

Design and fabrication of an indigenous molecular beam ultraviolet photoelectron spectrometer⁺

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Abstract. An ultraviolet photoelectron spectrometer for the study of van der Waals molecules has been designed and fabricated indigenously. The spectrometer consists of an HeI discharge lamp, a molecular beam sample inlet system, an electrostatic lens, a 180° hemispherical electrostatic analyser and a channeltron detector. Performance of the spectrometer is illustrated with an example.

Keywords. UVPES; molecular beam; van der Waals molecules.

1. Introduction

A conventional photoelectron spectrometer is adequate to study the photoelectron spectra of molecular aggregates where the interaction energy is much above thermal energy. Investigations of systems where the interaction energy is close to or less than thermal energy as in van der Waals systems cannot be undertaken by such an instrument. The species under investigation will have only very short life time under ordinary conditions of temperature and pressure. The concentration also will be very low. In order to overcome the problem of low concentration associated with equilibrium systems, molecular beam techniques (Ramsay 1985) have been widely used. The important features of a molecular beam are: unidirectional motion with small velocity dispersion corresponding to low temperatures of relative translation motion and low temperatures of rotational degrees of freedom. Almost all physical tools have been used in conjunction with molecular beam techniques to yield valuable structural, thermodynamic and spectroscopic information.

In spite of these developments in other branches of spectroscopy, the use of molecular beams in photoelectron spectroscopy is very recent. A free jet expansion is a cheaper alternative to a skimmed and collimated molecular beam, though the average chamber pressure would be rather high. This is a problem since the photoelectron transmission will be affected by electron–molecule collisions. However, by confining the expansion zone and providing a large pumping system in the ionization region, this difficulty can be overcome.

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In the double chamber photoelectron spectrometer described below, the photoionization and the subsequent kinetic energy analysis of the electrons are carried out in two different chambers. A slit for electron entrance is the only connection between the two chambers. Apart from the pumping provided in the ionization chamber, another oil diffusion pump is also provided with the pumping port right opposite to the molecular beam so as to keep the average chamber pressure to a minimum.

2. Design and fabrication

The basic apparatus is similar to a conventional one (Jayaram and Hegde 1986) developed in our laboratory. The discharge lamp is of design similar to that described in the literature (Poole *et al* 1974). A bigger analyser of 154 mm mean dia is used for better resolution. The detection and counting systems are also similar to that described by Jayaram and Hegde (1986). The basic spectrometer assembly is shown in figure 1. Other parts of the instrument are the nozzle, the ionization box, the electrostatic lens and the data acquisition system. These are described in detail below.

The nozzle: These are generally glass or metal tubes of 6 mm OD and 3 mm ID terminating as nozzles. The glass nozzles were made by blowing 6 mm OD tubes. The metal nozzles were made out of stainless steel rods of 6 mm OD. These were drilled (3 mm ID) so that the tip of the drill just meets the other end of the rod. The metal pieces were ground from the closed end on an optical grinding wheel so

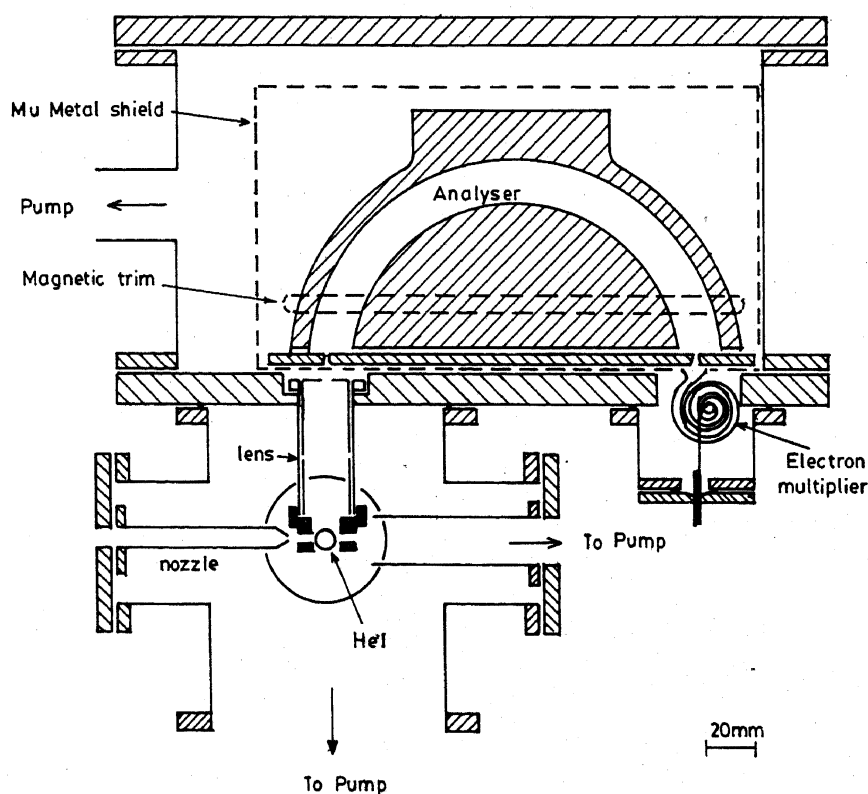


Figure 1. Cross-sectional view of the molecular beam ultraviolet photoelectron spectrometer.

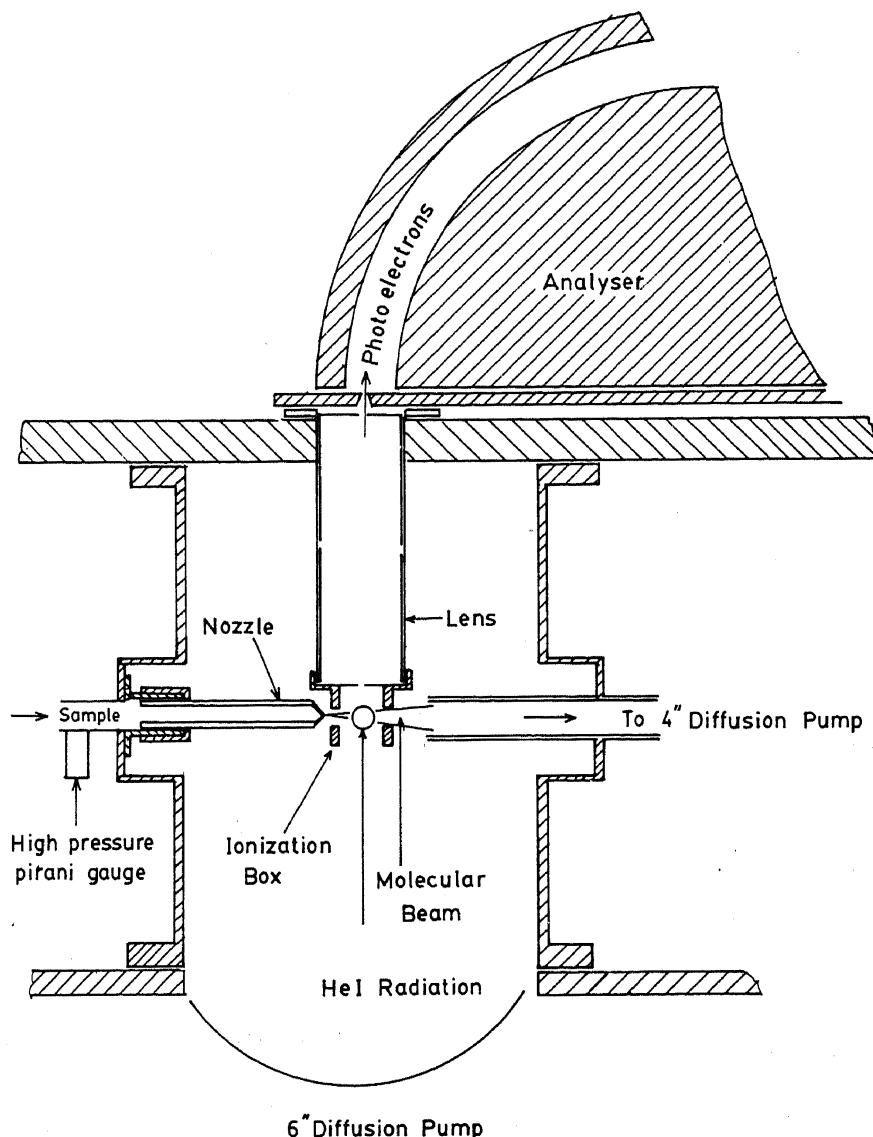


Figure 2. Enlarged view of the ionization region. The molecular beam intercepts at 120° with the He I radiation.

as to obtain the desired nozzle diameter. The surface finish was checked and the nozzle diameter was measured with the help of magnifying lenses. A high pressure pirani gauge (1 to 999 torr) is connected to the nozzle to measure the stagnation pressure. The nozzle holder was designed to adapt nozzles of different sizes. A needle valve controls the stagnation pressure. The nozzle assembly is shown in figure 2.

The ionization box: In order to reduce the gas pressure inside the expansion chamber, an ionization box is needed. This is also important because a higher pressure in the expansion chamber will affect the photoelectron transmission. The ionization box is made of stainless steel. A slit of 2 mm dia provided on top of the box is used for the photoelectron collection. Four holes of 6 mm dia are provided on the sides. The bottom is kept open. Through one hole the helium lamp capillary is admitted and the hole opposite is left open to reduce the background emission intensity. The nozzle tip is just outside the other hole and a pumping port is kept close to the

opposite hole so that the outgoing gases can find their way to the vacuum pump. The bottom of the ionization box is right above the throat of the 6" diffusion pump. These details are shown in figure 2.

The electrostatic lens: Since the ionization region is far removed from the analyser, a lens is needed to transport the photoelectrons from the ionization box to the analyser entrance slit. The lens system was designed as described in the literature (Lessettre *et al* 1963). The assembly consists of a pair of identical hollow cylindrical tubes of 19 mm diameter and 32 mm length machined out of stainless steel and mounted co-axially as shown in figure 2. The spacing is kept at 0.2 mm.

Data acquisition: The electrons emerging from the lens are energy analysed by the same kind of analyser described in the literature (Jayaram and Hegde 1986). Detection, amplification and recording are carried out as described by Jayaram and Hegde (1986). The ratemeter analogue output is fed into an A/D card and the data is acquired by an IBM personal computer. Inputs like scan-time, scan-energy, discharge current, stagnation pressure etc., are fed into the computer and it is then set for data acquisition. The spectra of 1000 data points are averaged over the desired number of scans and

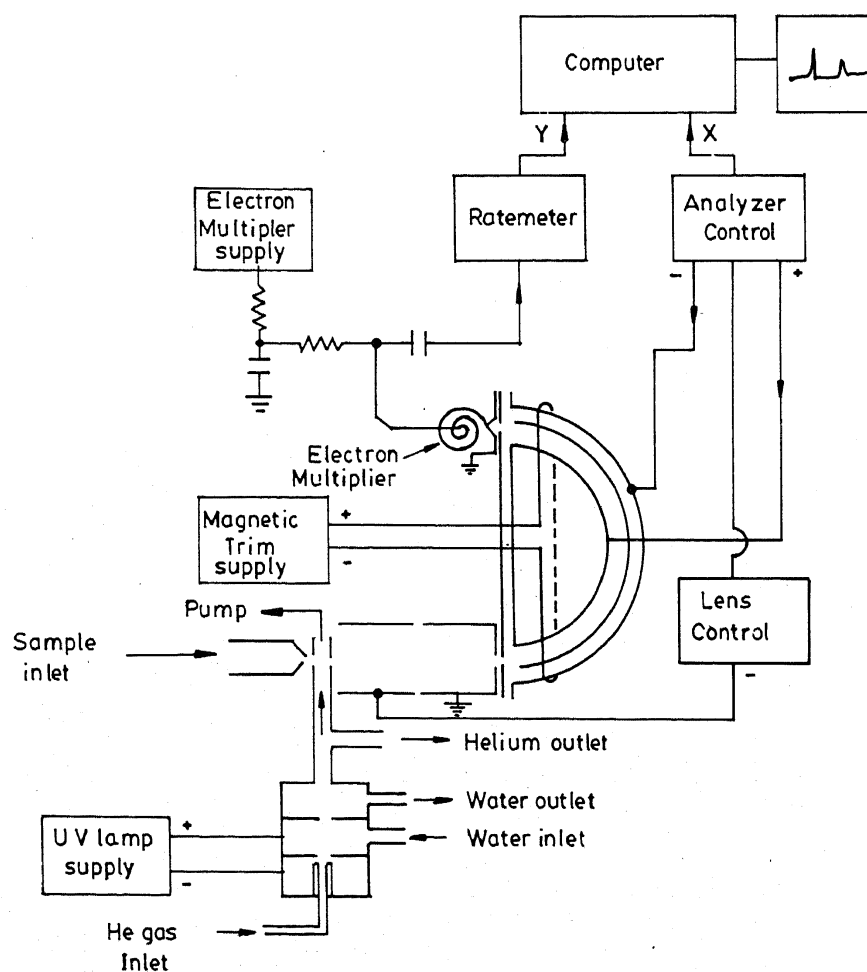


Figure 3. Block diagram of the spectrometer control.

are stored on to the magnetic disk. Manipulations like spectrum addition, subtraction, shifting, curve fitting, normalising etc., can be done with the stored data. The spectrum can be plotted by a colour plotter or printed by a dot matrix printer. The block diagram of the spectrometer control is shown in figure 3.

Operation of the instrument: After obtaining a vacuum in the range of 10^{-6} torr, the helium discharge lamp is switched on. The calibrant gas (Xe or Ar) is admitted through the needle valve. The analyser and lens voltages are adjusted to detect the peaks and are set for maximum signal intensity. Since the lens voltage is a function of the voltage across the analyser, a variable gain amplifier connected to the analyser ramp can scan the lens voltage. The magnetic trim supply is suitably adjusted to obtain the maximum signal intensity. The discharge current is also adjusted. Now, the sample is let in and the spectra are acquired. Typical spectra are shown in figure 4. The operating resolution of the instrument is 50 meV.

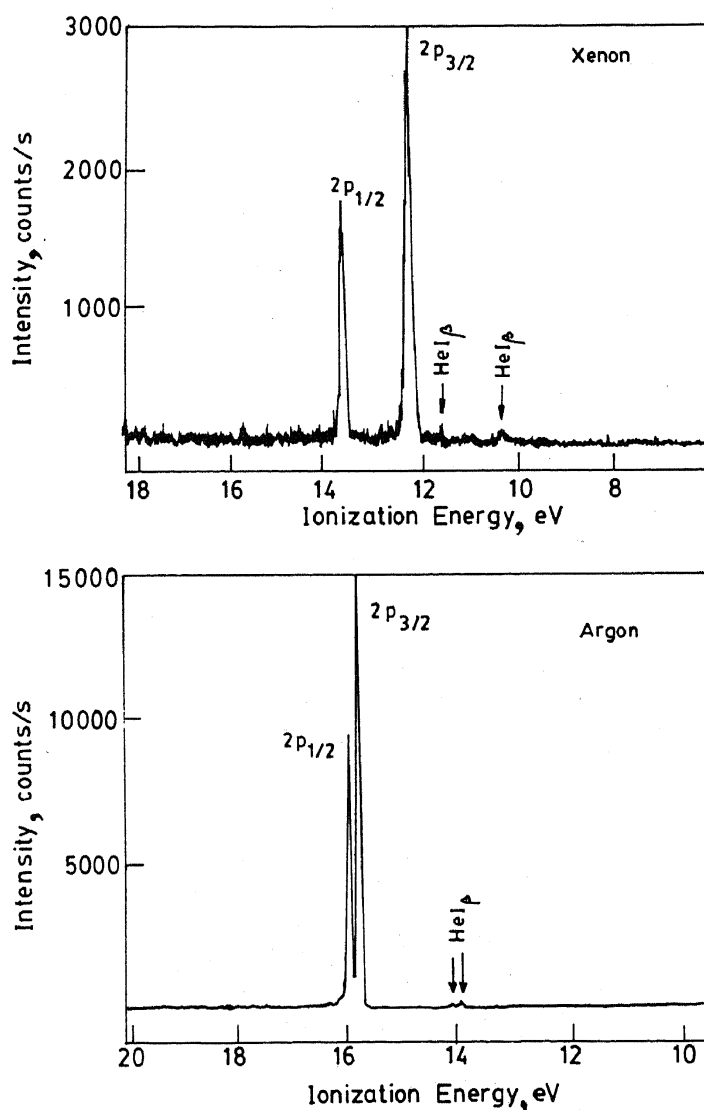


Figure 4. Hel UPS of Ar and Xe; note the weak $He I_{\beta}$ features.

3. Performance of the spectrometer

Using the apparatus described above, we have investigated the photoelectron spectra of the dimers of methanol and ethanol. We have also studied the van der Waals molecule Xe...HCl. These results are discussed in detail elsewhere (Pradeep *et al* 1991). As an illustrative example, we provide a brief discussion of the photoelectron spectrum of the methanol dimer obtained using this instrument.

We used a 0.1 mm glass nozzle and the alcohol vapours were expanded into the ionization box at different stagnation pressures. The PE spectra of methanol at increasing stagnation pressures are shown in figure 5. The spectrum marked (a) in the figure is due to the monomer. When we compare the spectra at higher nozzle pressures with that of the monomer, a few striking features come to the fore. Additional features develop on each of the bands and the spectrum becomes more complex as the pressure increases. Since in this kind of nozzle expansion, it is well established (Odotola *et al* 1979; Cook *et al* 1980) that the dimer fraction dominates (more than the other clusters), it is certain that the spectrum marked (e) has significant contribution from the dimer. When the features due to the monomer are stripped off from the spectrum marked (e), we get the spectrum given in figure 6, which we attribute to the pure dimer.

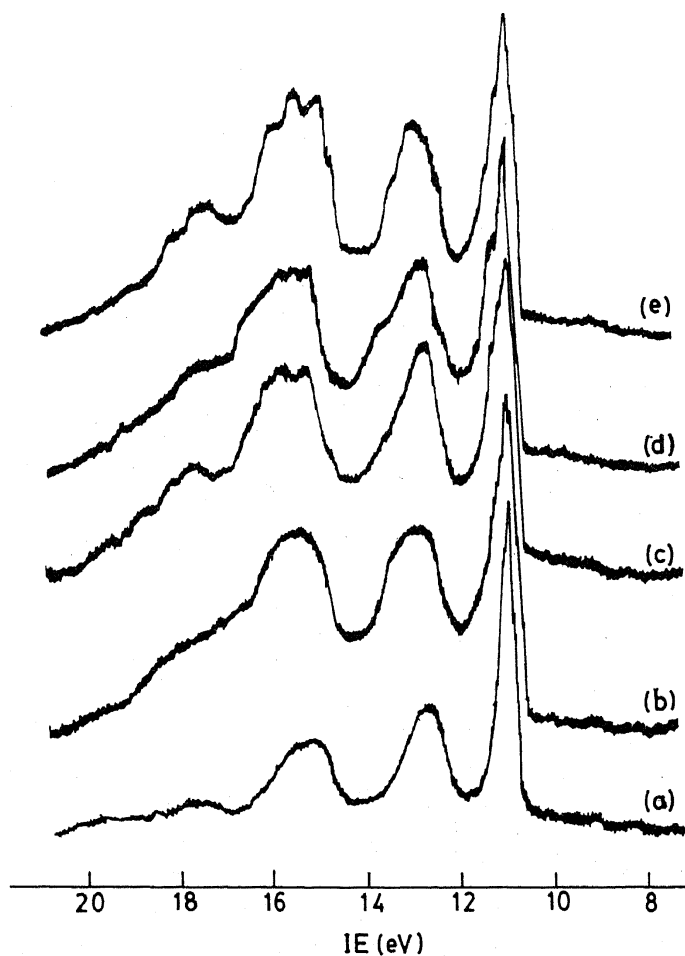


Figure 5. HeI photoelectron spectra of methanol at various pressures. The pressures are in the order, (a) < (b) < (c) < (d) < (e). The spectrum marked (a) is due to the monomer.

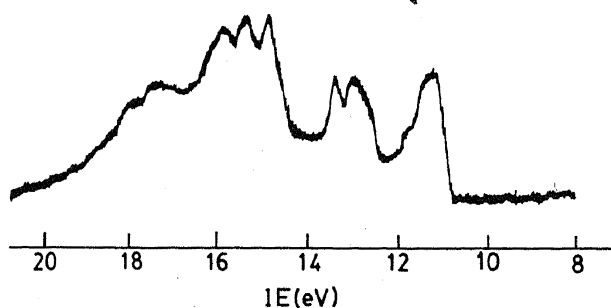


Figure 6. HeI photoelectron spectrum of pure methanol dimer obtained after stripping.

The spectral assignments have been carried out on the basis of molecular orbital calculations.

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