7.12 Photoelectron Spectroscopy

(7 points)

Introduction

The energy required to ionize a molecule is the difference between its total energy and that of its positive ion. This energy is a small difference (ca. 10eV) between two large (>500 eV) quantities and often the correlation between experimental and theoretical data is poor. A better correlation exists with the energy of the orbital occupied by the electron to be removed. Thus if we determine the ionization energies of a molecule using Photoelectron Spectroscopy as in this experiment, we are in effect measuring directly the molecular electron energy levels.

Relevant lecture courses and topics

Courses: Quantum Mechanics, Molecular Energy Levels, Molecular Spectroscopy, Valence and Electronic Spectroscopy. *Topics*: Electronic structure, Molecular Orbitals, Franck-Condon factors, Quantum theory. *Web site*: http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/712.html

Format

This experiment combines theoretical with practical work. In the theoretical portion you will complete several Pre-lab tasks whose aim is to help you to understand the principles of the experiment. These exercises must be completed before you start experimental work. As these form an integral part of the experiment, they must be written up as part of your report when you have the experiment signed off.

Safety

Do not open the side panels of the photoelectron spectrometer. If you are not sure how to use the gas regulators, ask a demonstrator or technician for advice before proceeding.

Theory

Ionization

Prior to the development of photoelectron spectroscopy only the first ionization energy of atoms and molecules was readily measured, using methods such as optical spectroscopy (Rydberg series) or electron impact (mass spectrometric appearance potentials).

Ionization energy measurements are related, in the most direct way, to the electron energy levels of atoms and molecules, and so are of considerable theoretical interest. The accurate prediction of the first ionization energy of a molecule, I_1, is an important objective of molecular quantum theory. It is this first energy which has been the primary objective, since, at least in "complex" molecules (more than 3 atoms!), the values of the higher ionization energies, I_2, I_3, etc., corresponding to the removal of more tightly bound electrons (leading to the formation of excited ions), have been much less readily available, and when known have often not had the degree of confidence required for theoretical tests.

The transition from the molecular ground state to each of the possible states of an ion determines an ionization energy. We can distinguish between ionization energies which correspond to the removal of more than one electron (multiple ionization) and those in which only one electron is lost. The one electron ionization potentials I_1, I_2, ... I_i (which you will measure in this experiment) are numerically equal to the orbital energies (by Koopman's Theorem).

Photoelectron spectroscopy gives I_1, I_2, etc. by measuring the kinetic energies E of electrons ejected from the molecule by high energy photons:

$$E_1 = h\nu - I_1 \quad \text{etc.}$$

This equation shows that when energy is absorbed by the molecule, it is divided into two portions; one portion is used to ionize the electron, while the rest of the energy is left with the electron in the form of kinetic energy. It is this latter energy which is measured in PES experiments.

Examples of many photoelectron spectra and their interpretation will be found in Ref. 2. A fuller discussion is given in Ref. 3, while Ref. 4 is a simpler survey.

Experimentally, we illuminate molecules in the gas phase with monochromatic light at an energy which is much larger than the ionization energies. Typically we need to use UV or even X-ray energies for this. Electrons are thrown out of the molecule, and their energy spectrum (i.e. the range of their translational energies) is determined.

Pre-lab 1: Partition of energy between ion and electron

The energy of the principle emission from the helium lamp used in this experiment is 21.22 eV. The first gas you will study is argon, from which electrons can be removed to create the Ar^+ ion in either the $^2P_{1/2}$ or the $^2P_{3/2}$ state. The ionization energies are 15.759 and 15.937 eV. To which state does each ionization energy relate? How do you know (hint: consider Hund's Rules)? Calculate the velocity of an electron removed from Argon to create each of these states if the atom absorbs a photon of energy 21.22 eV. The mass of an electron is 9.109 x 10^{-31} kg and 1eV=1.602 x 10^{-19} J.

Conservation of momentum results in energy partition between the electron and the ion in the inverse ratio of their masses; in the least favourable case (H_2) the mass ratio is ca. 10^4 and thus the error in equating the electron energy with ($h\nu$ - I) is about 1 part in 10^4; for larger ions it will usually be much less than this.

A photoelectron energy spectrum shows the number of electrons having kinetic energy between E and $E + \Delta E$ as a function of that energy. An ideal spectrum would consist of a number of lines equivalent in order and spacing to the orbital energies in a conventional energy-level diagram of the ground-state of the molecule. Each line is associated with the formation of a positive ion in either its ground or some excited state.

Pre-lab 2: MO diagram and PES spectrum for nitrogen

Look up, if you do not already know, the MO energy level diagram for the nitrogen molecule. Sketch it in your lab notebook and, assuming electrons can be removed from any energy level, sketch what the PES spectrum should look like, in the absence of any effects due to vibration or rotation.

The relative intensities of the lines in such a spectrum will be governed by the numbers of each type of electron present, i.e. by the orbital degeneracy, and, provided that the total light absorption is small, by the photoionization cross-sections σ_i. The relative intensities should be independent of pressure until electron-molecule collisions become important.

σ_i decreases as ($h\nu$ - I) increases, so the peaks corresponding to high ionization potentials should be larger than those for the lower ones, but not by factors greater than about two under the conditions used in this experiment. The spectral slit width increases nearly linearly with electron energy and bands for I.E. near 21.22 eV (the energy of the exciting radiation used in the experiment) are correspondingly weaker than those of lower I.E.

Franck-Condon effects

Energy partition between the vibrationally excited ion and the electron is affected by the degree to which the ion formed upon loss of the electron is vibrationally excited. If a non-bonding electron is removed to form the ion, the geometry of the molecule should not change much upon ionization (as we would expect no significant change in the strength of the bonds). The ion will then generally be formed with no more vibrational energy than it had in the ground state and the Franck-Condon factor will be at its greatest for transitions for which $\Delta v = 0$.

In such a case, we expect a single strong peak in the electron energy spectrum at the energy appropriate to the $v'(0) \rightarrow v''(0)$ transition, or a short progression of peaks in which the $0 \rightarrow 0$ transition is much the strongest.

By contrast, if a bonding (or antibonding) electron is removed, there may be a significant change in molecular geometry. The ion may then be formed in a vibrationally excited state, and a series of peaks in the electron energy spectrum corresponding to the $0 \rightarrow 0$, $0 \rightarrow 1$, $0 \rightarrow 2$, ... transitions will appear, with intensities again determined by the appropriate Franck-Condon factor.

If the energy resolution is less than the gap between vibrational energy levels <u>in the ion</u>, the spectrum appears as just a broad band, commencing at the electron energy corresponding to the $0 \rightarrow 0$ transition. If the resolution of the instrument is sufficient to resolve this structure, the vibrational frequencies of the ion can be determined. Because the vibrational frequency is related to the molecular force constant (i.e., the bond strength), this parameter can in principle be determined from the spectrum.

<u>Pre-lab 3: Molecular vibration and Franck-Condon Factors</u>

If you are to fully interpret your PES spectra, it is important that you properly understand the effect that vibration has on the appearance of the spectra. Draw a diagram showing two Morse curves, for the ground state of N_2 and for the molecular ion after removal of a bonding electron. Show a few vibrational energy levels and wavefunctions in each potential well and use your diagram to explain in one paragraph why transitions linking the two states should show significant vibrational structure.

The PES Instrument

The instrument in the Teaching Laboratory uses a helium resonance line light source ($h\nu$ = 21.22 eV) produced by passing a continuous electric discharge through a low-pressure flow of helium. The energy of the electrons is determined using an electron energy analyzer based upon the focusing properties of the electrostatic field in a cylindrical condenser [5].

The main vacuum chamber containing the analyzer, the electron detector and electron multiplier is pumped by an oil diffusion pump backed by a rotary pump. The vacuum and gas handling systems are shown diagramatically on the front face of the instrument, and photographs of the (gold-plated!) interior of the main chamber are kept in a file beside the instrument (for interest only).

Experimental

Layout

Before starting, familiarize yourself with the controls of the instrument and its layout. The internal arrangement of the instrument is traced on the front panel. Lines in black denote connections between gas inlets and reservoirs, or between reservoirs and the main chamber. Lines in green show connections to rotary or diffusion pumps. Red lines show connections to pressure gauges. Work out the flows of gas through the instrument by studying the tracing on the front panel; take time to understand the layout.
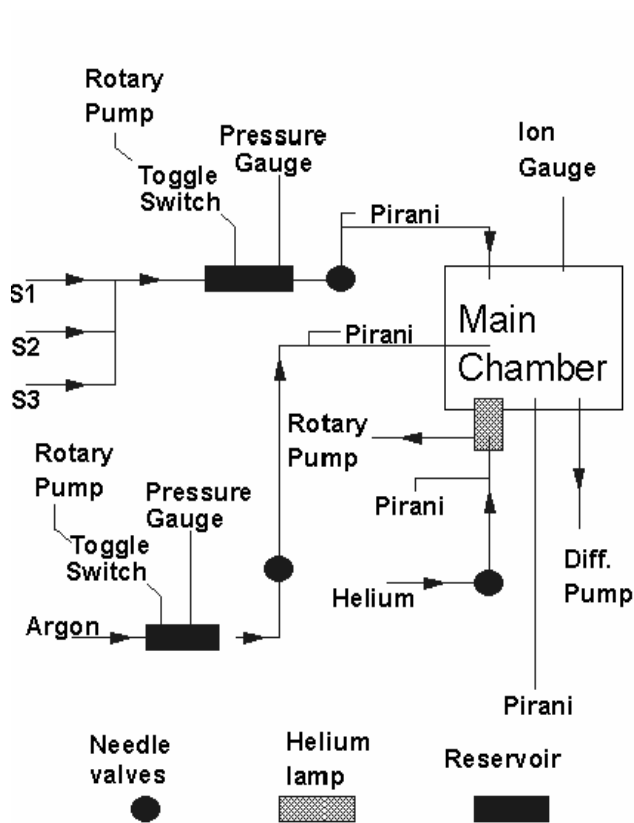

Fig. 1. A schematic of the photoelectron spectrometer.

Note: A complex instrument of this sort can be seriously damaged by rough handling. <u>In particular, the needle valves need only to be turned *gently* to close and open them. If you turn them hard you will ruin them.</u> Needle valves are extremely expensive and are time-consuming to replace; any repair work will probably mean that you have to abandon the experiment. If in any doubt about use of the needle valves, gas cylinders, or any other part of the spectrometer, consult a demonstrator.

The instrument has two gas reservoirs which can be (separately) connected to the main ionization chamber, or pumped out. Check for any additional instructions beside the instrument, since you may be using both or just one of these reservoirs.

The electronics rack controls the helium lamp and detector voltages. A PC, attached to the instrument, is used to control data gathering, display the spectrum and to send it to a suitable plotter.

Setting up: Initial check

When you start the experiment

☒ all needle valves should be closed,
☒ electronics in the rack should be off,
☒ the red diffusion pump light indicator should be on.

Check that the instrument is in this state; if it is not, consult a demonstrator or technician before proceeding.

a) Start by checking the helium supply. Helium is provided from the large gas cylinder to the rear of the instrument. The regulator will probably have been left closed. Turn it on as follows.

Ensure that the blue needle valve is closed (turned fully <u>clockwise when viewed from above</u>). Closing the needle valve at this stage will prevent a sudden surge of gas from passing into the instrument when the regulator is opened.

b) Check that the regulator valve (the winged handle in the centre of the regulator) is closed. In regulators of this sort, the valve is "closed" when the winged handle has been turned fully <u>anti-clockwise when viewed from above</u>. Turn this handle gently anti-clockwise until you come to a stop, then turn it back slightly. Do not leave it set hard against the stop and do not turn it clockwise yet, or you will risk a sudden release of gas into the apparatus and possible damage to the gas line.

c) Now that the regulator is closed, it is safe to open the main valve on the cylinder. Cautiously open this until a pressure registers on one of the regulator pressure gauges; gas is now at full cylinder pressure within the regulator.

d) Slowly turn the winged handle clockwise when viewed from above. There will be almost no resistance initially, but soon you will feel slight resistance as the handle is turned. Watch the low pressure gauge on the regulator, and once a positive pressure registers, stop turning. You have now set a low pressure for the regulator output.

e) Open the blue needle valve one turn to allow helium into the connection to the instrument.

Electronics

Check that the channeltron slider (middle panel, to the right between the meters) on the electronics panel is in the 'off' position, then press the Power button. Turn on the PC monitor. The PC may already be on but if it is not, turn it on.

Start the PES program by double-clicking on the "PESexperimentnew" icon. When the control panel appears, maximize it so that all controls are visible.

Main chamber pressure

The ionization gauge at the lower left of the front panel shows the pressure in the main chamber. Check the pressure now as follows:

Turn the knob on the front of this gauge to 10^{-3}, then momentarily move the switch just below the meter to 'on'. The filament at the top of the instrument should light. If it does not, or lights for only a few seconds and then goes out, check the setting of the knob, check that all needle valves are closed, and that the diffusion pump is on (red light towards the bottom right of the front panel lit). Wait 30 seconds then try again. If the filament will not stay on, consult the technician. Once the pressure in the chamber has settled, record it. It should be below 1×10^{-3} mm Hg. Having checked that the pressure is within acceptable limits, turn the ionization gauge off; it will not be needed again. (The filament produces a high background count rate which would swamp your spectrum if it were left on).

Helium lamp

Once lit, you will be able to view the spectrum of the helium lamp through a grating situated on the front panel. Before lighting the lamp, look through the grating. You will observe a broad continuous rainbow-like spectrum from scattered ambient light which you can compare in a moment with the spectrum of the helium lamp.

Open the helium needle valve about half a turn, wait ten seconds, and press the 'helium' button on the electronics rack to provide power to the lamp. The analogue meter showing current supplied to the lamp (electronics rack) will jump from 0 to around 15mA. The helium pressure should settle somewhere between 1 and 0.3 torr. If it is not within this range adjust the pressure using the needle valve.

Check the spectrum of the lamp through the grating; the continuous band due to room light should now have a few strong lines superimposed upon it. You should also be able to see the peach-coloured emission from the lamp directly by lifting out the grating, which is the size and shape of a 35 mm slide. If you still see only the background spectrum of room light, consult a demonstrator.

Introduction of samples

You are now ready to admit gas into the sample reservoir. The argon spectrum, which you will record first, consists of a pair of lines whose position is accurately known, and can be used to calibrate the spectra of other samples by providing an accurate scale by which to measure the voltage at any position in the spectrum. (A similar procedure is widely used in IR spectroscopy: a gas-phase calibrant showing lines of accurately known wavelength may be used to superimpose calibration lines on the spectrum of a sample.)

Filling the Argon reservoir

Check that the regulator and needle valve on the argon cylinder are closed. Ask the technician for two bladders which can be used for argon. Either fill these with argon yourself if you are confident about using the gas cylinder, or ask the technician to do this for you. Clamp the outlet of the bladders and then fit them to the two inlet tubes on the left of the instrument.

Pump out both reservoirs as follows:

a) Close the needle valve connecting the reservoir to the main chamber; open the needle valve which connects the reservoir to the bladder so that the connecting tube can be pumped out, but do not unclamp the bladder.

b) Open the toggle valve on the reservoir by lifting it so that it is at right angles to the plane of the panel. The indicator on the circular pressure gauge nearby will quickly settle near 760 mm - the reservoir is now pumped down.

c) Close the toggle valve.

d) With the toggle valve connecting the reservoir to the pump now both closed, open the clamp on the bladder to allow gas to expand into the reservoir. Leave the bladder connected and the clamp undone.

e) Repeat with the second reservoir.

f) Open the needle valve connecting either reservoir to the main chamber about one turn to give a pressure of argon of roughly 0.8 torr. Turn on the channeltron, which supplies power to the detector, and set the voltage to approximately 2.2 kV. Do not move the slider to the top of its travel, or you may damage the detector.

Setting the electronics

You control data collection, though not the instrument itself, through the computer.

The **offset voltage** determines the position of the centre of the spectrum. To adjust this click on the offset knob and drag it, or type in the required value in the panel under the knob.

The **scan size** determines the span in electron volts from one side of the plotting area to the other. You can choose spans of 20V, 4V or 1V.

Most of the controls on the electronics unit are not operative. The remainder should not be altered.

You should find that the **Range** has been set to 10^3 and the **Discriminator** to around 0.07. You can ignore the other controls.

Although there are not many adjustable parameters available to you, the quality of your spectrum is intimately related to the values chosen for these, in particular the pressures used for both the sample and helium. This is because (a) the intensity of the light emitted from the lamp is strongly correlated with the helium pressure, and (b) if the sample pressure is too high the spectrum degrades because of many electron-gas molecule collisions, while if the pressure is too low the signal falls away because too few electrons are released.

The spectrum is also strongly dependent upon the setting of the discriminator.

Your initial task is to gather a series of argon spectra so that you can determine optimum values for these two pressures.

The equipment should now be running with helium flowing through the lamp and argon through the sample chamber. Start with a 20eV range, (which will ensure that you see the spectrum if there is one!) To begin accumulation of data, press the green "Start/Stop" button on the computer screen. The indicator next to this will change from "Stopped" to "Running". To stop data collection, press the "Start/Stop" button a second time. You can delete a spectrum by pressing the "Clear" button.

Gather counts for a short time (perhaps a couple of minutes) – you will see the spectrum develop on screen. If there is no evidence of peaks (you should see a doublet) ask for help from the demonstrator. Check that the plotter is turned on, then print out the spectrum by clicking the right mouse button and selecting the plot option. You can also use the mouse to change the appearance of the spectrum, for example if you wish to zoom in or out.

Once the spectrum has been plotted, change the pressure of argon or helium and repeat. You will probably need to try about four values of each pressure to determine the optimum pressures for both sample and helium.

After you have determined the best settings for the pressures, record a final spectrum using an expanded range to give the highest quality spectrum you can obtain. You can

assume that the optimum helium pressure will not change during the experiment, but you may need to make adjustments to the sample pressure when you change to different gases.

Nitrogen

Spectra of other sample gases are gathered in an entirely analogous way. Ask the technician to get samples of nitrogen for you; like the argon, these will be supplied in bladders, which are a convenient and safe way of transporting small quantities of gas.

The nitrogen spectrum will show three bands (band systems). Each arises from the creation of an ion in a different electronic state. The fine structure which should be visible is due to vibrational excitation of the ion (not the neutral molecule!).

Because of the presence of fine structure, a suitable choice of instrument parameters is important if you are to record a good spectrum. Investigate, in a systematic way, the effect of the adjustable controls on the appearance and quality of your spectrum.

Hydrogen

Record a spectrum on the 20eV range, then on an expanded range so that as many peaks as possible can be seen (you may see as many as 14 peaks). Use your experience optimizing the nitrogen spectrum to select appropriate control settings to give the best possible spectrum. The spectrum is fairly weak, and overlapped with considerable noise, so you will need to exercise some care in optimizing it.

Carbon dioxide

Record the spectrum on the 20eV range and each band on an expanded scale.

Calculations

Argon

Estimate the relative intensities of the two peaks. Why are there two peaks? What can be deduced from these intensities? What should the intensity ratio be? The argon ionization potentials are 15.759 and 15.937 eV. Use these figures to derive a relationship between the gap between two peaks on the printout, measured in cm, and the energy difference between them.

Nitrogen

Using the spectra recorded at different instrument parameter settings, discuss the effect which the settings have upon the appearance and quality of the spectra.

On a suitable spectrum, determine the positions of all peaks in the nitrogen spectrum. Deduce the vertical and adiabatic ionization energies for the three bands.

Calculate the vibrational frequency of the ion in the three states and, comparing this with the corresponding frequency for the molecule in its ground state [6], sketch possible potential energy curves for the ion.

Hydrogen

Measure the energy intervals between adjacent peaks, ΔG, and plot *vs* $(v+\frac{1}{2})$. Attach a copy of the resulting graph and calculated best fit line to your report. Calculate D_e and D_0 (why are there two dissocation energies?); compare with the value obtained from the cycle

$$H_2^+ + e^- \rightarrow H_2 \rightarrow 2H \rightarrow H^+ + H + e^-$$
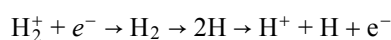
The ionization energy of H is 13.598 eV.

Carbon Dioxide

Measure the vertical and adiabatic ionization energies and the mean vibrational intervals. Sketch potential energy curves relative to the molecular dimensions for symmetric stretching, which indicate how Franck-Condon control of ionization accounts for the relative intensities of the peaks in each progression.

On the assignments for these peaks given in, for example, Ref. 2, predict what allowed transitions might be observed in the optical spectrum of the CO_2^+ ion. Calculate the wavelengths of the 0 - 0 transitions in each case, and estimate where the most intense emissions would be observed.

References

1. Stewart, *Ann. Reports*, 1961, **58**, 14.
2. *Molecular Photoelectron Spectroscopy*, D.W.Turner *et al.*, Wiley, 1970.
3. *Principles of Ultraviolet Photoelectron Spectroscopy*, J.W.Rabelais, Wiley, 1977. [Hooke Ca 115]
4. *Spectroscopy*, Vol III, Straughan and Walker, Methuen Science Paperbacks.
5. *Electron Optics*, O.Klemperer, 3rd ed, Cambridge University Press, 1971.
6. *Electronic Spectra of Diatomic Molecules*, G.Herzberg, Van Nostrand Reinhold, New York and London, 1950. [Hooke MF4 Vol 1].

a) Observation: Helium lamp will not light.
Indicates: No power.
Solution: Turn on power to the lamp by pressing the Helium Lamp button on the electronics unit.

b) Observation: Spectrum is of poor quality, showing little apart from noise (see also problem e).
Indicates: (i) Helium lamp not lit. (ii) Helium lamp is lit, but gives only an air discharge (lamp does not show pinky helium lines). (iii) No flow of sample into the ionization chamber.
Solution: (i) Press Helium Lamp button on electronics to provide power to lamp. (ii) Check that the helium cylinder is open, that the regulator has been adjusted to give a (small) positive pressure on the outlet, and that the helium needle valve has been opened to give a (small) flow of helium through the lamp. (iii) Check that sample is present in the reservoir and that the appropriate needle valve is slightly open.

c) Problem: Spectrum shows only a large sloping and featureless (but perhaps noisy) background.
Indicates: (i) Helium lamp not lit or no helium flow through the lamp. (ii) Too little sample. (iii) Sample contaminated with air, giving a spectrum consisting of the oxygen and nitrogen spectra overlaid.
Solution: (i) See above. (ii) Check that sample is present in the reservoir and that the appropriate needle valve is slightly open. (iii) Evacuate sample reservoir then refill with a fresh sample, ensuring that air is pumped out of the tube connecting the reservoir and the gas balloon before gas is fed into the reservoir.

d) Problem: Spectrum is strong, but shows poor resolution.
Indicates: (i) Sample pressure too high, so electrons are striking molecules or each other before reaching the detector. (ii) Diffusion pump is off, as shown by the red diffusion pump indicator light being out.
Solution: (i) Reduce rate of flow of sample into chamber. (ii) Ask the technician to reset the diffusion pump.

e) Problem: Spectrum shows a large number of (perhaps quite impressive!) peaks equally spaced across the entire scan range which seem to be independent of instrument parameters.
Indicates: Not a wonderful spectrum, unfortunately, since in a real spectrum the peaks would get progressively closer together (reflecting the diminishing gap between successive vibrational levels). Setting of the discriminator is wrong.
Solution: Adjust the discriminator to reduce the number of counts per second (which you can judge using the meter on the electronics rack).

f) Problem: The red diffusion pump indicator light on the right side of the instrument is off.
Indicates: Diffusion pump cut-out has operated (sensing either a reduction in pressure of the cooling water or, more probably, too high a pressure of gas in the chamber)
Solution: Reduce the flow of sample and/or helium through the sample chamber, then ask a technician to reset the pump.