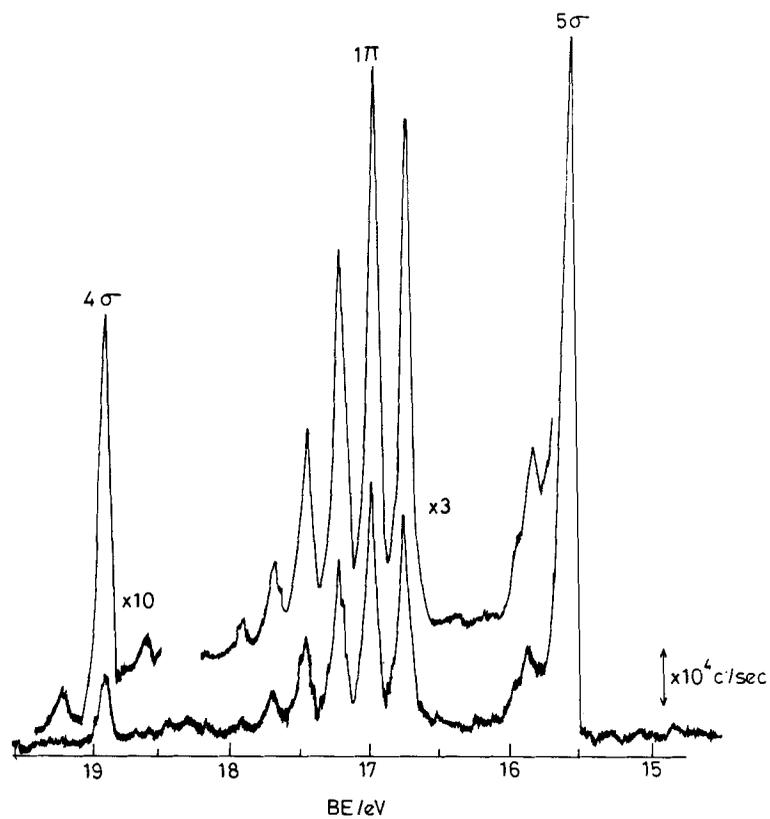


Figure 6. HeI UPS of N₂.

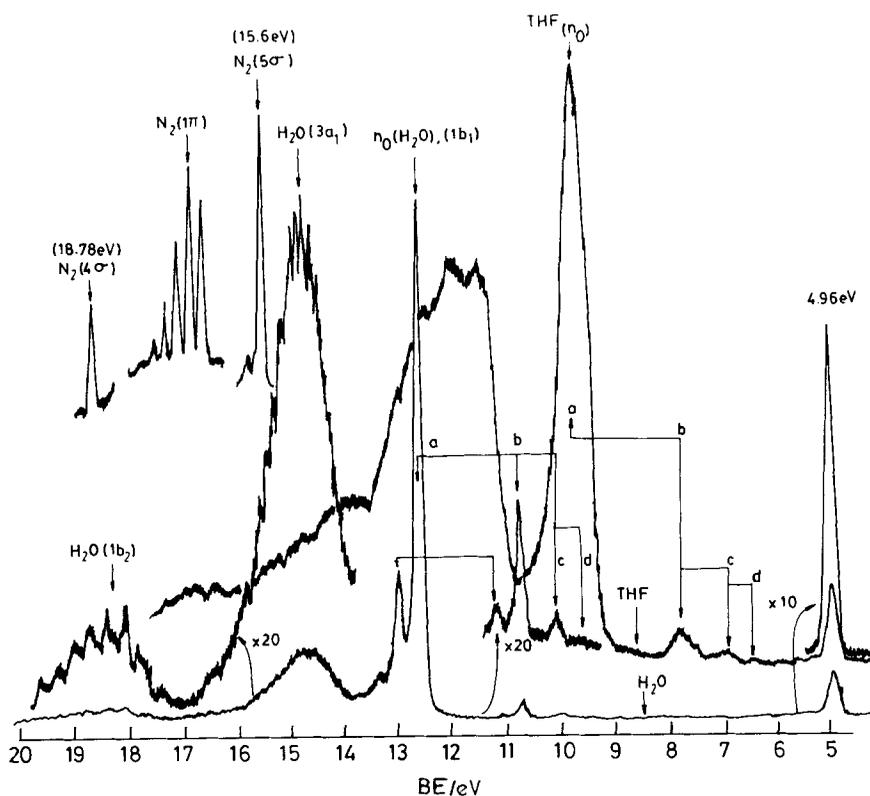


Figure 7. HeI UPS of H₂O and THF; notice autoionization peak of He at 4.96 eV; also satellites due to HeI β , HeI γ , HeI δ radiation marked b,c,d.

In figure 7, photoelectron spectra of H₂O and THF are given. Spectra of air (only the N₂ part) are also shown, which were taken for calibration. Autoionization peak of helium at 4.96 eV is also shown. The N₂ (5 σ) peak at 15.6 eV and the autoionization peak at 4.96 eV provide spectra for complete internal calibration of H₂O and THF bands. Expanded bands of 1b₂ and 3a₁ of H₂O are also shown. Assignment of each of the photolines can be found in Turner *et al* (1970) and Kimura *et al* (1981).

In the helium discharge lamp, in addition to the resonance radiation due to the 2¹P – 1¹S transition (HeI $_{\alpha}$), 3¹P – 1¹S, 4¹P – 1¹S, and 5¹P – 1¹S (HeI $_{\beta}$, HeI $_{\gamma}$, HeI $_{\delta}$) are also emitted and the energies of these radiations are 23.08, 23.74 and 24.04, respectively (Eland 1984). 1b₁ band of H₂O due to these radiations also appear as satellites marked by b, c and d in figure 7. Taking the intensity of HeI $_{\alpha}$ (21.22 eV) of 100%, HeI $_{\beta}$ and HeI $_{\gamma}$ are 3% and 0.5% respectively as can be seen from the figure 7. Generally, these satellites are seen for the more intense lines as can be seen for n₀ band in THF. The photoelectron spectra shown here are comparable to those obtained from commercial spectrometers (Kimura *et al* 1981).

The spectrometer has also been employed to study molecular interactions, and systems such as diethyl ether-iodine (Rao *et al* 1986) and BF₃ · H₂O (Durrant *et al* 1986) have been investigated.

Acknowledgements

The authors thank Professor C N R Rao, FRS for his encouragement. Financial support from the Department of Science & Technology, Government of India is gratefully acknowledged.

References

- Durrant M C, Hegde M S and Rao C N R 1986 *J. Chem. Phys.* (In print)
- Eland J H D 1984 *Photoelectron spectroscopy* (London: Butterworths)
- Heilbornner E and Maier J P 1977 in *Electron spectroscopy* (eds) C R Brundle and A D Baker (London: Academic Press)
- Hegde M S and Basu P K 1978 *Curr. Sci.* **47** 160
- Kimura K, Kastumata S, Achiba Y, Yamazaki T and Iwata S 1981 *Handbook of HeI photoelectron spectra of fundamental organic molecules* (Tokyo: Japan Sci. Societies Press)
- McDaniel E W 1964 *Collision phenomena in ionized gases* (New York: John Wiley)
- Seviere K D 1972 *Low energy electron spectroscopy* (New York: Wiley-Interscience)
- Rao C N R, Basu P K and Hegde M S 1979 *Appl. Spectrosc. Rev.* **15** 1
- Rao C N R, Hegde M S and Kamath P V 1986 *J. Mol. Struct. (Theor. Chem.)* **135** 409
- Turner D W, Baker C, Baker A D and Brundle C R 1970 *Photoelectron spectroscopy* (New York: Wiley-Interscience)