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HIGH TEMPERATURE UV PHOTOELECTRON SPECTROSCOPY

Sefik Süzer
(Ph.D. thesis)

March 1976

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HIGH TEMPERATURE UV PHOTOELECTRON SPECTROSCOPY

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HIGH TEMPERATURE UV PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

A commercial spectrometer, the model PS-18 Perkin Elmer Photoelectron Spectrometer, was modified to achieve better vacuum to reach temperatures of up to 800°C. It was also provided with a better data handling system.

Atomic vapors of Ca, Sr, Ba, Zn, Cd, and Hg were studied by HeI (or NeI) radiation, using photoelectron spectroscopy. Several satellite lines were observed and were attributed to initial state configuration interaction in the ground states of these atoms. The relative intensity ratios of the 2D lines of Zn, Cd, and Hg were studied by different radiations, using both HeI and HeII lines.

Pb in the form of atomic vapors was studied by HeI radiation. Relativistic effects were observed to cause the ratio of the peaks arising from $Pb^+(s^2p; ^2P_{1/2})$: $Pb^+(s^2p; ^2P_{3/2})$ states to be 1.000:0.071 instead of 1.000: 2.000 as given by the simple L-S picture. Several final states inaccessible from an s^2p^2 initial state configuration were observed and attributed to admixtures of the configurations sp^2d and s^2d^2 .

Atomic and molecular bismuth were studied by HeI radiation. Atomic Bi showed again satellites due to admixtures of configurations in the ground state. Molecular Bi_2 lines were observed and assigned to the

corresponding states of Bi_2^+ . The ordering of $(\sigma_g, 6p)$ and $(\pi_u, 6p)$ was observed to be reversed from N_2 , and this reversal was correlated with the increase in the internuclear distance in the isoelectronic series N_2 , PN , P_2 and Bi_2 .

I. INTRODUCTION

The largest portion of this thesis deals with observation of satellites which give information about the electron-electron correlation in the valence shells of atoms, using the experimental technique of photoelectron spectroscopy. High temperature techniques had to be applied to obtain the samples in atomic form, since very few elements exist in the form of neutral free atoms at room temperature.

As the name electron-electron correlation implies, it involves the correlated motion of two or more electrons confined in a region of space. In the case of the "independent particle" or "Hartree-Fock" approximation this effect is most important for the orbital into which two electrons of opposite spin are put. This approximation inherently neglects the correlation of electrons among themselves. "Configuration Interaction" is a formalism which takes this into account and improves the description of such a system. In this formalism one writes the wave function as a linear combination of all possible configurations of the same symmetry, i.e.,

$$\Psi = c_1 \Phi_1 + c_2 \Phi_2 + c_3 \Phi_3 + \dots \quad (1)$$

where the Φ_i 's are the independent particle wave functions of different configurations. One of the coefficients (say c_1) is going to be large compared to the others, and this configuration (Φ_1) is called the "main" one. In the course of photoionization one of the electrons is removed to infinity from the atom, but the remaining one finds itself without the necessity to correlate any longer. Hence photoionization can be

viewed as breaking the parts of the wave function ($\phi_1, \phi_2, \dots$ etc.) which were otherwise held together. Very simplistically one can say that the photon ionizes electrons from different configurations ($\phi_1, \phi_2, \dots$ etc.); this results in observation of ionic states corresponding to removal of an electron from ϕ_1 and removal of an electron from ϕ_2 and so on. Their observed experimental intensities will be roughly proportional to the squares of the coefficients $c_1^2, c_2^2, \dots$ etc. Since one of them (c_1) is larger than the others, its intensity will dominate over the others; we now call it "the main photoemission line" and the others with much smaller intensities are termed "the satellite lines". As an example, one writes the ground state wave function of He as;

$$\Psi = c_1 \phi(1s^2) + c_2 \phi(1s2s) + c_3 \phi(2s^2) + c_4 \phi(2p^2) \dots (2)$$

In the photoemission spectrum of He one would see $\text{He}^+(1s;^2S)$ carrying a large portion of the intensity (main line) from the main configuration and $\text{He}^+(2s;^2S), \text{He}^+(2p;^2P), \dots$ etc. in relatively small intensities, resulting from the admixtures of the other configurations.

Chapter II gives the experimental details. Chapter III deals mainly with satellites observed in Group IIA and Group IIB atoms. Chapter IV deals with satellites and relativistic effects in the valence shells of Pb atom, and Chapter V again discusses the satellites in atomic Bi and also attempts to assign the photoelectron spectrum of the Bi_2 molecule.

II. EXPERIMENTAL

A. General Description

The experiments can simply be described as follows. The gaseous samples are bombarded by UV photons of known energy. Some of the photoelectrons produced enter an electrostatic energy analyser. The photoelectrons are deflected in an electrostatic field maintained between two concentric curved plates, the inner one being positively charged. For a particular field value, only electrons of a particular energy pass through the exit slit and enter an electron detector. The electron energy is proportional to the potential drop across the plates;

$$E = e.V \quad (1)$$

and the proportionality constant is fixed for a given geometry and analyzer design. The kinetic energy of the electron can be determined from knowledge of the electrostatic field; in turn the electron kinetic energy can be used to find the characteristic of the sample, "the binding energy", defined by the following energy conservation equation;

$$h\nu = E_k + E_b \quad (2)$$

E_b is the binding energy and $h\nu$ is the photon energy.

The applications of this technique to atomic, molecular, and solid-state problems have been discussed in great detail.^{1,2,3,4}

B. Perkin Elmer PS-18 Photoelectron Spectrometer

1. The Original Instrument

The instrument used in this work is a commercial spectrometer, the model PS-18 Perkin Elmer Photoelectron Spectrometer. The design principles and details are given elsewhere² and a schematic illustration of the spectrometer is given in Fig. 1.

An intense beam of photons of energy 21.21 eV (95% or higher spectral purity) is produced by an electrical d.c. discharge in helium. The photons are directed into the ionization chamber through a capillary tube which collimates the photon beam and also helps to prevent contamination of the discharge tube by the sample, since there is no window in between. The photoelectrons are produced in the ionization chamber and are allowed to enter the electron analyzer through a slit of dimensions 0.006" $\times$ 0.5" and analyzed by the electrostatic deflection in a field between two concentric curved plates, and pass through the exit slit, the width of which can be continuously varied up to 1/16 inch (1.6 mm). The electrons passing through the exit slit enter the electron multiplier (Mullard B419BL). The analyzer is encased in a metal shield to protect it from external magnetic fields. The magnitude of the analyzing potential is controlled by a potentiometer driven by the recorder pen scanning mechanism and the chart abscissa is calibrated in eV binding energy.

The main vacuum chamber is pumped through a water-cooled baffle valve, by means of an oil-filled 3-inch diffusion pump (Edwards Pump, model EO2) backed by a two-stage rotary pump. The helium discharge tube is pumped differentially by another rotary pump. The base pressure in the

main vacuum chamber is about 5×10^{-6} torr and goes as high as 10^{-3} torr when running a sample. This rise is due to (i) He leaking into the chamber which is kept at about 300 microns in the discharge tube, (ii) the sample leaking into the chamber through the entrance slit. Sample pressures of typically 10-30 micron are used.

The upper part of the discharge tube is the anode which is made out of copper and delivers the heat into the ionization chamber where solid samples can be heated up in vacuum. The temperature is controlled by the air (or water) cooling jacket around the copper anode. Temperatures of up to 400°C can be obtained with this arrangement.

Some of the spectra were taken using this original arrangement, but it has several shortcomings and had to be modified to fit our requirements.

2. Shortcomings of the PS-18 Spectrometer

(a) Vacuum system

i. The water-cooled baffle is not effective for keeping the oil from creeping up into the main chamber, nor for keeping the diffusion pump oil from being contaminated with the sample. Hence better trapping is needed between the pump and main chamber.

ii. The helium rotary pump contaminates the discharge tube; hence the oil cracks in the discharge tube when the lamp is turned on.

iii. The automatic control solenoid valves are not reliable nor are they clean.

(b) Data collection system

Only one analog spectrum is produced for each scan, so no multiple runs can be made. For a better signal-to-noise ratio one needs to put a

larger time constant (integrating over a larger time interval) which means a larger time overall. The longer time is undesirable due to fluctuations both in the photon flux and in the sample pressure in the ionization chamber. One needs to be able to take fast spectra with multiple runs added onto each other.

(c) High temperature system:

Only 400°C can be reached, whereas this work requires higher temperatures.

The next section will describe the modifications to overcome these problems.

3. Modifications of the PS-18 Spectrometer

(a) Vacuum system

ii. A right-angle liquid nitrogen trap with a larger area of water-cooled baffle is placed between the diffusion-pump and the main vacuum chamber. This enables us to reach a base pressure of better than 1×10^{-7} torr, and more important no oil creeps up into the chamber.

ii. The helium pump-out line is passed through the outside jacket of the L.N. trap, which prevents any rotary pump oil from getting into the discharge tube, enabling us to keep the tube cleaner.

iii. All the automatic control solenoid valves are bypassed and replaced by manual ones.

All three modifications were suggested and designed by Gene Miner of LBL.

(b) Data collection system

The original analyzer power supply is replaced by a digital supply

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with a 4096-step and 0-20 volt range. The digitally controlled analyzer supply provides control signals so that photoelectron counts are accumulated in 256, 512, 1024, 2048, or 4096 channels of a multichannel analyzer memory in an MCS mode. The schematics and parts of this are shown in Fig. 2. Mr. Joseph Katz and Mr. Vincent Randolph suggested and designed the necessary electronics.

This system enables us to take a spectrum of 7, 14, 28, or 56 eV range in 1, 2, 4, 8, or 16 minutes and store it in 1024, 2048, or 4096 channels of memory. Several scans can be taken and added together. The data can be taken from an X-Y plotter, dumped on a magnetic tape/or paper tape, or printed out on paper. We have been able to take spectra for as long as 42 hours non-stop which corresponds to several hundreds of scans with this system. Also data manipulations are possible (fitting, deconvoluting, and area determinations).

Figure 3 shows the same spectrum taken with two different systems. The upper one is the original analog spectrum of Cd taken at 290°C which took about 2.5 hours for the whole region. The lower one is the same spectrum taken with our new digital system for the same amount of time and the same temperature. The $^2P_{1/2}$ and $^2P_{3/2}$ (see chapter for explanation of Cd spectrum) peaks of Cd^+ around 14.7 eV can hardly be picked up from the background in the upper spectrum whereas they clearly show up in the lower one, relative intensities being the same. Since most of this work is devoted to satellite lines of few per cent intensity this was a very important improvement.

(c) High temperature system

C. S. Fadley, et al.⁵ were the first to construct high temperature

devices for use in photoelectron spectrometers. They built an oven and used it to study vapors of europium and ytterbium. Their idea was to use non-inductively wound tantalum wires enclosed by boron nitride plates and heat the sample by passing d.c. current through the wires. Banna, et al.⁶ used a similar oven in their work. Many different designs have been suggested. Khodeyev, et al.⁷ used an oven similar to that of Fadley, et al. to study lead and bismuth vapors. Some others suggested Laser heating⁸ as a cleaner way. The Perkin Elmer PS-18 utilizes the heat generated in the d.c. discharge plasma of helium to heat the samples, but as mentioned earlier can only go up to 400°C.

We wanted to construct an oven which would be easily demountable and cleanable and relatively cheap, to study reactive samples such as atoms. Fadley's design was attractive and simple. Tantalum wire was a good choice for its ruggedness and inertness. Boron nitride was chosen for easy machining and finally a tantalum ionization chamber and tantalum shields were chosen again for inertness and easy cleaning. Essential components of the oven are shown schematically in Fig. 4. The whole assembly fits onto the anode of the PS-18 system.

The tantalum wires are non-inductively wound and encased in two cylinders of boron nitride. The wire concentration is more on the lower half of the boron nitride than the upper one, giving effectively higher temperature around the slit which we found to improve electron flux through the slit into the analyser. Fig. 5 shows the removable components; each component is explained in the caption. The samples are loaded into the stainless steel capsule and put in the upper part of the tantalum ionization tube, the tantalum cover is put around it and the whole thing

is inserted into the boron nitride heater which again is enclosed with tantalum heat shield and the screws both ground and hold the different parts together. Fig. 6 shows how each component is put together and Fig. 7 shows all the components assembled together.

C. Present System and the Experimental Procedure

1. Performance of the high-temperature system

We have been able to use the oven up to temperatures of 800°C which required 1.5 amp. current (45 Watt) through the wires for heating metals to vaporize them. The spectra have been reproduced at least three times for each sample. Fig. 8 shows the spectra of N_2 at two different temperatures. Assignments are taken from earlier work.² At high temperatures we see a new peak at 16.40 eV apparent binding energy due to thermal excitation of N_2 molecules into the $v = 1$ vibrational state in the ground state which is 0.291 eV separated from the $v = 0$ vibronic state (hot bands). At room temperature only $v = 0$ state is populated, but at 700°C the $v = 1$ state is becoming populated too. This feature was first observed by S. T. Lee et al.⁹

2. Use of the high temperature system

The samples, usually in the form of small pieces, are loaded into the stainless steel crucible in air and the oven assembled and put into the spectrometer in about 10 min.. Hence oxides are also introduced together with the metals, but usually do not give any appreciable vapor pressure; as a result no interference is detected. The metal samples used are 99.5% or better pure and we do not detect any impurity lines except in Sr where appreciable Ba impurity lines are observed. (see Chapter III) The gas pressure is never measured directly but the optimum operating temperature is determined for a count rate of $(1-4) \times 10^3$ counts/sec on the most intense peaks. Then the same spectra are taken at temperatures of

± 30 C from the optimum to differentiate between the inelastic loss peaks and the real photoionization peaks. Almost every spectrum contains one or more of these inelastic loss peaks, but they are easily identified. The temperature is monitored on top of the sample compartment outside the vacuum chamber by a thermocouple which reads approximately $15-25^{\circ}\text{C}$ lower than the temperature in the ionization chamber.

Since this work deals mostly with reactive metals, the ionization chamber and the other parts of the instrument (deflection plates, anode of the discharge tube etc.) get coated with the metals or oxides of them which charge up very quickly; as a result the electron flux into the analyzer is reduced and a loss in the resolution is detected as well. Coating these parts of the instrument with graphite (Dry graphite lubricant, Crown 8078) helps to keep the electron flux and the resolution for longer periods of time. Frequent disassembling and cleaning is necessary. Under these conditions a FWHM of 0.050 eV measured with Ar peaks (about 5eV kinetic energy) is continuously achieved, which corresponds to about 1% energy resolution.

3. Calibration of the Spectra

The constant in equation (1) is given more precisely,⁴ for the central ray of electrons and for the 127° cylindrical analysers, as;

$$E_o = \frac{V}{2} \ln \frac{r_1}{r_2} \quad (3)$$

r_1 = Radius of the inner plate.

r_2 = Radius of the outer plate.

V = Potential difference between the plates

E_0 = Kinetic energy of the central ray of electrons.

Hence the absolute value of E_0 can be calculated, for the present spectrometer $r_1 = 9$ cm and $r_2 = 11$ cm which gives the value of c as .10033. However, it is more instructive to use some other known lines for internal calibration of individual spectra because usually the apparent binding energies are shifted due to charging effects. Table I gives the photoemission lines commonly used in this work for calibration. The calibration gas (or gases) are introduced into the spectrometer together with the samples in a separate run.

4. Transmission of the Spectrometer

In a cylindrical analyzer of a set resolution the transmission of the electrons is proportional to their kinetic energies (i.e. $\Delta E/E =$ constant for the spectrometer). Hence the area under each peak divided by the central kinetic energy (E_0) gives a measure of the relative intensities of the individual peaks. There are three important factors which affect the relative intensities;

(a) Angular distributions:

The relative strength of each peak is a function of the collection angle and the total cross-section is dependent on this angle through the relation:^{10, 11, 12} for unpolarized light and randomly oriented atoms;

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

θ = Angle between the photon direction and photoelectron direction

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σ_{total} = Total integrated cross-section

$\sigma(\theta)$ = Differential cross-section at θ

β = Asymmetry parameter

θ can change from 0° to 180° . For the present spectrometer $\theta = 90^\circ$

reducing the equation (4) to

$$\frac{\sigma(90^\circ)}{\sigma_{\text{total}}} = \frac{1}{4\pi} \left(1 + \frac{\beta}{2} \right) \quad (5)$$

β itself can change between $-1 \leq \beta \leq 2$, hence a quantitative comparison of the relative intensities requires the knowledge of the asymmetry parameter.

(b) Inelastic scattering of electrons

Finite sample pressure causes the electrons to be scattered inelastically. The scattering probability is also a function of the energy of electrons; hence it affects the transmission of electrons at different kinetic energies. Corrections for this effect can be made by extrapolation methods,¹³ i.e. one measures the relative intensities of two different peaks at different sample pressures and extrapolates them to zero pressure. No such a correction is made for any spectra in this work. However, this effect is not very pronounced for kinetic energies over 5 eV and for moderate sample pressures (10 μ).

(c) Charging effects

As already mentioned the samples condense on or around the ionization region or the analyzer which causes charging and in turn affects both the resolution and the transmission of the electrons. This causes very severe discrimination especially for 1-2 eV energy electrons. Graphite coating greatly reduces this effect. Again it is not expected to affect

the electrons with 5 eV or higher energy.

5. Performance of the He Discharge Lamp:

The capillary discharge produces many discrete as well as continuous lines of HeI and HeII. Fig. 9 shows the photoemission spectrum of Hg. Table II summarizes the lines and their relative intensities measured for the Hg $^2D_{5/2}$ line without taking the photoelectric cross-section changes into consideration. The HeI line at 21.21 eV dominates and gives about 95% of all the distinct lines. Table II also gives the NeI and ArI lines used in parts of this work as well as the HI and OI impurity lines observed in the present set-up due to incomplete removal of H_2O .

D. Possible Improvements of the Instrument

The present Perkin-Elmer PS-18 Spectrometer can be improved in several ways:

- i. The vacuum system can be improved by making some parts bakable to get rid of water completely, which would help to solve the charging problem and the impurity lines out of the discharge tube.
- ii. Incorporating a carbon or polystyrene⁶ window to filter out the low energy lines and also the impurity lines.
- iii. Incorporating a pre-accelerating set-up before the entrance slit to increase the transmission of low energy electrons.
- iv. Incorporating an oven which can go to temperatures higher than 800°C.

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Table I. Photoemission Lines Used for Internal Calibration of the Spectra.

Gas	He	Ne	Ar	Kr	Xe	N ₂ (adiabatic)		
Ionization from	1s	2p	3p	4p	5p	$\sigma_u 2s$	$\pi_u 2p$	$\sigma_g 2p$
Binding Energy (eV)	24.580	21.656 21.559	15.937 15.759	14.665 14.000	13.436 12.130	18.759	16.691	15.579

Table II. Exciting Radiations Used in this Work.

Source	Type of transition	Commonly cited as	Wavelength ^(a) (in Å)	Energy (eV)	Relative intensity	Remarks
	$1s^2 \rightarrow 1s2p$	HeI α	584.334	21.217	100 ^(b)	
	$1s^2 \rightarrow 1s3p$	HeI β	537.030	23.086	4.5	
	$1s^2 \rightarrow 1s4p$	HeI γ	522.213	23.741	0.6	
		...	..	..	..	
He		...				
Capillary						
Discharge	$1s \rightarrow 2p$	HeII α	303.782	40.812	4	
	$1s \rightarrow 3p$	HeII β	256.317	48.370	0.25	
	$1s \rightarrow 4p$	HeII γ	243.027	51.016	0.06	
		...	..	..	..	
		...			-	
	—	HI γ	1215.67	10.199	-	Impurity lines from H ₂ O
	—	OI	1306.029	9.493	-	
	—	OIII	320.979	38.326	-	
Ne						
Capillary	—	NeI	743.718	16.6704	30 ^(c)	
Discharge			735.895	16.8476	100	
Ar						
Capillary	—	ArI	1066.659	11.623	-	
Discharge			1048.219	11.828	-	

(a). Ref. 15.

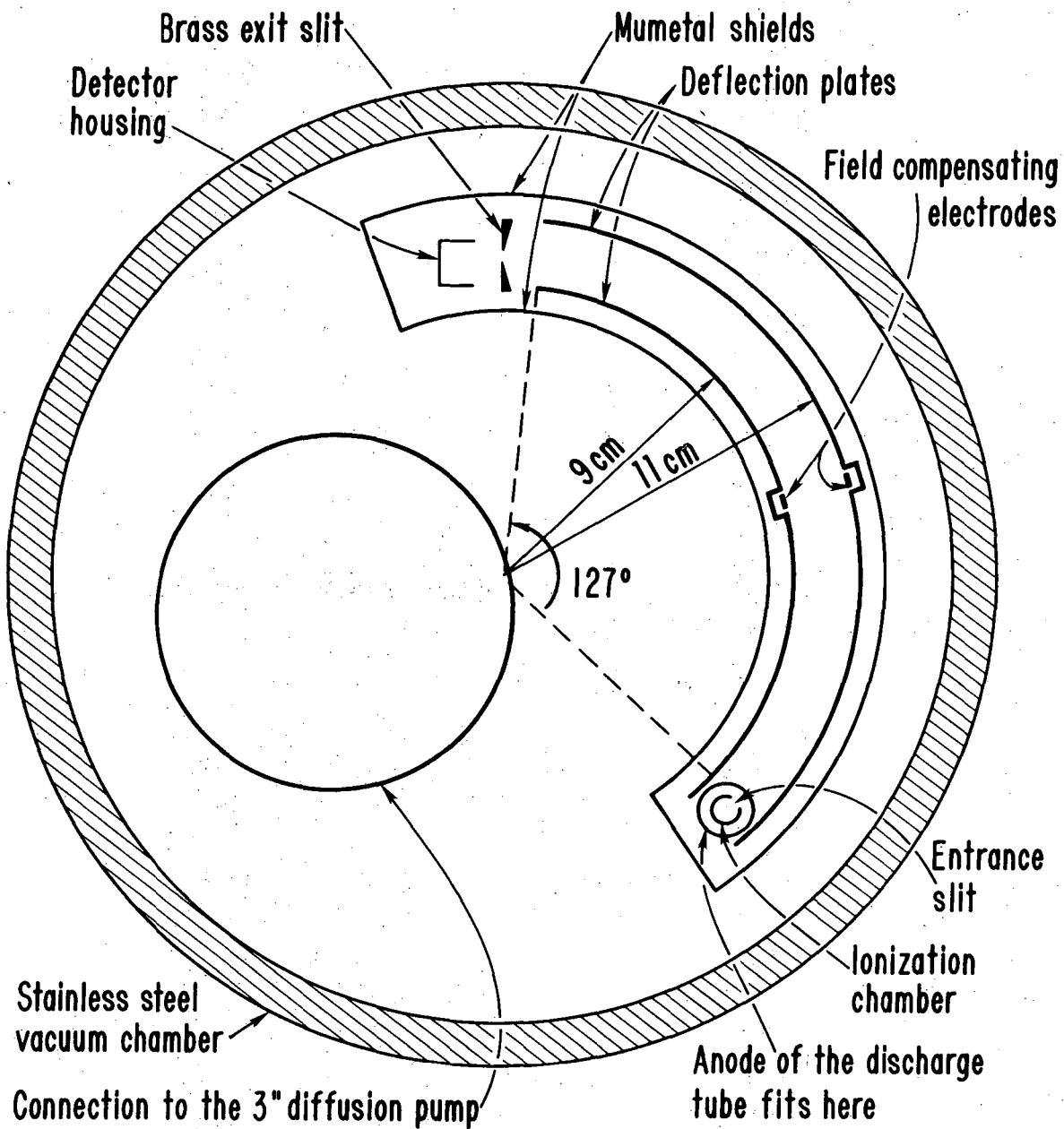
(b). Relative to $^2D_{5/2}$ line of Hg without taking the cross section effects into consideration.

(c). Relative to $^2S_{1/2}$ line of Ba (the main one).

FIGURE CAPTIONS

- Fig. 1 Schematics of the PS-18 Spectrometer.
- Fig. 2 Schematics of the Digital Data Collection of the PS-18 Spectrometer.
- Fig. 3 Spectra of Cd taken with, (a)- the original data collection system, (b)- the new digitally controlled system. ("I" refers to an inelastic loss and "s" lines are from HeI and HeII).
- Fig. 4 Schematics of the oven and the ionization chamber.
- Fig. 5 Components of the oven assembly. (From left to right) Screws which hold the different parts together and ground them. Tantalum heat shield and the defining slit. Boron nitride; the heating wires are in between the two layers of boron nitride. Tantalum spacer (fits to the window in the middle of the boron nitride). Tantalum removable cover. Ionization chamber (tantalum). Sample crucible.
- Fig. 6 Oven partly assembled.
- Fig. 7 Oven with all the parts put together.
- Fig. 8 Spectra of N_2 taken at, (a)-700°C, (b)-room temperature. The "hot band" at 16.4eV only shows up in (a). Assignments are from Ref. 2.
- Fig. 9 Spectrum of Hg. He discharge lamp produces both HeI and HeII radiations with varying intensities.

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Figure 1

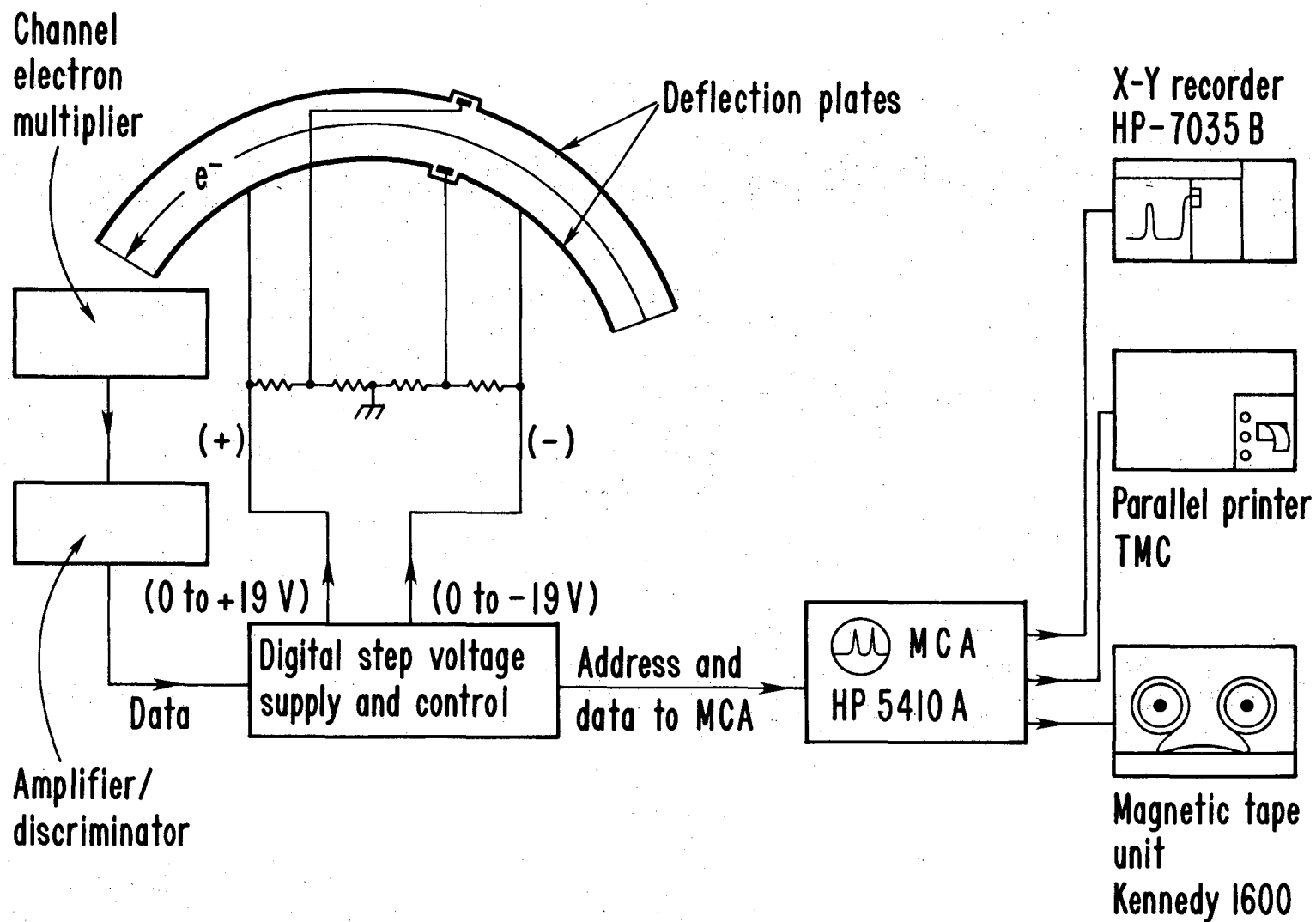
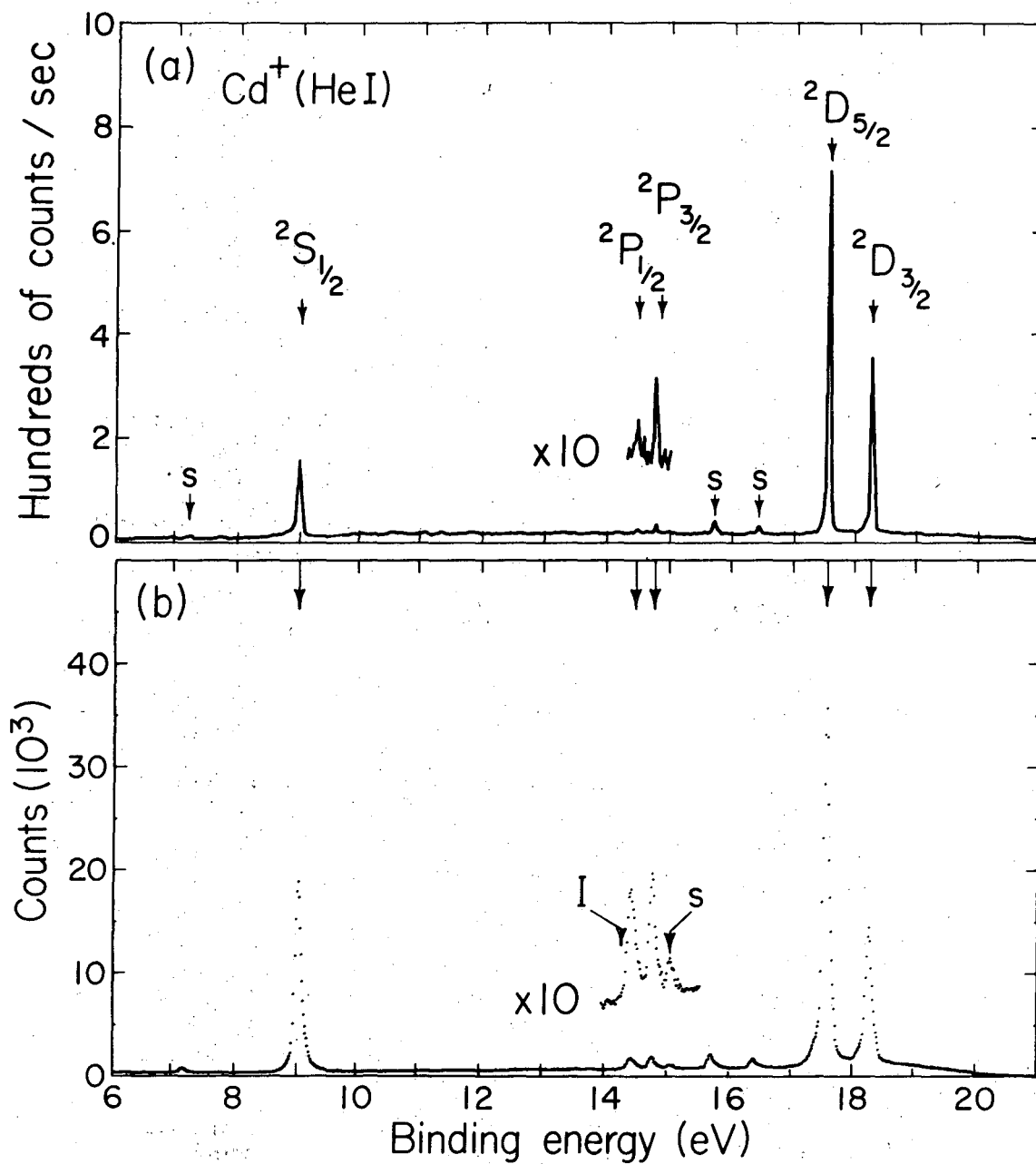


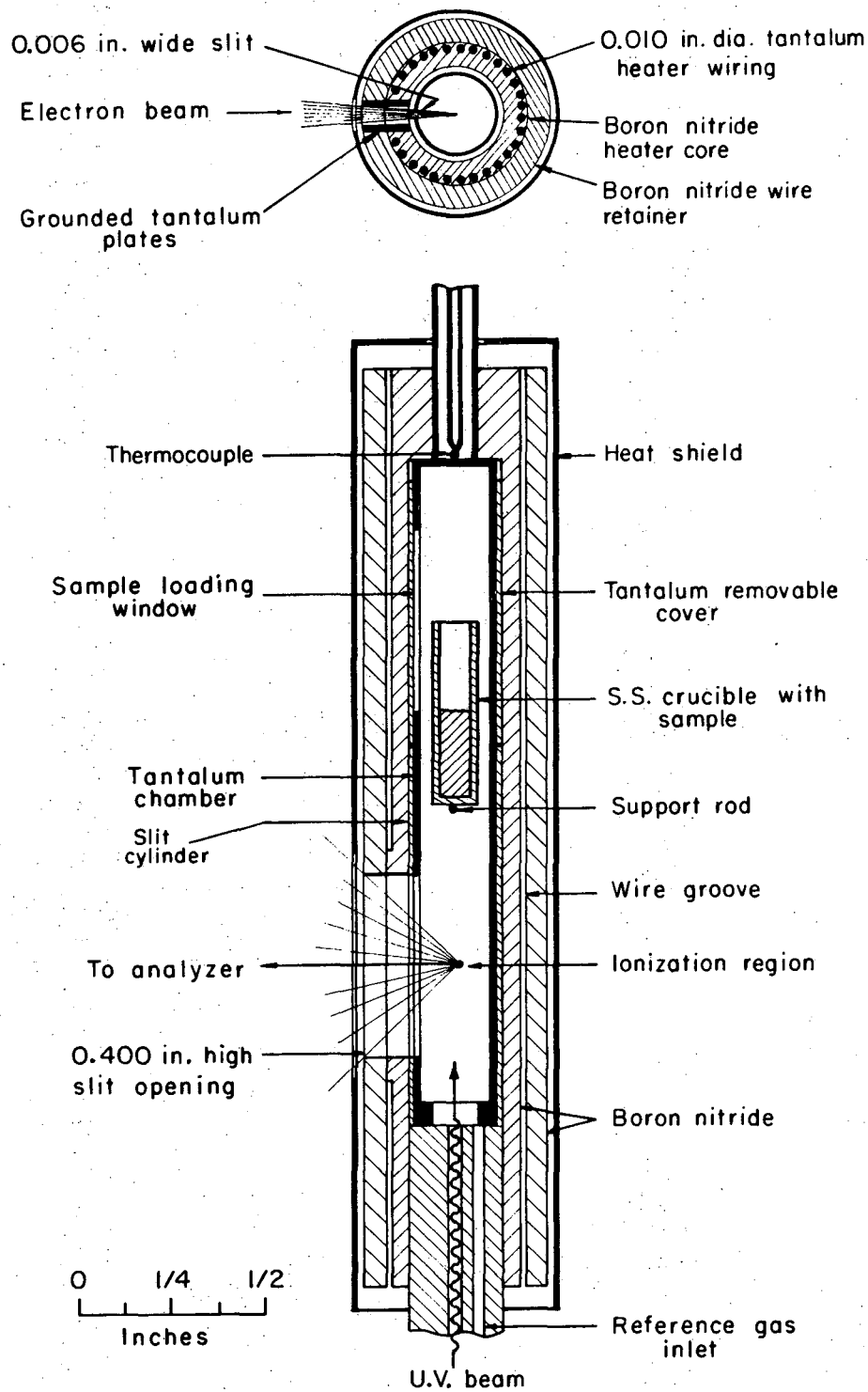
Figure 2

XBL 761-2032



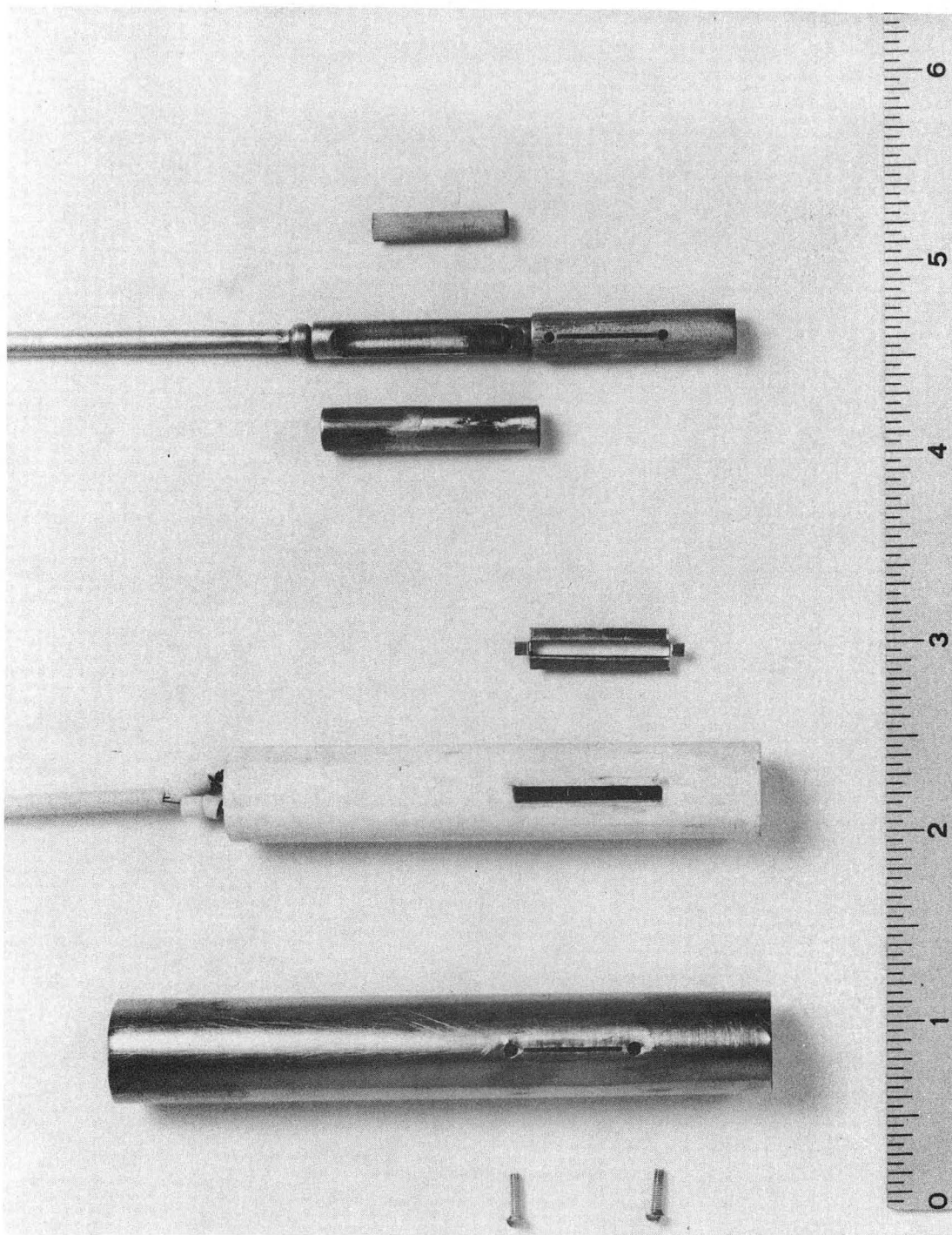
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Figure 3



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Figure 4



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Figure 5

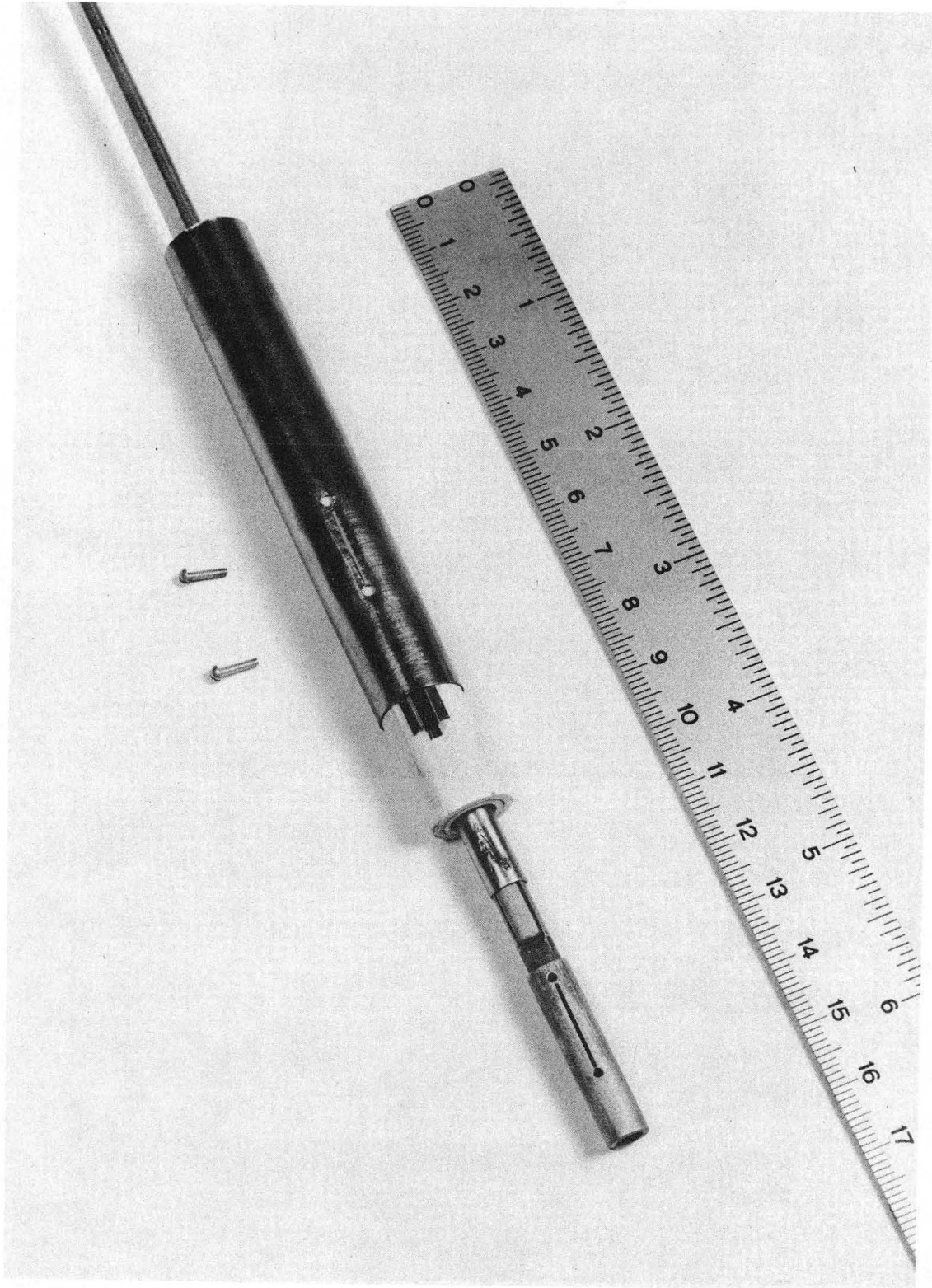


Figure 6

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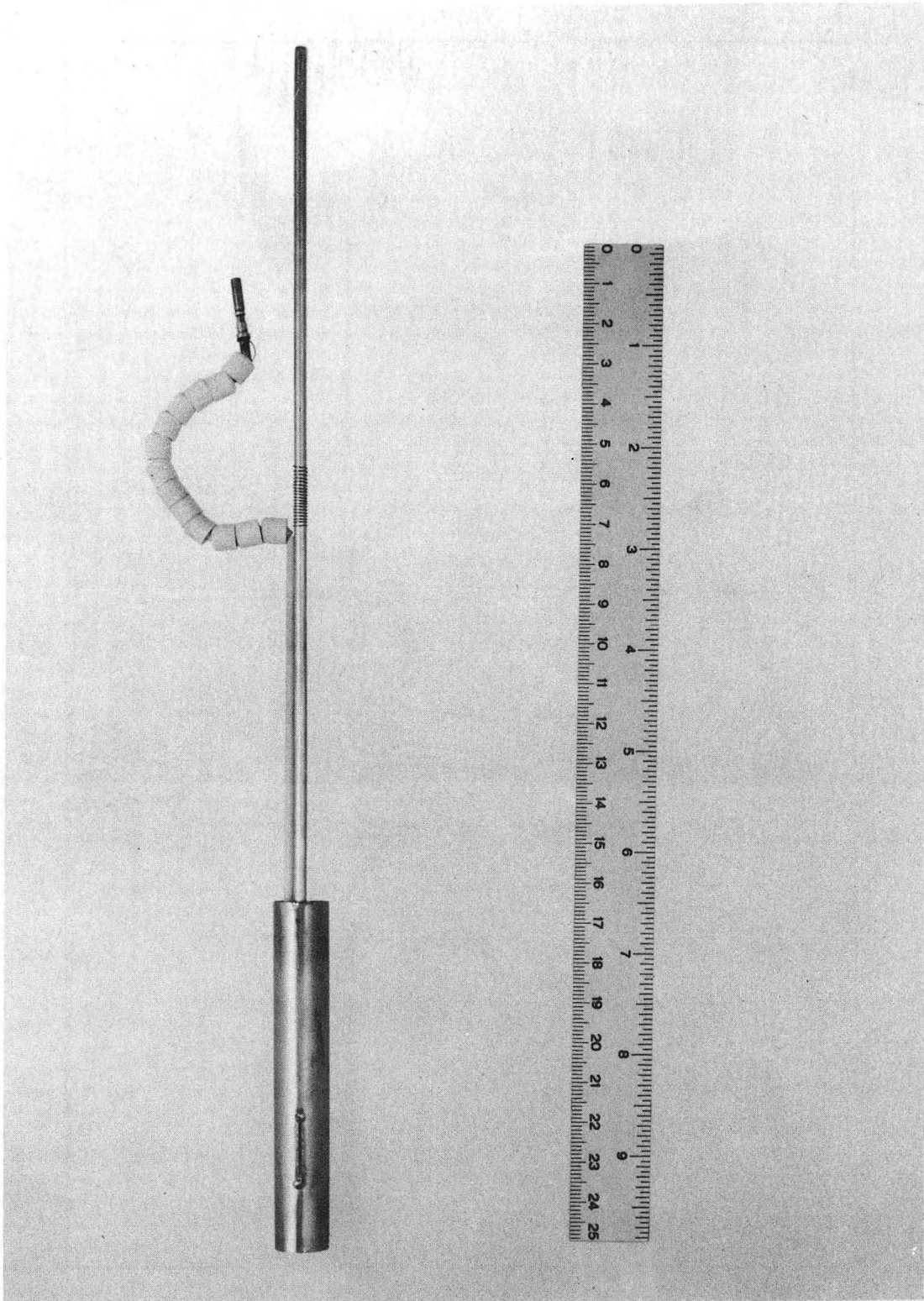
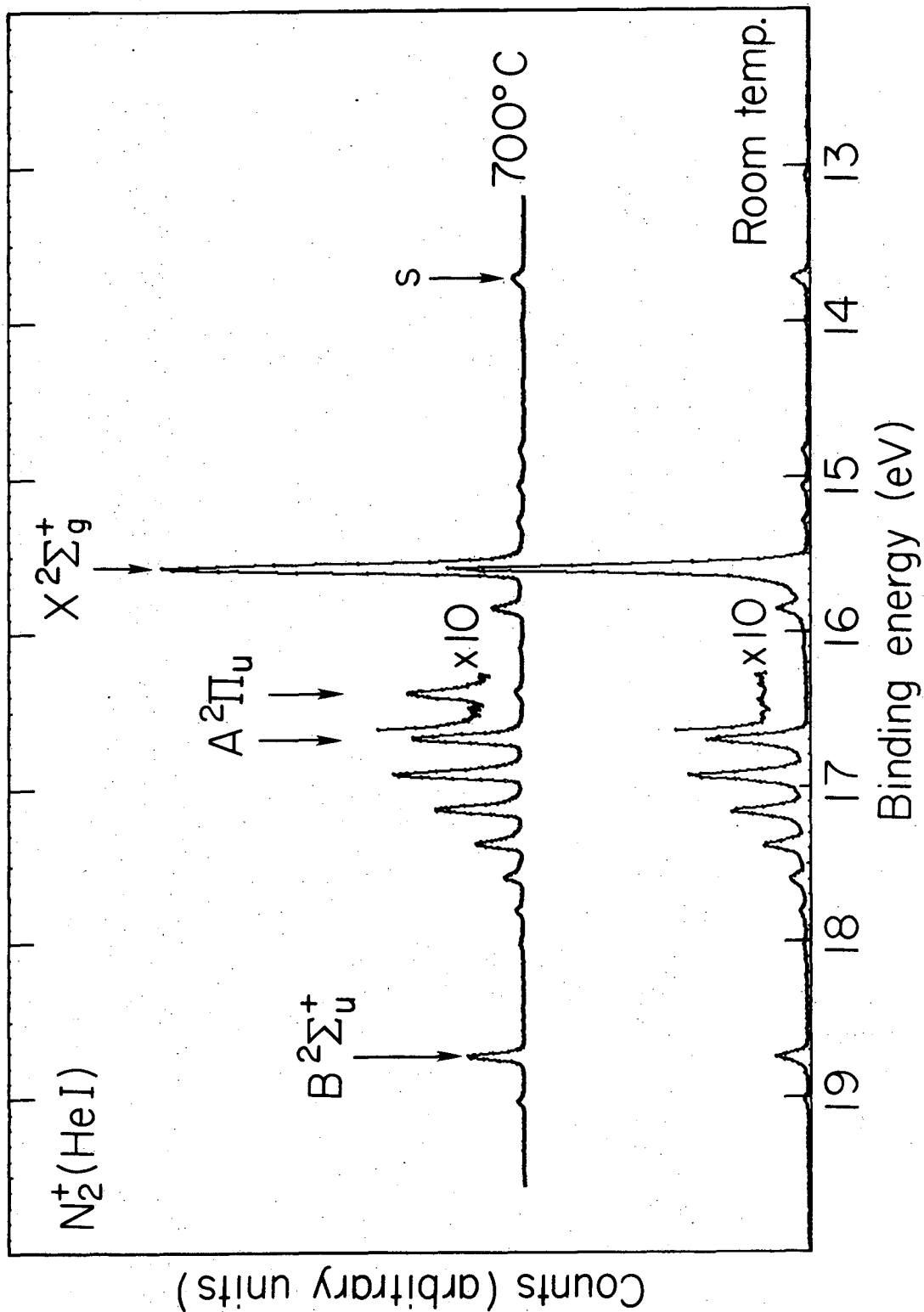


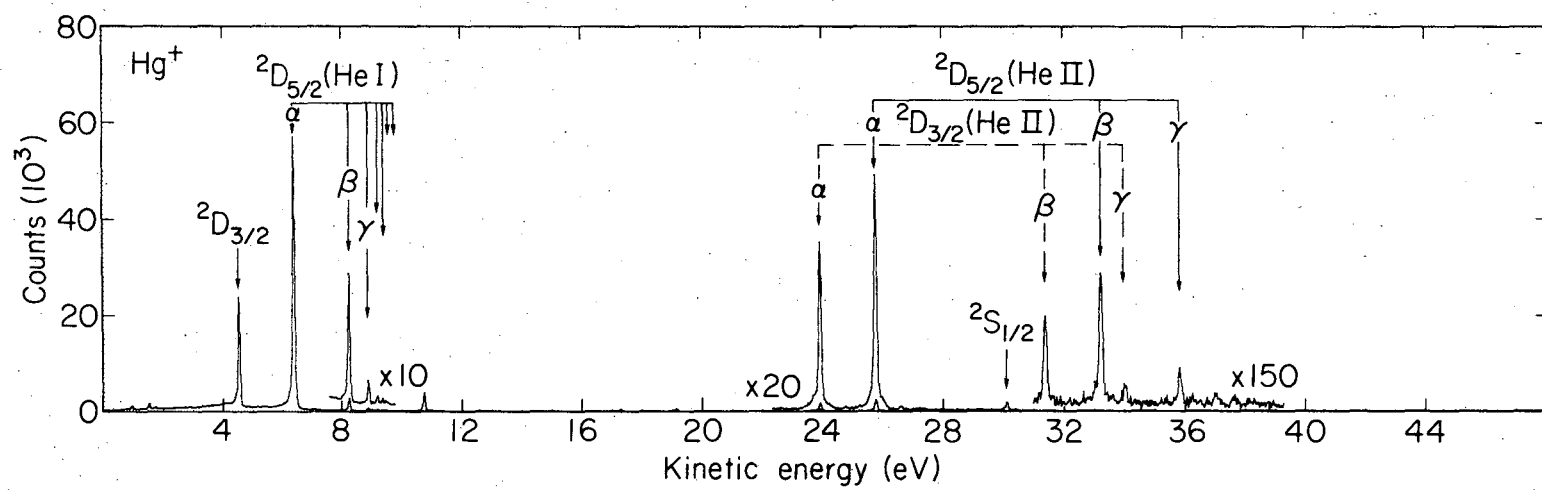
Figure 7

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Figure 8



-29-

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Figure 9

III. CORRELATION SATELLITES IN THE ATOMIC PHOTOELECTRON SPECTRA OF GROUP IIA AND GROUP IIB ELEMENTS*

Abstract

Atomic vapors of Ca, Sr, Ba, Zn, Cd, and Hg were studied by photoelectron spectroscopy in a special high-temperature cell using HeI (and in some cases NeI or HeII) resonance radiation. In addition to strong lines obtained by photoemission from the nominal $ns^2 + (n-1)d^{10}ns^2$ configurations, weaker lines were observed that are attributed to admixtures of the configurations np^2 , $(n-1)d^2$, etc. (in Group IIA elements) or np^2 , in Group IIB elements, into the ground-state. In the Group IIA cases, the satellite intensities are consistent with expectations based on multi-configuration Hartree Fock results. Photoelectron spectroscopy thus appears to provide incisive information about the details of electron correlations in these atoms. Intensity ratios of spin-orbit partners fall near the multiplicity ratios in Zn and Cd, but deviate in Hg due to relativistic effects, in agreement with expectations based on earlier work.

*This chapter has been submitted to Phys. Rev. A in co-authorship with S. T. Lee and D. A. Shirley.

A. Introduction

Quantum states of multi-electron atoms are commonly labeled by their dominant configurations in one-electron orbital bases. For example, the ground-state of the helium atom is designated ($1s^2; ^1S$), while the Group II elements are described as ($ns^2; ^1S$) if only the valence electrons are considered. Such a simple description cannot be rigorously correct, of course, because it implicitly neglects electron correlations. Correlations may be treated theoretically by admixing additional configurations of the same symmetry: thus the ground-state of calcium would be described by

$$\Psi(^1S) = a(4s^2) + b(4p^2) + c(3d^2) + \dots \quad (1)$$

This theoretical approach (configuration interactions) is commonly used to carry atomic or molecular calculations beyond the Hartree-Fock limit. The total energy is usually employed as a criterion of quality of the computation.

The experimental situation is much less straightforward. Conventional spectroscopic methods usually involve excitation of an N-electron (bound) excited state. The selection rules are governed by the total symmetries of both states. Configuration mixing may be manifested as deviations from interval rules, irregularities of intensities, etc., but conventional spectroscopy is not particularly sensitive to details of electron correlation.

Photoelectron spectroscopy provides a relatively direct measure of configuration mixing. A photoelectric transition excites an N-electron

system to an N-electron final state in which, however, one electron is unbound. Thus a calcium atom in our example would be taken, by photoionization of a valence electron, to a state in Ca^+ plus a free electron. The total N-electron final state must have ^1P symmetry. Thus the (dipole) selection rules are as stringent for photoelectron spectroscopy as for conventional spectroscopy, when applied to the total system. However, the N-electron ^1P state can be made up of any one of a wide variety of states in Ca^+ plus a continuum state of symmetry appropriate to satisfy the selection rules. In particular, any one-electron state in Ca^+ that can be reached by removal of an electron from a basis configuration in Eq. (1) should be reached by photoemission. For example, the $\text{Ca}^+(4p^1; ^2\text{P})$ states are accessible from the $b(4p^2)$ part of the Ca ground-state wave function in Eq. (1), with the second electron leaving in a continuum s or d state. Similarly, $\text{Ca}^+(3d^1; ^2\text{D})$ states are accessible from the $c(3d^2)$ portion of the Ca ground-state wave function, etc. None of these states could be reached by a one-electron process if the Ca ground-state were simply $4s^2$: thus observation of the ^2P , ^2D , etc., lines gives a measure of the extent to which the $4p^2$, $3d^2$, etc., configurations are admixed into the ground-state. A rigorous quantitative interpretation would require further theoretical developments, to correct for differences in photoelectric cross sections for the different $n\ell$ orbitals and for two-electron processes.

In this paper we report experimental photoemission studies of vapors of the Group IIA metals Ca, Sr, and Ba and the Group IIB metals Zn, Cd, and Hg, in which several satellite peaks arising from electron correlation have been observed. We have reported similar results for

Cd^1 and Pb^2 earlier, while Berkowitz et al.³ have reported satellite peaks in Hg. The alkaline earth atoms have been treated theoretically by Kim and Bagus⁴ using the multi-configuration Hartree Fock method. They found that considerable electron correlation must be included to bring the calculated generalized oscillator strengths into agreement with experiment. Their calculations included the configurations np^2 and $(n-1)d^2$ in the ground states, and they found appreciable mixture of these configurations. Judging from their results, we would expect to find satellite peaks corresponding to np and $(n-1)d$ ionic states in the photoemission spectra of alkaline-earth atoms. Group IIB atoms would be expected to show similar correlation effects.

In this paper, experimental details are given in Section B and results in Section C. Section D-1 discusses the nature of these satellites and D-2 deals with the relativistic effects on the branching ratios of the spin-orbit components. Conclusions are given in Section E.

B. Experimental

The experiments were carried out in a Perkin-Elmer PS-18 photo-electron spectrometer modified for high-temperature work. The details of the modifications have been given in Chapter II.

The spectrum of Hg was taken at about 55°C and that of Cd at about 290°C using the original heated probe provided with the PS-18 spectrometer. The Cd spectrum reported here is different from that of the earlier work¹ in that digital data acquisition was employed, as described earlier.² Zinc was run at 380°C, Ca at 740°C and Sr at 650°C using our high-temperature cell and HeI radiation. Barium spectra were taken at 700°C using both HeI and NeI radiation. The HeI spectrum of Ba showed very strong autoionization features, in agreement with results reported by other workers.⁵ These features are absent in NeI spectrum. Because of this phenomenon, we shall report here only the NeI spectrum of Ba. The HeI spectrum will be discussed in a separate paper.

At lower pressure, our He lamp produces sufficient HeII radiation (ca. 5% HeI) to record the HeII spectra of Zn, Cd and Hg. This was actually done, to see how the relative peak intensities changed with photon energies.

Samples were loaded in air, then introduced into the spectrometer. Oxides, which were invariably present in the samples, did not show up in the spectra because of their low vapor pressures. All samples were 99% pure, and no impurity peaks were found in the spectra except in the case of Sr. The first Sr sample used (from Alfa Inorganics) was stated to be of > 99.5% purity and contained ca. 0.3% of Ba. Because of the

strong resonant absorption of HeI radiation in barium, the Ba peaks showed up in fair intensity in the Sr spectra. Strontium samples of 99.99% purity (from Orion) were then tried, but without much success, because the Ba peaks gained in intensity as the percentage of Ba increased with time. However, all impurity peaks could be identified by comparison with the HeI spectrum of pure Ba; thus they did not affect the interpretation of the Sr spectra.

Peak areas were corrected for the change of the spectrometer transmission with electron kinetic energy using the approximate relation $\Delta E/E = \text{constant}$. All the observed lines are broad in comparison with the instrumental resolution due to the effects of charging in or around the ionization region. This also affects the transmission function of the spectrometer, which severely discriminates against the low-energy electrons. No correction was made for this effect or for the inelastic scattering of the electrons due to a finite sample pressure. The latter was shown to affect the area ratios of peaks at different energies.⁶ However, neither of these effects is expected to be very important for high-energy electrons. Hence the area ratios reported for the HeII results, should be reliable. Those for the low energy satellites must be regarded as only qualitatively correct.

C. Results

The HeI spectra of Ca and Sr and the NeI spectrum of Ba are shown in Fig. 1. Peak assignments were done by comparison of their binding energies with optical data.⁷ These assignments and derived parameter are set out in Table I.

The spectrum of atomic Ca($4s^2, ^1S$), (Fig. 1a), shows one main peak at 6.11 eV corresponding to the $Ca^+(4s, ^2S)$ final state and four additional peaks at 7.82, 9.24, 12.60, and 13.16 eV, corresponding respectively to ($3d, ^2D_{3/2,5/2}$), ($4p, ^2P_{1/2,3/2}$), ($5s, ^2S_{1/2}$) and ($4d, ^2D_{3/2,5/2}$) final states. The peak designated by I at 9.04 eV is an inelastic loss peak, resulting from excitation of the transition ($4s^2 \rightarrow 4s\ 4p, ^1P_1$) in neutral Ca by monoenergetic electrons from the $Ca \rightarrow Ca^+ 4s$ transition.

The spectrum of atomic Sr($5s^2, ^1S$), (Fig. 1b), again shows one main peak at 5.69 eV, from the ($5s, ^2S_{1/2}$) final state, and five additional peaks at energies 7.53, 8.64 (plus 8.73), 11.61, 12.30 and 13.25 eV, corresponding respectively to final states ($4d, ^2D_{3/2,5/2}$), ($5p, ^2P_{1/2,3/2}$), ($6s, ^2S_{1/2}$), ($5d, ^2D_{3/2,5/2}$) and ($4f, ^2F_{5/2,7/2}$). The peak designated by I is again an inelastic loss peak from the transition ($5s^2 \rightarrow 5s5p, ^1P_1$) in neutral Sr. The peaks marked with stars are from transitions in the Ba impurity.

The NeI spectrum of atomic Ba($6s^2, ^1S$), (Fig. 1c), shows a main peak at 5.21 eV ($6s, ^2S_{1/2}$), [the most intense NeI lines actually are a doublet with 0.18 eV separation],⁸ and five additional peaks at 5.81 (plus 5.91), 7.70 (plus 7.92), 10.46, 10.92 and 11.20 eV corresponding respectively to ($5d, ^2D_{3/2,5/2}$), ($6p, ^2P_{1/2,3/2}$), ($7s, ^2S_{1/2}$),

($6d, {}^2D_{3/2,5/2}$) and ($4f, {}^2F_{5/2,7/2}$) final states of Ba^+ . The peak designated by I is an inelastic loss peak ($6s^2 \rightarrow 6s\ 6p, {}^1P_1$ in neutral Ba), and those marked by A's are believed to be Auger lines arising from ionization of core electrons by NeII radiation.

The HeI photoelectron spectra of Zn, Cd and Hg are shown in Fig. 2. Figure 2 also depicts the 2D lines of these atoms taken with HeII in the same run as also shown on Figs. 3, 4, and 5. Assignments and derived parameters are tabulated in Table II. The area ratios of the main lines taken at different photon energies are given in Table III. The spectrum of atomic Zn ($3d^{10}4s^2, {}^1S$), (Fig. 2a) shows three main peaks at binding energies, 9.39, 17.17 and 17.50 eV, corresponding to the Zn^+ final states ($3s^{10}4s, {}^2S_{1/2}$), ($3d^94s^2, {}^2D_{5/2}$) and ($3d^94s^2, {}^2D_{3/2}$); and two additional peaks at 15.40 and 15.51 eV corresponding to ($3d^{10}4p, {}^2P_{1/2}$) and ($3d^{10}4p, {}^2P_{3/2}$) final states embedded between 2D lines excited by the HeI β (23.08 eV) radiation. The peak I is an inelastic loss peak ($3d^{10}4s^2 \rightarrow 3d^{10}4s4p, {}^1P_1$). The peaks at 18.6 and 18.8 eV cannot be identified with any known transitions.

The spectrum of Cd ($4d^{10}5s^2, {}^1S$), (Fig. 2b), shows, in agreement with our earlier work,¹ two satellites at 14.45 eV and 14.76 eV corresponding to ($4d^{10}5p, {}^2P_{1/2}$) and ($4d^{10}5p, {}^2P_{3/2}$) final states. There is also an inelastic loss peak (I), near the (${}^2P_{1/2}$) line. The statistical accuracy of the present spectrum is much better.

The Hg spectrum (Fig. 2c) shows satellites at 16.83 eV and 17.96 eV corresponding to ($5d^{10}6p, {}^2P_{1/2}$) and ($5d^{10}6p, {}^2P_{3/2}$) final states. These have been reported before by other workers,³ and are included here for comparison. The line I is again an inelastic loss peak.

The Figures 3, 4, and 5 show also some other inelastic lines designated I_A and I_B and OIII is a radiation at 38.33 eV coming from H_2O impurity.

D. Discussions1. The Nature of Satellite Peaks

Recent theoretical analyses^{9,10} have been made of the manner in which correlation effects can lead to satellites in photoemission spectra. There are three mechanisms that describe the breakdown of the one-electron picture: initial-state configuration interaction (ISCI), final ionic state configuration interaction (FISCI), and continuum-state configuration interaction (CSCI), or interchannel coupling. FISCI is well-known in atoms,¹¹ molecules,¹² and solids,¹³ while ISCI was reported for Hg by Berkowitz, et al.³ and by Süzer et al. for Cd¹ and Pb².

The distinction among these three mechanisms is not completely unambiguous, because precise statements about configuration interaction can only be made within the context of a particular basis set. In the Group IIA and Group IIB elements, however, the FISCI mechanisms is expected to be relatively unimportant, because the final-ionic states have only one electron outside a closed shell or major subshell (for helium, FISCI could be rigorously excluded¹⁰). The initial states of these closed-shell atoms possess near-degenerate configurations that are known to mix strongly with the ground-state. This phenomenon is termed "internal correlation" by McKoy and Sinanoğlu.¹⁴ In Group IIA elements both the np and the (n-1)d shells are empty and low-lying, while in Ba the 4f shell is also available for configuration mixing. In Group IIB atoms, the (n-1)d shell is filled, but the np shell is expected to mix substantially. We therefore believe that ISCI rather than FISCI is

dominant in the spectra reported here, and a qualitative interpretation neglecting FISC I seem justified.

The importance of interchannel coupling (CSCI) is difficult to evaluate, and it may constitute a sizable correction to the interpretation of our spectra in terms of ISC I alone. In their study of the $2p$ satellites in the photoionization of Hg, Berkowitz et al.³ calculated that $\sim 80\%$ of the intensity arose via ISC I. This supports our approach. The other 20% was calculated to arise via "conjugate shakeup", in which the photon's angular momentum is transferred to one of the passive electrons. We note that conjugate shakeup can be regarded as a specific configuration interaction that falls under the general category of interchannel coupling. The $2D$ and $2F$ final states in our spectra could not arise via conjugate shakeup, but CSCI through continuum channels could lead to these states. In general CSCI is expected to be most important near threshold and/or for ions with closely-spaced states of the same symmetry. Thus it should be a good approximation to neglect CSCI in interpreting these satellite spectra, especially for the lowest-energy ionic states.

Even within the constraint of interpreting the spectra entirely in terms of ISC I, we still do not have enough theoretical information for a complete quantitative interpretation. In particular, the relative photoemission cross-sections from various subshells are unknown, as is the angular dependence (our spectra were taken in 90° geometry with unpolarized radiation). Our results are set out in the tables to facilitate a more complete interpretation when more theoretical parameters become available. We give below an approximate interpretation in which

line intensities are compared directly with ISCI admixture coefficients, neglecting cross-section differences, angular dependences, and FISC and CSCI effects.

The ground-states of Group IIA and Group IIB atoms can be approximated as

$$\psi(^1S) \cong a(ns^2) + b(np^2) + c(n'd^2) + d(n''f^2) + \dots \quad (2)$$

with

$$n' = n-1 \text{ if available}$$

$$n'' = n-2 \text{ if available}$$

The photoionization spectrum should therefore be dominated by the primary ionic state $(ns; ^2S)$, with satellites corresponding to $(np; ^2P)$, $(n'd; ^2D)$, $(n''f; ^2F)$, etc. Within the approximations discussed above, the satellite intensities should vary roughly as $a^2 : b^2 : c^2 \dots$ etc. . Kim et al.⁴ did a multi-configuration Hartree-Fock calculation to evaluate the generalized oscillator strengths of IIA atoms by including $(np)^2$ or $(np)^2$ and $(n'd)^2$ configurations in the ground-state. We compare the squares of mixing coefficients a^2 , b^2 , c^2 etc. from their results, with our experimentally observed intensities of the corresponding satellites in Table III. There is an almost constant value of 9% for the calculated intensities of $(np)^2$ configuration. Experimentally the intensities of the $(np, ^2P)$ lines decrease going down the Periodic Table from 10% in Ca and 5% in Ba. This agreement is qualitatively good in view of the experimental accuracy and the assumptions made in the comparison. By contrast, the experimental $(n'd, ^2D)$ intensities are much higher than the calculated values and the discrepancy gets worse going down the

Periodic Table. For Ba it is 22% experimentally, compared to 1.1% calculated. This suggests either that the difference between the photoionization cross sections of ns and n'd electrons is very large in the comparison or that another mechanism also contributes to the satellite intensities. The other possible contributors are autoionization and interchannel coupling. We have measured the spectrum of Ba using ArI (11.83 eV) radiation, and found that the relative intensities of the 5d lines remained essentially the same as in the NeI case. This indicates that the two aforementioned mechanisms are probably not major contributors to the discrepancy, because their contributions are expected to be strongly dependent on the photon energy. Similar conclusions can be drawn for Ca and Sr, because we observed about the same relative intensities of (n'd, 2D) lines in the HeI and NeI spectra. This leads us to conclude that the differences in photoionization cross-sections are too large for such a comparison to be meaningful for the (n'd; 2D) lines. One factor that could account for part of the enhanced intensity of the 2D lines is the $(2\ell+1)$ multiplicity of the final continuum states. The d electron would go into p or f waves with a total multiplicity of $3 + 7 = 10$, compared to 3 for the s electrons, which go into p waves.

In the spectra of Ca^+ , Sr^+ , and Ba^+ , a few weaker satellites with relative intensities less than 2% were also detected; they correspond to higher excited states of these ions. Their existence can again be accounted for by ISCI, by interchannel coupling, or by a combination of the two. For the excited $[(n+1)s; ^2S]$ lines, FISCI (or shakeup) is also a possible mechanism. Here it is even more difficult to differentiate the individual contributions. We note, however, energy considerations

alone give a fairly good indication of how important the ISCI effects on satellites are, while no such *a priori* rule is available for the inter-channel coupling effects. Thus the increase of satellite intensities toward lower binding energy is consistent with the ISCI interpretation.

For Group IIB atoms, the satellite intensities of the satellites amount to - 20% of the primary peak. Again both ISCI and interchannel coupling can be contributory, and it is difficult to distinguish between them. However, by comparing with IIA atoms, we tend to believe that ISCI is the dominant mechanism. Unfortunately no CI calculations on Group IIB atoms are available for comparison with these spectra.

2. Relativistic Effects on the Branching Ratios of Spin-Orbit (s-o) Components

It is widely recognized that the presence of s-o coupling can cause the branching ratios of s-o components to deviate from the statistical ratios. Recently, Walker et al.¹⁵ found the $^2D_{5/2} / ^2D_{3/2}$ branching ratios for Cd and Hg to be significantly greater than the statistical value 3/2 for photoemission at 584Å. These deviations were attributed¹⁵ mainly to two causes, the difference in the initial state wavefunctions for $d_{5/2}$ and $d_{3/2}$ bound orbitals and the difference in photoelectron kinetic energy. It was further pointed out that the effect of energy difference is important only at lower photon energies, when the photoelectron energy is not too large compared to the s-o splitting. As the photoelectron energy becomes much larger than the s-o splitting, its effect diminishes and the deviation from the statistical ratio will be predominantly due to difference in wavefunctions. Furthermore, the

generalization has been made that if the partial cross-section is rising, the ratio of cross-sections is greater than statistical, and vice versa.

In Hg,⁶ the wavelength dependence of the $^2D_{5/2} / ^2D_{3/2}$ ratio was observed to follow the generalization. The marked deviation (dropping from 2 to 1.3 for the range $600\text{\AA} \geq \lambda \geq 200\text{\AA}$) of the ratio from the statistical is understandable in view of the large s-o splitting, and is to be attributed to the difference in the initial state wavefunction. In view of this, it is interesting to see how the ratios for Zn and Cd behave, and thus how important are the relativistic effects. We have measured the ratios for Zn, Cd and Hg using both HeI and HeII radiation (Table IV). Our results for Hg, after being adjusted for angular dependence using β asymmetry parameters given in Ref. 6, are in good agreement with those reported by Dehmer et al.,⁶ except at 584Å. The agreement tends to support our expectation that the results for HeII radiation are less susceptible to the influence of inelastic loss and charging, and thus are more reliable. Turning to Zn and Cd, in view of the experimental accuracy, the $^2D_{5/2} / ^2D_{3/2}$ branching ratios at both 304 and 256Å can be regarded as little different from 1.5, in contrast to Hg. This behavior of the ratio suggests that the relativistic effects in Zn and Cd are too small to cause an appreciable difference in the initial state wavefunction, and thus the ratio is around 1.5 at higher photoelectron energy. The deviation of the ratio in Cd at 584Å is most probably due to the photoelectron energy difference.

In the case of open shells, s-o coupling introduces still another relativistic effect on the branching ratio.³ As the s-o coupling gets larger, it may then be more appropriate to use the j-j coupling scheme,

and the components with lower J value lies lower in energy when the shell is less than half-filled. In the j-j coupling description, as one goes down the series Zn, Cd and Hg, $(p_{1/2})^2$ will mix increasingly stronger than the $(p_{3/2})^2$ configuration, with the $(ns)^2$ primary configuration due to increasing s-o splitting. As a result the observed ${}^2P_{3/2} / {}^2P_{1/2}$ branching ratio will to a first approximation be given by the ratio of the squares of the corresponding mixing coefficients. Depending upon the magnitude of this relativistic effect, the observed ${}^2P_{3/2} / {}^2P_{1/2}$ ratio may differ significantly from the statistical value 2 given in the L-S coupling limit. Experimentally the ${}^2P_{3/2} / {}^2P_{1/2}$ branching ratio (Table IV) is 1.7 for Zn and 2.0 for Cd, but decreases to a dramatically low value of 0.28 for Hg. This indicates again that relativistic effects are significant in Hg, but small in Zn and Cd, in accord with the conclusion drawn from the ${}^2D_{5/2} / {}^2D_{3/2}$ ratio. The ${}^2P_{3/2} / {}^2P_{1/2}$ ratio of 0.28 for Hg is in good agreement with the work of Hotop and Mahr,¹⁶ who measured a value of 0.25 from their high resolution spectrum of Hg. It is significant to note that the measured ratio is much smaller than the value of 0.8 calculated by the relativistic configuration interaction method.³ This large discrepancy is surprising in view of the fact that the relativistic calculation has actually included the conjugate 'shake-up' mechanism, which would be expected to be the major contributor in the interchannel coupling. However, the calculation did not include the effects of the difference in the partial cross-sections arising from the differences in the photoelectron kinetic energy and in the initial state wavefunctions.

For the alkaline earth atoms, the experimental resolution did not

permit us to resolve the s-o doublets (e.g. $^2D_{5/2,3/2}$, $^2P_{3/2,1/2}$ etc.). In any event, the s-o splittings are not large (e.g. 6p splitting is 0.21 eV for Ba^+ vs. 1.13 eV for Hg); thus we do not expect the relativistic effect to be significant. In fact, the branching ratio observed for 6p doublets (Table I) is not much different from the statistical ratio, corroborating our expectation.

E. Conclusions

This work has demonstrated the feasibility of doing ultraviolet photoelectron spectroscopic measurements on high-temperature atomic metal vapors up to 750°C. Satellite lines have now been identified in a total of six Group IIA and IIB elements. The lines were attributed mainly to initial state configuration interaction. A complete quantitative interpretation awaits further theoretical progress on cross-section calculations as well as on estimates of the magnitude of final-state and coupled-channel contributions. Especially after these refinements are made, photoelectron spectroscopy holds promise of becoming a decisive method for studying electron correlation. Finally, intensity ratios for the spin-orbit split components of p and d shells were found to deviate from statistical value in Hg but not in Cd and Zn, supporting and extending the results of earlier work.

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Table I. Observed States of Ca^+ , Sr^+ and Ba^+

Ion	Final state	Apparent relative intensity(a)	Binding energy, eV(a)	Energy from optical data, eV(b)
Ca^+	$4s\ ^2S_{1/2}$	100	6.11(2)	6.111
	$3d\ ^2D_{3/2,5/2}$	.5	7.82(2)	7.805; 7.811
	$4p\ ^2P_{1/2,3/2}$	10.3	9.24(2)	9.254; 9.262
	$5s\ ^2S_{1/2}$	1.6	12.60(2)	12.579
	$4d\ ^2D_{3/2,5/2}$	1.5	13.16(2)	13.158; 13.161
	$4s\ 4p\ ^1P_1$	—	9.04(2) ^(d)	9.044 ^(d)
Sr^+	$5s\ ^2S_{1/2}$	100	5.69(2)	5.692
	$4d\ ^2D_{3/2,5/2}$	4.5	7.53(2)	7.497; 7.541
	$5p\ ^2P_{1/2,3/2}$	6.5	8.64; 8.73(2)	8.632; 8.732
	$6s\ ^2S_{1/2}$	1.0	11.61(2)	11.611
	$5d\ ^2D_{3/2,5/2}$	0.6	12.30(2)	12.300; 12.309
	$4f\ ^2F_{5/2,7/2}$	0.4	13.25(2)	13.250
$\text{Sr}^{(c)}$	$5s\ 6p\ ^1P_1$	—	8.38(2) ^(d)	8.382 ^(d)
Ba^+	$6s\ ^2S_{1/2}$	100	5.21(3)	5.211
	$5d\ ^2D_{3/2,5/2}$	22.1	5.81; 5.92(3)	5.816; 5.915
	$6p\ ^2P_{1/2,3/2}$	1.5; 3.2	7.70; 7.92(3)	7.723; 7.933
	$7s\ ^2S_{1/2}$	0.7	10.46(3)	10.463
	$6d\ ^2D_{3/2,5/2}$	0.7	10.92(3)	10.908; 10.934
	$4f\ ^2F_{5/2,7/2}$	0.5	11.20(3)	11.195; 11.222
$\text{Ba}^{(c)}$	$6s\ 6p\ ^1P_1$	—	7.45(3) ^(d)	7.450 ^(d)

^aThis work, Xe and N_2 were used for calibration. Areas were corrected for $(\Delta E/E)$ the Ca and Sr were taken with HeI radiation, the Ba with NeI.

^bReference 7.

^cInelastic loss peaks in neutral Ca, Sr and Ba originate from $^2S_{1/2}$ lines (see text).

^dApparent binding energy.

Table 11. Observed States of Zn^+ , Cd^+ and Hg^+

Ion	Final state	Apparent relative intensity ^(a)	Binding energy, eV ^(a)	Energy from optical data, eV ^(b)
Zn^+	$3d^{10} 4s^2 S_{1/2}$	100	9.59(2)	9.591
	$3d^{10} 4p^2 P_{1/2}$	7	15.40(2)	15.400
	$3d^{10} 4p^2 P_{3/2}$	12	15.51(2)	15.509
	$3d^9 4s^2 D_{5/2}$	611	17.17(2)	17.166
	$3d^9 4s^2 D_{3/2}$	429	17.50(2)	17.503
$\text{Zn}^{(c)}$	$3d^{10} 4s4p^1 P_1$	—	15.19(2) ^(d)	15.187 ^(d)
Cd^+	$4d^{10} 5s^2 S_{1/2}$	100	8.99(2)	8.991
	$4d^{10} 5p^2 P_{1/2}$	5	14.45(2)	14.462
	$4d^{10} 5p^2 P_{3/2}$	10	14.76(2)	14.770
	$4d^9 5s^2 D_{5/2}$	622	17.58(2)	17.576
	$4d^9 5s^2 D_{3/2}$	305	18.27(2)	18.274
$\text{Cd}^{(c)}$	$4d^{10} 5s5p^1 P_1$	—	14.40(2) ^(d)	14.401 ^(d)
Hg^+	$5d^{10} 6s^2 S_{1/2}$	100	10.43(2)	10.435
	$5d^{10} 6p^2 P_{1/2}$	25	16.83(2)	16.816
	$5d^{10} 6p^2 P_{3/2}$	7	17.96(2)	17.947
	$5d^9 6s^2 D_{5/2}$	1719	14.84(2)	14.837
	$5d^9 6s^2 D_{3/2}$	781	16.70(2)	16.700
$\text{Hg}^{(c)}$	$5d^{10} 6s6p^1 P_1$	—	17.13(2)	17.152

^aThis work, Xe and Ar used for calibration. Areas corrected for ($\Delta E/E$).^bReference 7.^cInelastic loss peaks in neutral Zn, Cd and Hg (see text). Originates from $2S_{1/2}$ lines.^dApparent binding energy.

Table III. Comparison of Experiment with MCHF Calculations

Calculated mixing coefficients: Ratios of the squares of the coefficients normalized to (ns^2) (a) $\psi = a(ns)^2 + b(np)^2 + c(n'd)^2$				Experimentally observed intensities normalized to ns peak (b)		
	a^2	b^2	c^2	$a'^2(ns^2S)$	$b'^2(np^2P)$	$c'^2(n'd^2D)$
Mg $n = n' = 3$	1.00	0.075	0.0010	—	—	—
Ca $n = 4$ $n' = 3$	1.00	0.087	0.0034	1.00	0.103	0.045
Sr $n = 5$ $n' = 4$	1.00	0.085	0.0055	1.00	0.065	0.045
Ba $n = 6$ $n'' = 5$	1.00	0.092	0.011	1.00	0.047	0.221

^aReference 4.

^bThis work. Observed intensities of satellites. Areas are the total of the spin-orbit doublets). See Section IV-A.

Table IV. Experimentally Observed line Intensities for Zn, Cd and Hg

λ Å	State	Area Ratios		
		Zn	Cd	Hg ^(a)
	$2S_{1/2}$	0.23	0.33	0.13(0.08) (0.025) ^(b)
584	$2D_{5/2}$	1.42	2.0	2.20(2.28) (2.00)
	$2D_{3/2}$	1.00	1.00	1.00(1.00) (1.00)
	$2S_{1/2}$	—	—	0.04(0.03) (0.027)
304	$2D_{5/2}$	1.46	1.53	1.38(1.36) (1.37)
	$2D_{3/2}$	1.00	1.00	1.00(1.00) (1.00)
	$2S_{1/2}$	—	—	—
256	$2D_{5/2}$	1.48	1.56	1.32(1.31) (1.32)
	$2D_{3/2}$	1.00	1.00	1.00(1.00) (1.00)
	$2S_{1/2}$	—	—	—
243	$2D_{5/2}$	—	—	1.30 (1.30) ^(c)
	$2D_{3/2}$	—	—	1.00 (1.00)

^aValues in parentheses are branching ratios, where angular dependence is corrected as was done in reference 3.

^bValues in this column are taken from reference 3 for comparison.

^cEstimated from Fig. 4 of reference 3.

FIGURE CAPTIONS

- Fig. 1. Photoelectron spectra of: (a) Ca(HeI radiation, 740°C); (b) Sr(HeI radiation, 650°C); and (c) Ba(NeI radiation, 700°C). Peaks of interest in this work are labeled by spectroscopic symbols. "S" denotes a peak arising from satellite lines in the incident radiation, and "I" an inelastic loss peak. Asterisks denote peaks in the Sr spectrum that arise from autoionizing Ba impurities (see text). Peaks labeled "A" in the Ba spectrum are tentatively identified as Auger transitions arising from excitation by NeII radiation.
- Fig. 2. Photoelectron spectra of Zn, Cd, and Hg, with notation as in Fig. 1. Inserts denote HeII - excited ^2D lines taken from the parts of Figs. 3, 4, and 5.
- Fig. 3. HeI and HeII photoelectron spectrum of Zn taken in the same run. I_A is an inelastic loss peak and OIII is impurity radiation at 38.33 eV coming from water.
- Fig. 4. Spectrum of Cd as in Fig. 3. I_B is another inelastic peak.
- Fig. 5. Spectrum of Hg as in Fig. 3 and 4.

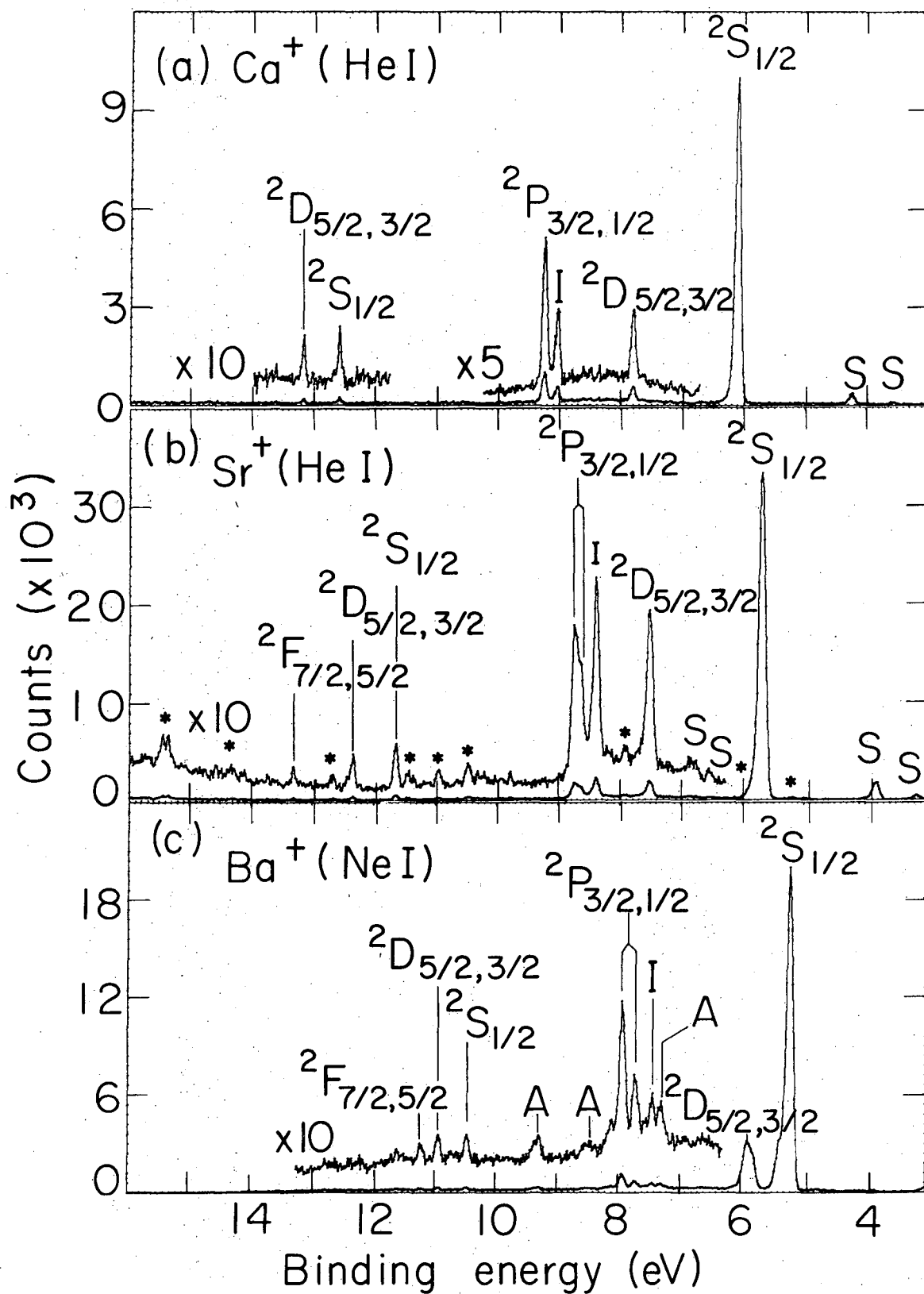


Figure 1

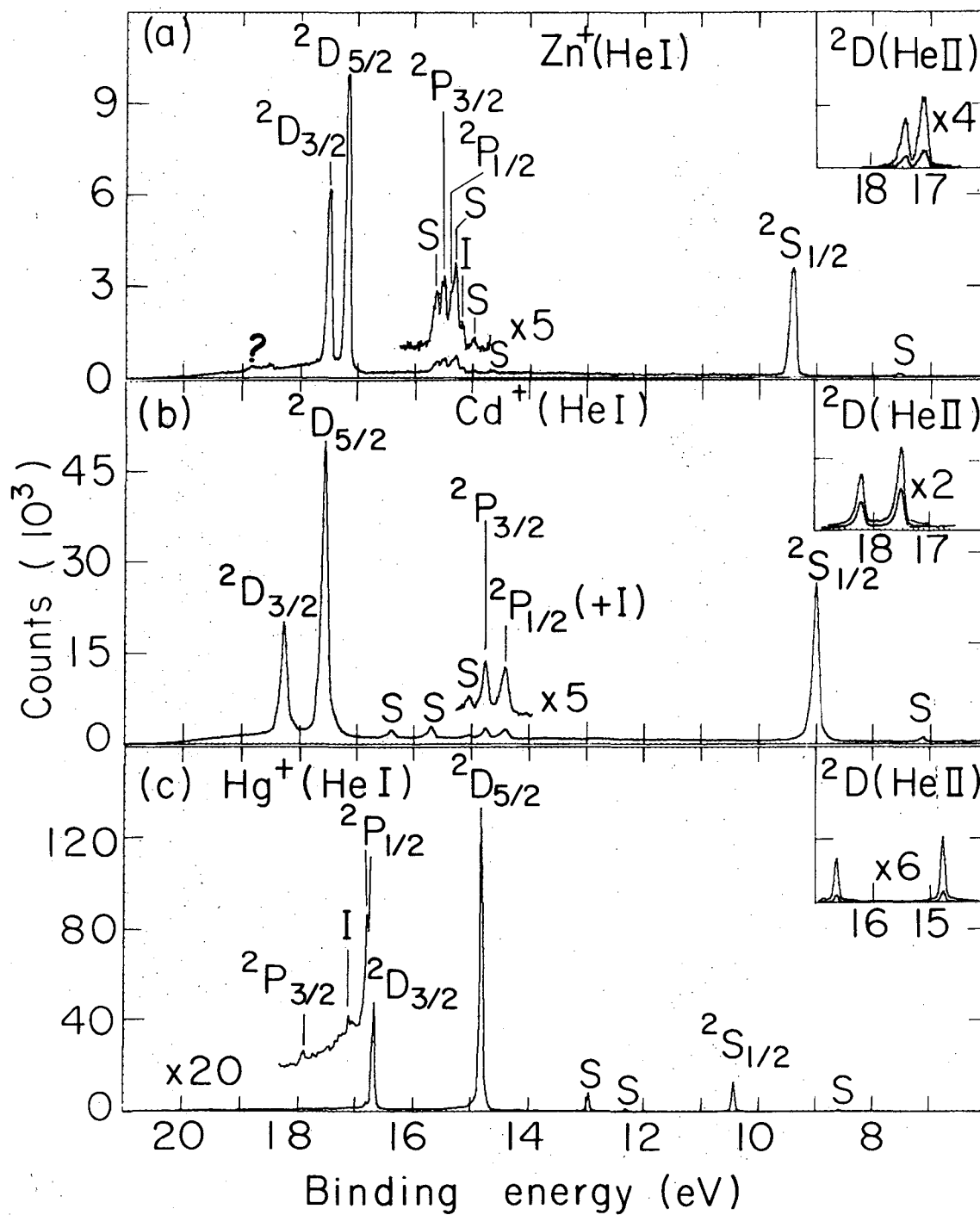


Figure 2

XBL7512-9907

00004503433

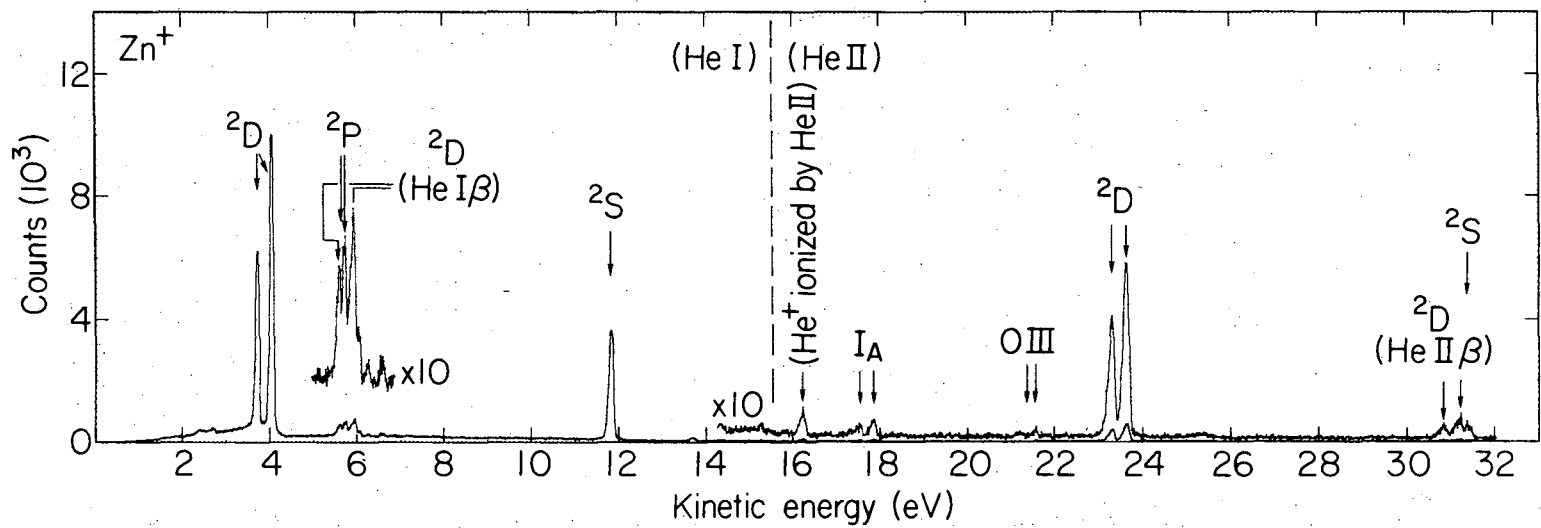


Figure 3

XBL 761-2039

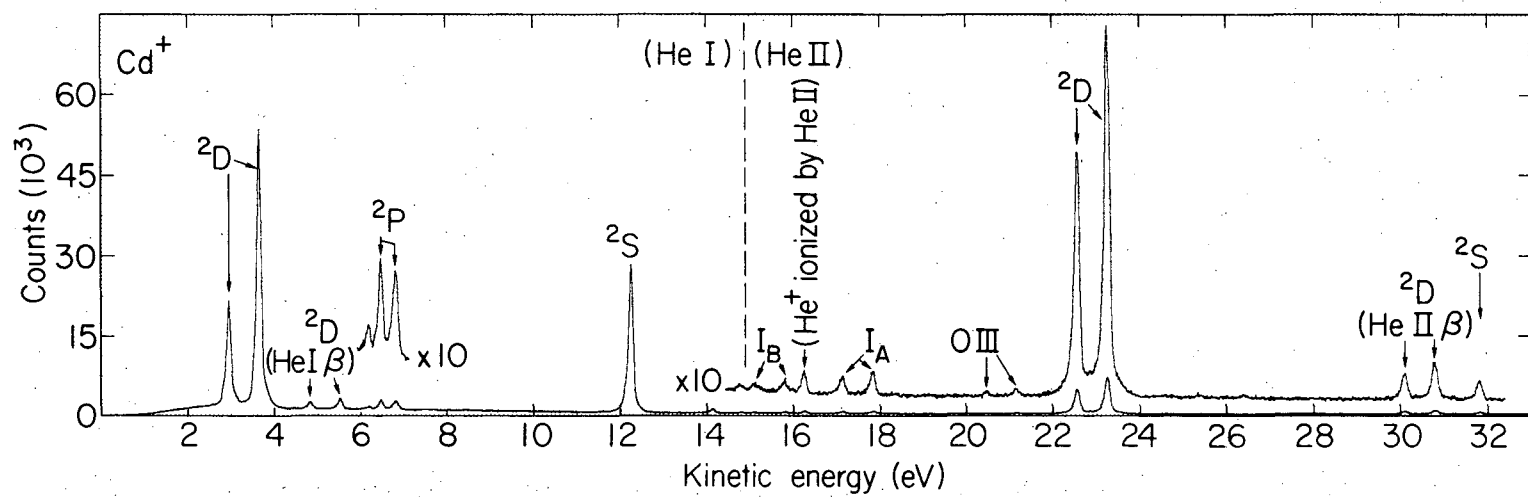
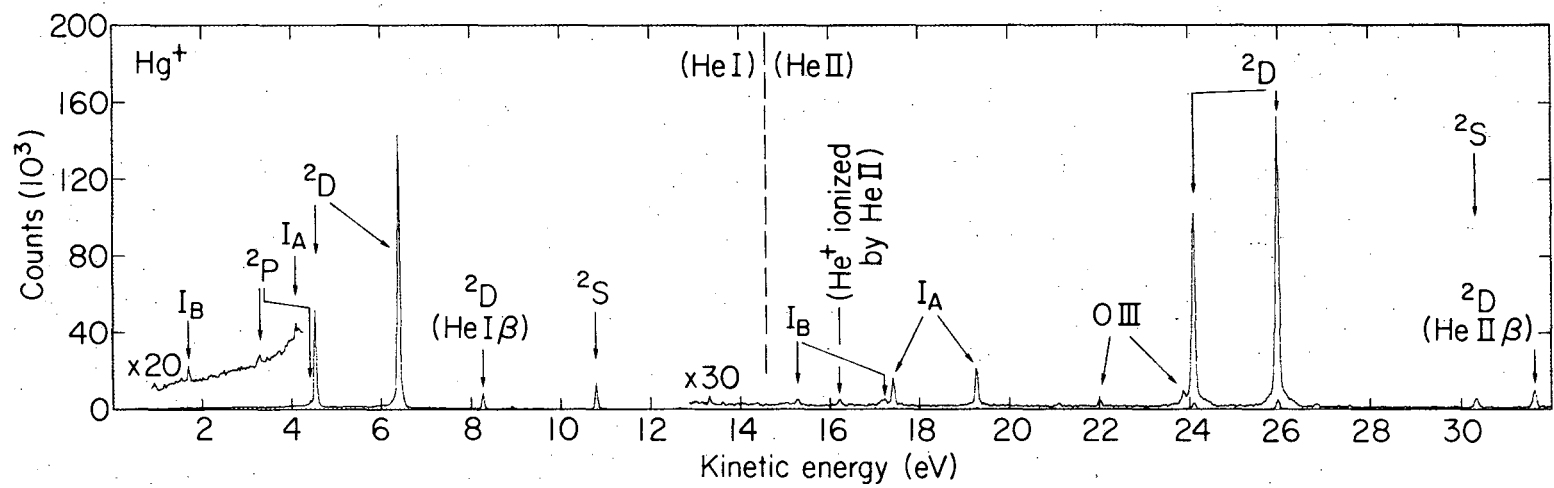


Figure 4

XBL 761-2035



-59-

Figure 5

XBL 761-2040

IV. RELATIVISTIC AND CORRELATION EFFECTS IN THE 21.2-eV PHOTOEMISSION SPECTRUM OF ATOMIC LEAD*

Abstract

Photoelectron spectra were obtained for atomic lead in the 700-800°C range, using HeI radiation (21.2 eV). Relativistic effects were obvious, most notably in the relative intensity of 1.000:0.071 in the peaks arising from $\text{Pb}^+(s^2p; ^2P_{1/2})$: $\text{Pb}^+(s^2p; ^2P_{3/2})$ states. This is a consequence of the $\text{Pb}(s^2p^2; ^3P_0)$ ground state being in fact mostly $s^2p_{1/2}^2$. Correlation effects were also apparent. Several final states inaccessible from an s^2p^2 initial-state configurations were reached; this was explained by admixtures of the configurations sp^2d and s^2d^2 into the initial state. All transitions that would be allowed by the presence of these peaks were actually found. These "direct" observations of configuration interaction give an operational meaning to this concept that is not available to most spectroscopic methods. Energy-loss peaks were observed at higher pressure and attributed to excitation of optical levels in neutral Pb by photoelectrons.

* This chapter was published in J. Chem. Phys. 63, 3473 (1975) in co-authorship with M. S. Banna and D. A. Shirley.

A. Introduction

This is the second in a series of papers reporting photoelectron spectroscopic studies of atomic species in the gas phase, using samples heated to high temperatures. In the first paper¹, on atomic cadmium, we reported the observation of initial-state configuration interaction (ISCI). This paper is addressed to atomic lead.

When an N-electron system absorbs a photon, the process is usually constrained to obey electric dipole selection rules. This constraint is often quite restrictive for ordinary absorption spectroscopic experiments in which the N electrons are all bound in the final state. For photoelectron spectroscopic transitions, of the form

$$N \rightarrow (N - 1)^+ + e^- \quad (1)$$

however, any state of the N-1 electron system can in principle be reached if dipole selection rules can be satisfied for the overall system, with the continuum state of the photoelectron included. This substantially removes the restrictions imposed by the dipole selection rule, and the strongest remaining selection rule is that the transition must be accessible via one-electron operators.

Two important implications follow directly. First, most or all of the electronic states of the N-1 electron system that are reached by one-electron operators will appear in the photoelectron spectrum. The electron kinetic energies yield the level energies directly. Thus a more or less complete array of final states is obtained, with each at its correct energy.

Second, correlation effects, as manifested through configuration interaction, can be observed directly. This follows because those eigenstates of the (final) $N-1$ electron system possessing a given symmetry are described as admixtures of the nominal $N-1$ electron configurations of that symmetry. Thus each eigenstate may consist in part of the nominal lowest-energy $N-1$ electron configuration, and may be directly accessible by photoemission from the ground state. In addition, the ground state itself may be comprised of several admixed configurations, allowing transitions to states that would not be reached if only the dominant configuration were present. This latter effect is in fact the important one in the systems that have been studied to date. In neutral cadmium¹ and mercury², for example, admixtures of the configuration $(np^2; ^1S)$ into the nominal ground-state configuration $(ns^2; ^1S)$ allows the $[np; ^2P_{1/2}]$ and $[np; ^2P_{3/2}]$ final states to be reached.

Group IV elements, with a nominal s^2p^2 ground-state configuration, present an important series that has received considerable theoretical attention. In carbon, the first member of the series, Bagus et al.³⁻⁵ have shown that explicit correlation effects must be introduced to account for the observed 3P , 1D , 1S multiplet separations as well as their ratios $(^3P - ^1D)/(^3P - ^1S)$. In lead, the last member, these effects are expected to be similar magnitude, and relativistic effects should be important as well.⁶

In this paper we report the observation of correlation and relativistic effects on the HeI photoionization spectrum of Pb vapor. Experimental details are given in Section B and results in Section C. Relativistic and correlation effects are discussed in Section D. Section E

deals with the inelastic loss spectrum. Conclusions are given in Section F.

B. Experimental

The experimental details were given in Chapter II.

C. Results

The He I photoelectron spectrum of Pb at 715°C is shown in Fig. 1. Assignments of the peaks were made by comparison of their binding energies with optical data.⁹ These assignments and derived parameters are shown in Table I.

The spectra from atomic $\text{Pb}(6s^2 6p^2; ^3P_0)$ is expected to show four peaks at binding energies 7.415 eV, 9.160 eV, 14.593 eV, and 18.353 eV, arising respectively from transitions to the $(6s^2 6p; ^2P_{1/2})$, $(6s^2 6p; ^2P_{3/2})$, $(6s 6p^2; ^4P_{1/2})$, and $(6s 6p^2; ^2P_{1/2})$ final states of Pb^+ . In addition to these four lines, we have also observed four weaker peaks at 15.61 eV, 15.96 eV, 16.06 eV, and 16.58 eV binding energies, corresponding respectively to the $(6s 6p^2; ^4P_{3/2})$, $(6s^2 6d; ^2D_{5/2})$, $(6s^2 6d; ^2D_{3/2})$ and $(6s 6p^2; ^4P_{5/2})$ final states. Also, three more peaks show up in the spectrum. The peaks designated in the figure by HI and OI are assigned to impurity lines; i.e., photoionization of Pb to the $\text{Pb}^+(^2P_{1/2})$ line at 7.4 eV through excitation by the resonant radiation from the impurities HI and OI (atomic hydrogen and oxygen). The peak at 9.85 eV can be identified neither with any known transition nor as any sample impurity.

The first unusual feature noticed in the spectrum is the inversion of the intensities of $(s^2 p; ^2P_{1/2})$ and $(s^2 p; ^2P_{3/2})$, with the former

dominant. This is explained in Section D-1. It is a consequence of relativistic effects (j-j coupling).

A second feature is the presence of the aforementioned four extra peaks. These are attributed to the correlation effects, as discussed in Section D-2.

Finally, in going to higher temperatures, we see new peaks arising from inelastic losses. In Section E we present the spectrum and discuss the nature of these transitions.

D. Discussion

1. Relativistic Effects

Spin-orbit coupling splits the 6p shell into $p_{1/2}$ and $p_{3/2}$ subshells, with the former being lower in energy. For the two-electron case we have three configurations; $(p_{1/2})^2$, $(p_{1/2}p_{3/2})$ and $(p_{3/2})^2$. The ground state of p^2 ($J = 0$) can, in general, be written in terms of j-j coupled states as

$$\Psi = c_1 (p_{1/2})^2 + c_2 (p_{3/2})^2.$$

In terms of L.S coupled states this corresponds to a mixture of 3P_0 and 1S_0 states. The relative weights of the two configurations will depend on the strength of the spin-orbit coupling. Relativistic Hartree-Fock (RHF) calculations⁶ predict the ratio $(c_2/c_1)^2 = .081$, showing that j-j coupling is a better approximation for Pb than is L-S coupling, which gives the ratio as 0.5.

Photoionization from the outer 6p subshells yields $^2P_{1/2}$ and $^2P_{3/2}$ states of Pb^+ ($6s^2 6p$), corresponding to the removal of an electron from $6p_{1/2}$ or $6p_{3/2}$ subshells, respectively. Hence the intensities of the observed lines give a measure of the relative weights of these subshells in the ground state. From Table I, our experimental intensity ratio is .071, in very good agreement with the RHF prediction. However, one would have to correct for any differences in the photoionization cross sections before a final comparison could be made. The photoionization cross sections may be considerably different for each individual subshell, because the radial functions are different (RHF calculations for the mean values of $\langle r \rangle$ give respectively 3.07 and 3.52 atomic units for the $6p_{1/2}$ and $6p_{3/2}$ subshell,⁶ compared to the non-relativistic value¹⁰ of 3.46). Also, the RHF calculation did not include some correlation effects that we will show to be important, which again may affect the calculated intensity ratio.

Removal of an s electron from ($s^2 p^2$; 3P_0) gives $^4P_{1/2}$ and $^2P_{1/2}$ (sp^2) lines. But for Pb^+ , ($6s 6p^2$; $^4P_{1/2}$) corresponds to $6s(6p_{1/2})^2$ and $^2P_{1/2}$ corresponds to $6s(6p_{1/2} 6p_{3/2})$ in j-j coupling. On this argument alone we would expect to see an intense $^4P_{1/2}$ line and a relatively weak $^2P_{1/2}$ line, but from Table I the relative intensities are .075 and .110, respectively. While the cross sections may be somewhat different for these two processes, we believe that the main reason for the $^2P_{1/2}$ intensity being so high is configuration interaction in the final state. A discussion of correlation effects is given below.

2. Correlation Effects

Final-state correlation effects have been reported in the photoemission spectra from noble gases,¹¹ molecules,¹² and solids.¹³ Berkowitz, et al.⁸ reported that the quasi-degenerate $6p^2$ configuration mixed into $6s^2$ in the ground state of Hg, giving satellites in the He I photoemission spectrum of atomic Hg, and we reported a similar result for Cd¹.

In open-shell atoms or molecules, the quasi-degenerate configurations are known to mix strongly with the ground state. This effect was termed "internal correlation" by McKoy and Sinanoglu.¹⁴ For the $6s^2 6p^2$ ground-state configuration of Pb, $6p^4$ is perhaps the conventional configuration to be admixed, but Desclaux⁶ found this mixing to be very small, because it involves promotion of two 6s electrons into the energetically unfavorable $6p_{3/2}$ subshell. Bagus et al.³⁻⁵ reported configurations of the type $2s2p^2 3d$ to mix substantially into the ground state of carbon ($2s^2 2p^2$), although the 3d shell is not quasi-degenerate with 2p. But in Pb, the 6d shell lies very close in energy to 6p, and it is of course quasi-degenerate. Hence we expect 6d mixing to be important in the ground-state of Pb. Because the spin-orbit coupling constant is small both the $6d_{3/2}$ and $6d_{5/2}$ subshells are expected to contribute.

In Table II, we give the configurations expected to mix strongly with $6s^2 6p^2$, their final states upon photoionization, and their spectroscopic designations. We used the j-j coupling scheme and coupled the two p electrons (or two s-electrons) to the remaining two electrons to get the $J = 0$ initial state. We have listed only the final states which can be reached by (21.2 eV) He I radiation (these states can all be regarded

as resulting from the ionization of a 6d electron, in an approximate description).

From Tables I and II one can see that configurations I.A would give $^4P_{3/2}$, which is observed to be 0.024 the intensity of the main line; I.B and I.C would give $^4P_{5/2}$, also observed, in intensity 0.040; I.D and I.E would give $^2D_{5/2}$ and $^2D_{3/2}$ derived from the s^2d configuration, again observed, with intensities of 0.022 and 0.019. Configurations II.F and II.G would give $^2D_{5/2}$ and $^2D_{3/2}$ derived from the configuration sp^2 . These were not observed to be present. This is easily understood, because they can mix directly only with the $(6s_{1/2})^2(6p_{3/2})^2$ part of the ground state (they would involve three-electron excitation from the $(6s_{1/2})^2(6p_{1/2})^2$ configuration and would therefore be expected to mix negligibly into this configuration).

Mixing of $6s^26d^2$ and $6s6p^26d$ configurations into the ground state of Pb can thus totally account for the presence of the satellites observed in this experiment. However it would be necessary to consider the mixing among final states as well as variations in photoionization cross-section before definite mixing coefficients could be derived from these experimental peak intensities. We are presently investigating techniques by which such quantitative comparisons with theory might feasibly be made.

Another mechanism has been suggested to account for the satellite structure, namely "conjugate shake-up",² in which the angular momentum of the radiation field is transferred to one of the passive electrons (i.e., the electron makes a transition to an empty orbital with higher l quantum number). We can write this process for Pb as follows:

Main process: $(6s_{1/2})^2(6p_{1/2})^2 + h\nu \rightarrow [(6s_{1/2})^2 6p_{1/2}]^2 P_{1/2} + \epsilon d \text{ or } \epsilon s$

Conjugate
shake up: $(6s_{1/2})^2(6p_{1/2})^2 + h\nu \rightarrow [(6s_{1/2})^2 6d_{3/2}]_{J=3/2} + \epsilon p$

or
/ $(6s_{1/2})^2(6p_{1/2})^2 + h\nu \rightarrow [(6s_{1/2})(6p_{1/2})(6p_{1/2})]_{J=1/2} + \epsilon p$

and $(6s_{1/2})^2(6p_{1/2})^2 + h\nu \rightarrow [(6s_{1/2})(6p_{1/2})(6p_{3/2})]_{J=3/2} + \epsilon p.$

Since $\Delta J = 0, \pm 1$ selection rules are operative, only $(sp^2; ^4P_{3/2})$ and $(s^2d; ^2D_{3/2})$ lines would be expected to be present in the spectrum. The $(sp^2; ^4P_{5/2})$ and $(s^2d; ^2D_{5/2})$ lines could only result from the $(6p_{3/2})^2$ part of the ground state, and would be extremely weak if not absent.

Hence we believe this mechanism does not contribute much to the observed intensity of the four satellite lines. The theoretical situation as to the importance of the conjugate shake-up mechanism is unclear. Detailed calculations have shown that this mechanism is unclear. Detailed calculations have shown that this mechanism is very weak for He¹⁵, although Berkowitz et al.² made estimates that suggested it could be as strong as the CI mechanism in mercury.

E. Inelastic Loss Spectra

When the Pb spectrum is taken at 765°C several strong inelastic loss peaks appear. Figure 2 shows the spectrum and Table III summarizes the results. All the observed five peaks are interpreted to result from electron impact excitation of neutral Pb by photoelectrons emitted in exciting the $^2P_{1/2}$ line, at a kinetic energy of 13.80(1) eV.

Lines 1 and 2 correspond to excitation of a $6p_{1/2}$ electron into the $6p_{3/2}$ subshell, with final states 3P_1 and 3P_2 . Intensities are in a ratio of $\sim 1:4$ which clearly deviates from the statistical ratio of 3:5. The final state 1D_2 , 2.66 eV away, corresponding to a $(6p_{3/2})^2$ configuration is not observed, which again is a consequence of strong j-j coupling. Lines 3 and 4 are the results of excitation from 6p to 7s and 6d shells. Line 5 cannot be identified by any known transition, and we tentatively assign it to an excitation from the 6s to the 6p shell. The breadth of this line indicates more than one final state, or perhaps that the excitation takes place in Pb_2 .

F. Conclusions

This work has demonstrated the feasibility of obtaining photoemission spectra of atomic Pb at temperatures of 700-800° C, with good resolution and signal/noise ratios. The spectra showed in a very direct way—through dramatic intensity ratios or the existence of satellite lines—that relativistic and correlation effects are indeed present in the $6s^2 6p^2$ ground-state configuration of lead. This may be contrasted with the relatively indirect nature of most spectroscopic methods for studying these effects. Further theoretical developments are necessary before a really quantitative interpretation of these peak intensities will be possible. With these developments, we believe that photoemission studies of this nature will be able to bring more operational meaning to the concept of configuration interaction.

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Table I. States of Pb^+ observed in photoemission from Pb Vapor.

Final States	Relative intensity ^a	Binding energy, eV ^b	Energy from optical data, eV ^c
$6s^2 6p \quad ^2P_{1/2}$	1.000	7.42(1)	7.415
$\quad \quad \quad ^2P_{3/2}$	.071 (5)	9.16(1)	9.160
$6s 6p^2 \quad ^4P_{1/2}$	.075 (5)	14.59(1)	14.593
$\quad \quad \quad ^4P_{3/2}$	.024 (5)	15.61(1)	15.611
$\quad \quad \quad ^4P_{5/2}$	.040 (5)	16.57(1)	16.576
$6s 6p^2 \quad ^2P_{1/2}$	.110 (5)	18.35(1)	18.353
$6s^2 6d \quad ^2D_{5/2}$	.022 (5)	15.97(1)	15.963
$\quad \quad \quad ^2D_{3/2}$	.019 (5)	16.06(1)	16.059
(?) ^d	.014 (5)	9.85(1)	---

^aRelative areas divided by their kinetic energies to correct for the spectrometer efficiency.

^bThis work. Values given are averages of three runs. Errors in last place are given parenthetically. The Xe lines at 12.130 eV and 13.436 eV and the Ar lines at 15.759 eV and 15.937 eV are used for calibration.

^cRef. 9.

^dNot identified.

Table II. Configuration which can mix with the ground state of Pb and their final ionic states of Pb^+ excluding the $^2\text{P}_{1/2}$ and $^2\text{P}_{3/2}$ states of s^2p .

	Initial state of Pb	Final state of Pb^+	J	Spec. design. ^a	Binding energy, eV ^a	Remarks
I.	$(6s_{1/2})^2 (6p_{1/2})^2_{J=0}$	$6s_{1/2} (6p_{1/2})^2_{J=0}$	$1/2$	$\left. \begin{matrix} 4\text{P}_{1/2} \\ 2\text{S}_{1/2} \end{matrix} \right\} \text{sp}^2$	14.593	Main line
II.	$(6s_{1/2})^2 (6p_{3/2})^2_{J=0}$	$6s_{1/2} (6p_{3/2})^2_{J=0}$	$1/2$	$\left. \begin{matrix} 4\text{P}_{1/2} \\ 2\text{S}_{1/2} \end{matrix} \right\} \text{sp}^2$	20.343	Not observed
I.A.	$(6p_{1/2} 6p_{3/2})_{J=1} (6s_{1/2} 6d_{3/2})_{J=1}$	$6s_{1/2} (6p_{1/2} 6p_{3/2})_{J=1}$	$3/2$ $1/2$	$\left. \begin{matrix} 4\text{P}_{3/2} \\ 2\text{P}_{1/2} \end{matrix} \right\} \text{sp}^2$	15.611 18.353	Observed Observed ^b
I.B.	$(6p_{1/2} 6p_{3/2})_{J=2} (6s_{1/2} 6d_{3/2})_{J=2}$	$6s_{1/2} (6p_{1/2} 6p_{3/2})_{J=2}$	$5/2$ $3/2$	$\left. \begin{matrix} 4\text{P}_{5/2} \\ 4\text{P}_{3/2} \end{matrix} \right\} \text{sp}^2$	16.576 20.389	Observed Not observed
I.C.	$(6p_{1/2} 6p_{3/2})_{J=2} (6s_{1/2} 6d_{5/2})_{J=2}$	$6s_{1/2} (6p_{1/2} 6p_{3/2})_{J=2}$	$5/2$	$\left. \begin{matrix} 4\text{P}_{5/2} \\ 4\text{P}_{3/2} \end{matrix} \right\} \text{sp}^2$	20.389	Not observed
I.D.	$(6s_{1/2})^2 (6d_{3/2})^2_{J=0}$	$(6s_{1/2})^2 6d_{3/2}$	$3/2$	$\left. \begin{matrix} 2\text{D}_{3/2} \\ 2\text{D}_{5/2} \end{matrix} \right\} \text{s}^2\text{d}$	16.059	Observed
I.E.	$(6s_{1/2})^2 (6d_{5/2})^2_{J=0}$	$(6s_{1/2})^2 6d_{5/2}$	$5/2$	$\left. \begin{matrix} 2\text{D}_{3/2} \\ 2\text{D}_{5/2} \end{matrix} \right\} \text{s}^2\text{d}$	15.963	Observed
II.F	$(6p_{3/2})^2 (6s_{1/2} 6d_{3/2})_{J=2}$	$6s_{1/2} (6p_{3/2})^2_{J=2}$	$5/2$ $3/2$	$\left. \begin{matrix} 2\text{D}_{5/2} \\ 2\text{D}_{3/2} \end{matrix} \right\} \text{sp}^2$	17.713 18.443	Not observed Not observed
II.G	$(6p_{3/2})^2 (6s_{1/2} 6d_{5/2})_{J=2}$	$6s_{1/2} (6p_{3/2})^2_{J=2}$	$5/2$ $3/2$	$\left. \begin{matrix} 2\text{D}_{5/2} \\ 2\text{D}_{3/2} \end{matrix} \right\} \text{sp}^2$	17.713 18.443	Not observed Not observed

a. Ref. 9.

b. Also borrows intensity from the main line at 14.59 eV.

Table III. Inelastic loss peaks observed in neutral Pb.

Peak	Transition from the ground state	Relative intensity ^a	Excitation energy, eV ^b	Energy from optical data, eV ^c
0	$6s^2 6p^2 \ ^3P_0^d$	---	---	---
1	$6s^2 6p^2 \ ^3P_1$	1	0.97 (1)	0.969
2	$6s^2 6p^2 \ ^3P_2$	4 ± 0.5	1.32 (1)	1.320
3	$6s^2 6p(^2P_{1/2})7s \ ^3P_1^o$	4 ± 0.5	4.37 (1)	4.374
4	$6s^2 6p(^2P_{1/2})6d \ \begin{cases} ^3D_2^o \\ ^3D_1^o \end{cases}$	4 ± 0.5	5.71 (1)	$\begin{cases} 5.709 \\ 5.710 \end{cases}$
5	$6s6p^2^e$	16 ± 1	10.52 (2)	---

- Areas divided by their kinetic energies, relative to peak 1.
- Values given are averages of two runs. The Pb^+ lines from Table I are used for energy calibration.
- Ref. 9.
- Zero loss line (i.e., the main peak).
- Assignment is tentative as explained in the text.

FIGURE CAPTIONS

Fig. 1. Photoemission spectrum of Pb vapor at 715°C using 21.21 eV HeI radiation. Lines marked HI and OI arise respectively from HI 10.199 eV and OI 9.493 eV radiation.

Fig. 2. Photoemission spectrum of Pb vapor at 765°C using 21.21 eV HeI radiation.

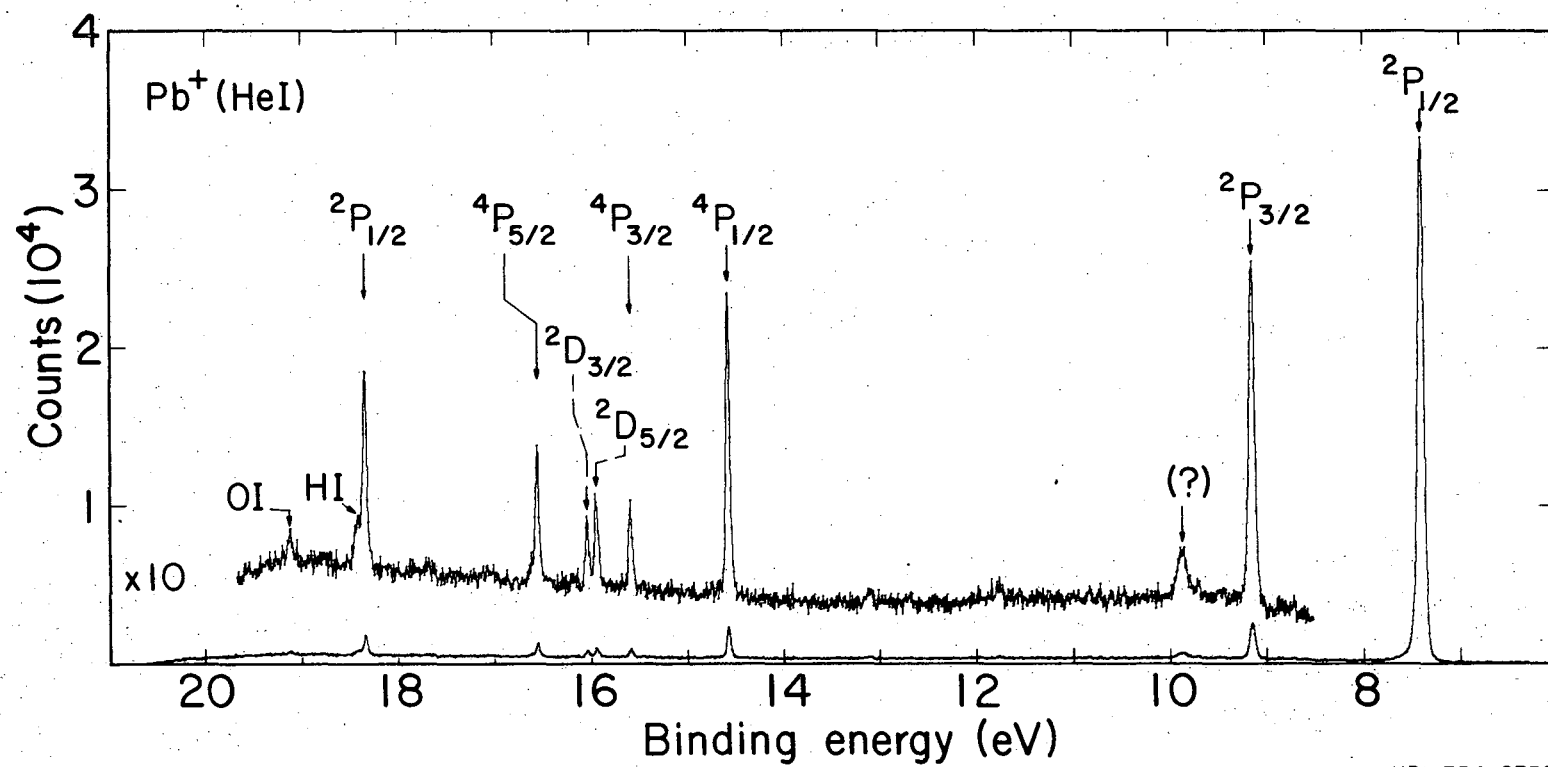


Figure 1

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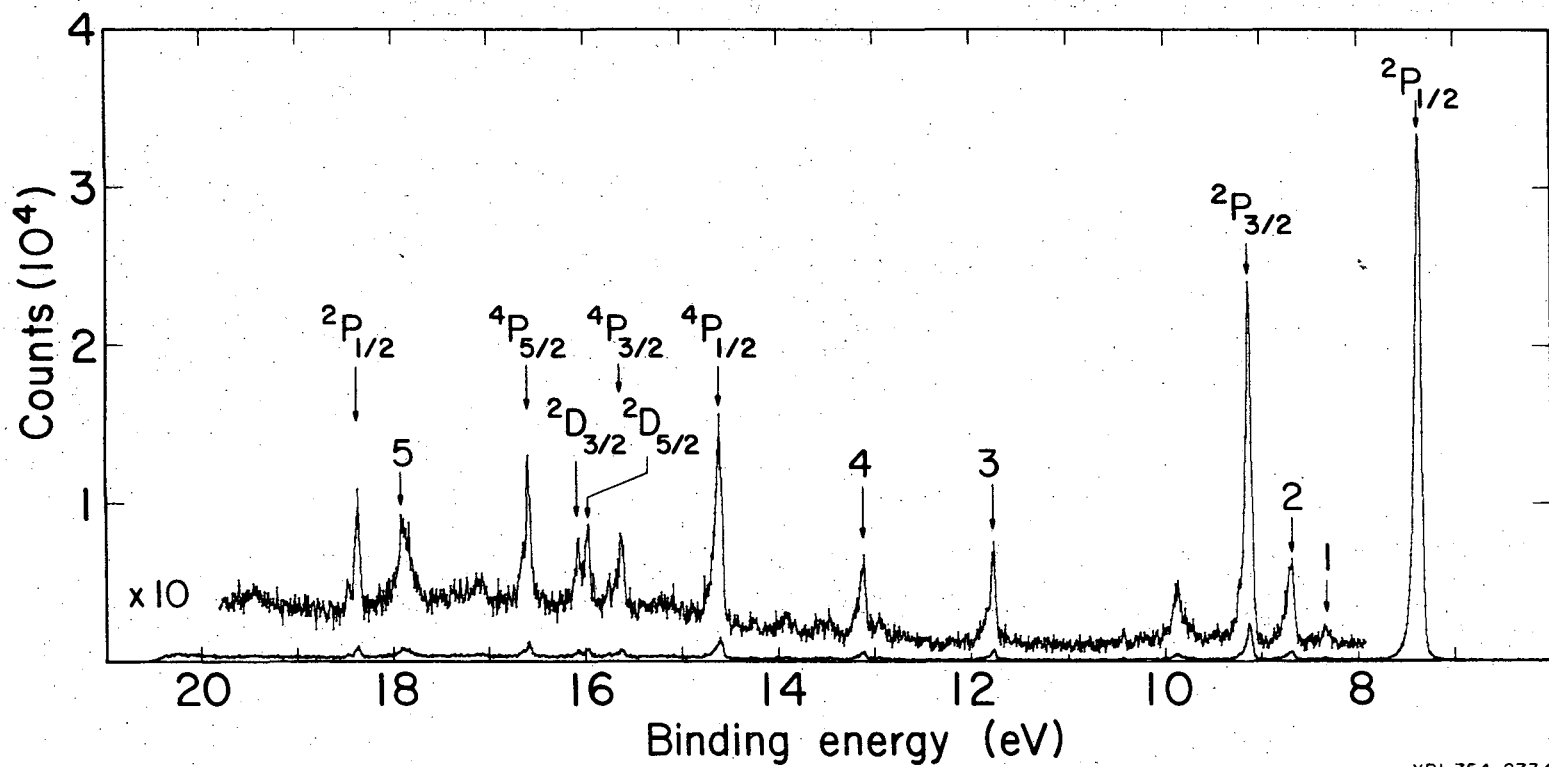


Figure 2

XBL 754-2734

V. PES OF ATOMIC AND MOLECULAR BISMUTH*

Abstract

Photoelectron spectra of Bi and Bi₂ were recorded by studying bismuth vapor at 750°C. The spectrum of Bi was found consistent with a j-j coupling description of the ground state. However, relativistic effects seemed to have little influence upon the relative photoionization cross sections of the ²P_{0,1,2} lines. Satellite peaks ¹D₂ at 11.49 eV, and possibly also ³D_{1,2} at 17.12 and ³F_{2,3} at 17.47 eV were observed. They were assigned to admixture of the configurations [(6s_{1/2})²(6p_{3/2})²]_{3/2}, [6s²6p6d²]_{3/2} into the main ground-state configuration [(6s_{1/2})²(6p_{1/2})²6p_{3/2}. An autoionization process at the energy of HeIγ radiation (23.74 eV) was suggested by the large intensity of the HeIγ spectrum. The photoelectron spectrum of Bi₂ showed three distinguishable bands at 7.53 eV, 8.94 eV, and 9.30 eV corresponding respectively to the ionic states ²Π_{u,3/2}, ²Π_{u,1/2}, and ²Σ_g⁺ due to ionization of a (π_u6p) or (σ_g6p) electron. A probable fourth band was observed at 14.87 eV, and was tentatively assigned to ²Σ_u⁺ of Bi₂⁺ formed from (σ_u6s) ionization. The spectrum of Bi₂ was found similar to those of lighter Group VA diatomics. A relationship between the equilibrium internuclear distance and the difference between the binding energies of (σ_gnp) and (π_unp) orbitals was established for the Group VA diatomics.

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A. Introduction

Recently photoelectron spectra of atomic vapors have been demonstrated¹⁻⁴ to be capable of providing unique information about electron correlation effects in the ground states of atoms. This is accomplished by observing directly in the spectra correlation satellite peaks due to configuration interaction in the initial state. The theory of correlation satellites has been extensively discussed,^{5,6} and will not be reviewed here. In this paper, we present a photoelectron spectroscopic study of atomic bismuth, which also shows relativistic and correlation effects.

The photoelectron spectrum of Bi was obtained from bismuth vapor at ca. 750 (± 20)°C. The composition of bismuth vapor has been well documented.⁷⁻¹⁰ At 800°C, bismuth vapor consists mainly of monoatomic and diatomic species in the ratio of 1:1.5 with less than 1% of heavier species. The same vapor composition was also observed in a recent ESCA study¹¹ where $4f_{7/2}$ lines were monitored. Therefore, bismuth vapor will also provide us a chance to study Bi_2 . As the heaviest, kinetically stable diatomic molecule, Bi_2 provides an interesting case to study the relativistic effects in molecular bonding. In the same context, it is interesting to compare the photoelectron spectrum of Bi_2 with those of other Group VA diatomic molecules.

B. Experimental

The experiments were carried out in a Perkin-Elmer PS-18 photoelectron spectrometer modified for high temperature work. The details of the modifications have been described in Chapter II.

The spectrum of bismuth was taken at $(750 \pm 20)^{\circ}\text{C}$, as determined by an iron-constantan thermocouple. The sample was introduced in the form of small pieces of metal. In this temperature range the vapor merely consists of atomic and diatomic bismuth.⁷⁻¹¹ From published thermodynamic data we estimated the dimer to monomer ratio under our experimental conditions as 1.7 ± 0.2 . No other lines were detected which could be identified with any other species or known sample impurities.

Peak areas were corrected for the change of the spectrometer transmission with electron's kinetic energy using the approximate relation $\Delta E/E = \text{constant}$. No other correction was made for inelastic scattering or charging effects.¹² Hence the area ratios reported here carry large experimental uncertainties, especially for the molecular bands.

C. Results

The HeI photoelectron spectrum of Bi and Bi₂ is shown in Fig. 1. Assignments of atomic peaks were made by comparison of binding energies with optical data.¹³ Some of the molecular lines of Bi₂ are easily distinguishable by their larger widths. This can be seen most clearly in Fig. 2, which depicts the portion of the spectrum between 6 and 11 eV binding energies. Additional identification was accomplished by noting the behavior of the line intensities with respect to the oven temperature. The intensities of the group of lines belonging to Bi₂ decreased with increasing temperature relative to that of atomic peaks, while the relative intensities within each group remained unchanged. In one experiment, the Bi vapor was superheated, and consequently only weak molecular lines were detected, thus confirming our identifications. Table I summarizes the experimental results for both Bi and Bi₂.

The spectrum of atomic Bi ($6s^2 6p^3 : ^4S_{3/2}$) shows four main peaks at binding energies 7.29 eV, 8.94 eV, 9.40 eV, and 16.73 eV corresponding respectively to the ($6s^2 6p^2 : ^3P_0$), ($6s^2 6p^2 : ^2P_1$), ($6s^2 6p^2 : ^3P_2$) and ($6s 6p^3 : ^5S_2$) states of Bi⁺ and 3 additional weaker peaks at 11.50 eV, 17.12 eV and 17.47 eV corresponding to the ($6s^2 6p^2 : ^1D_2$), ($6s^2 6p 6d : ^3D_2$ or 3D_1) and ($6s^2 6p 6d : ^3F_2$ or 3F_3) states of Bi⁺. The peaks designated by β or γ are from HeI β (23.09 eV) and HeI γ (23.74 eV) radiation, and the peaks designated by HI and OI arise by photoionization to the Bi⁺(3P_0) state by, respectively, the HI (10.199 eV) and OI (9.493 eV) radiation that are present due to traces of H₂O.¹⁴

The spectrum of diatomic Bi₂($^1\Sigma_g^+$) shows three distinct bands at

vertical binding energies 7.53 eV, 8.94 eV, and 9.30 eV corresponding respectively (see discussion) to the $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$ states of Bi_2^+ resulting from ionization of the $(\pi_u, 6p)$ orbital and the $^2\Sigma_g^+$ state of Bi_2^+ from the $(\sigma_g 6p)$ shell. A weaker line at 14.87 eV is also observed and tentatively attributed to Bi_2^+ , since its intensity followed those of the other molecular lines. It is assigned to the $^2\Sigma_u^+$ state arising from ionization of the $(\sigma_u 6s)$ orbital.

D. Discussion1. Atomic Bismuth

In the photoelectron spectrum of Pb, Süzer et al.² reported satellite peaks due to admixture of $(6s^2 6d^2)$ and $(6s 6p^2 6d)$ configurations into the $(6s^2 6p^2 : ^3P_0)$ ground state. Furthermore, it was confirmed that j-j coupling is appropriate for describing the ground state of Pb as a result of strong spin-orbit (s-o) interaction. Consequently, the ground state is better approximated by $\Psi = a(6p_{1/2})_0^2 + b(6p_{3/2})_0^2$ with $a \gg b$, as predicted by relativistic calculations.¹⁵ Being next to Pb in the periodic table and thus having a slightly larger s-o interaction, Bi $(6s^2 6p^3 : ^4S_{3/2})$ is certainly expected to follow the j-j coupling scheme closely. Therefore, the ground state of Bi can be approximated as a simple CI expansion

$$\begin{aligned} \Psi(^4S_{3/2}) = & a[(6s_{1/2})^2(6p_{1/2})^2(6p_{3/2})]_{3/2} \\ & + b[(6s_{1/2})^2(6p_{1/2})(6p_{3/2})^2]_{3/2} + c[(6s_{1/2})^2(6p_{3/2})^3]_{3/2}. \end{aligned} \quad (1)$$

The relative weights of a, b, and c depend on the magnitude of the s-o coupling constant. Qualitatively, simply on energy grounds ($6p_{1/2}$ lies lower than $6p_{3/2}$) and by analogy to Pb^2 , one expects the coefficients to fall in the order $a \gg b > c$. Furthermore, considering the near-degeneracy of 6d and 6p shells, and again by analogy to Pb, one may expect the ground state of Bi to have an admixture of configurations arising from $6p \rightarrow 6d$ excitations, e.g., $[6s^2 6p 6d^2]_{3/2}$.

Let us first concentrate on the main configuration in the ground state, i.e. $[(6s_{1/2})^2(6p_{1/2})^2(6p_{3/2})]_{3/2}$. Removal of an electron from the $6p_{3/2}$ shell gives one state 3P_0 (L-S designation) at 7.289 eV and the removal of an electron from the $6p_{1/2}$ shell gives two states 3P_1 , and 3P_2 (since the total J can couple to 1 or 2) at 8.942 eV and 9.401 eV, respectively. These three peaks are observed experimentally in the ratio of approximately 1:3:5 (Table I), close to their statistical ratios. This is a bit surprising considering that now the $6p_{1/2}$ and $6p_{3/2}$ shells are rather different from each other because of large s-o interaction [the calculated $\langle r \rangle$ values for $6p_{1/2}$ and $6p_{3/2}$ shells are respectively 2.56 and 2.94 a.u from Ref. 15]. This suggests that photo-ionization cross sections for these sub-shells are approximately the same, which agrees with the behavior of the 6p sub-shells of Pb^2 , but contrasts with that of Hg 5d sub-shells^{3,12} in which the observed ratio deviated from the statistical ratio. Perhaps angular distribution studies would clear up this point.

Removal of an electron from the 6s shell gives two states (again two possibilities for total J); only one of these i.e., 5S_2 could be observed at 16.730 eV, the other one 3S_1 is expected to have a binding energy higher than 21.21 eV. The intensity of the 5S_2 line is much lower than those of the 6p lines, again similar to the Pb case.

Turning to the secondary configurations in eq. 1, we note they can give rise to observable satellite peaks if their coefficients are large enough. Ionization of a $6p_{3/2}$ electron from $[(6s_{1/2})^2(6p_{1/2})(6p_{3/2})^2]_{3/2}$ gives the 3P_1 , and 3P_2 state of Bi^+ , but no new ionic states. However, the removal of the $6p_{1/2}$ electron gives the

$[(6s_{1/2})^2(6p_{3/2})^2]_2$ state at 11.49 eV with the L-S designation of 1D_2 , which can only arise in the spectrum through configuration interaction. The $\text{Bi}^+ 6s^2 6p^2 (^1S_0)$ state at 12.766 eV, which corresponds to $[(6s_{1/2})^2(6p_{3/2})^2]_0$ and would result from the removal of $6p_{3/2}$ electron from the last configuration in eq. 1, has not been observed. This confirms our expectation that the coefficient c is the smallest in eq. 1, because the configuration $[(6s_{1/2})^2(6p_{3/2})^3]_{3/2}$ involves two electron excitation from the $6p_{1/2}$ sub-shell into the $6p_{3/2}$ sub-shell and is highly unfavorable on energy grounds. The corresponding configuration was not observed in the Pb spectra.²

At least two more lines are observed at 17.12 eV and 17.47 eV, corresponding to states of the $6s^2 6p 6d$ configuration of Bi^+ . They can originate from the $6s^2 6p 6d^2$ configurations in Bi. Both configurations are favorable because the $6d$ shell is near-degenerate with the $6p$ shell. Again such configurations were found to mix with the main configuration, and to give satellite lines, in the Pb spectra.²

There are several anomalies in the intensities of the 3P lines of Bi^+ ionized by $\text{HeI}\gamma$ radiation, as shown in Fig. 1. In Table II we have listed the relative intensities of these lines excited by the different HeI resonance lines. It is known¹⁴ that in a cold cathode discharge lamp such as that used in the Perkin-Elmer spectrometer, the $\text{HeI}\beta$ line normally amounts to $\sim 5\%$ and the $\text{HeI}\gamma$ line $\leq 1\%$ of the dominant $\text{HeI}\alpha$ radiation. Our own experience with this lamp confirms this. Therefore, the observed $^3P_{0,1,2}$ line intensities (Table II) produced by $\text{HeI}\gamma$ radiation are unexpectedly large. They cannot reasonably be attributed to fluctuations of the lamp output. The observation was reproduced in three

independent runs. By contrast, the molecular lines of Bi_2^+ produced by HeI γ radiation are hardly detectable (Fig. 1) as expected. The possibility of impurities was carefully checked and ruled out by using NeI radiation, where no corresponding lines were observed. The first anomaly is thus an enhanced overall intensity in the HeI γ spectrum. Secondly, the ratio of $^3P_0 : ^3P_1 : ^3P_2$ in the HeI γ spectrum is 1 : 1.1 : 1.2, substantially different from the statistical ratio 1 : 3 : 5, which seems to be followed by the HeI α spectrum quite closely. The cause of the sudden rise of the 3P line intensities at HeI γ radiation (23.74 eV) and their unexpected intensity ratio cannot be determined at the present. We note, however, this is the type of behavior expected if a resonant state of Bi resulting from $5d \rightarrow np$ or $n'f$ excitation is reached by HeI γ radiation, and if this state subsequently autoionizes to give the 3P lines. Further study with a monochromatic light sources is needed to clarify this point.

The intensities in the HeI β spectrum (Table II) appear to reflect the expected HeI β radiation intensity. The observed ratio $^3P_0/^3P_1$, 1.5 seems to deviate appreciably from 1/3; however, the large experimental uncertainty precludes any definite conclusion.

2. Molecular Bismuth

From an analogy with N_2 , P_2 , etc., the ground-state valence electronic configuration of Bi_2 may be written as

$$(\sigma_g 6s)^2 (\sigma_u 6s)^2 (\sigma_g 6p)^2 (\pi_u 6p)^4 : 1\Sigma_g^+$$

where $(n\ell)$ denotes the dominant components of each molecular orbital.

Considering the large internuclear distance ($2.85\text{\AA}$)¹⁶ and the small vibrational frequency (172.71cm^{-1})¹⁷ of Bi_2 , one expects the bonding between the two bismuth atoms to be weak, and the core electrons to contribute little to the bonding. Thus the valence photoelectron spectrum of Bi_2 would divide into two groups of bands; the first group arising from 6p MO's would be found close to the atomic ^3P lines and the second from 6s MO's close to $(6s)^{-1}$ lines. The removal of a $(\pi_u 6p)$ electron would give the s-o partners $^2\Pi_{u,3/2}$ and $^2\Pi_{u,1/2}$ in the first group, with $^2\Pi_{u,3/2}$ lower in energy. The separation between the $^2\Pi$ states would be close to the 6p atomic s-o coupling constant, i.e. 1.25 eV ,¹⁸ as was found to be the case in diatomic halogens^{19,20} and in diatomic chalcogens.²¹⁻²³ By analogy with N_2^+ ,²⁴ PN^+ ,²⁵ and P_2^+ .²⁶ The $(\pi_u 6p)$ orbital would be comparatively bonding and thus the $^2\Pi$ bands of Bi_2^+ would be relatively broad due to vibrational structure whereas the other valence MO's would be comparatively nonbonding and give relatively sharp lines. With these considerations, it is rather a straightforward matter to assign the molecular spectrum of Bi_2 . Thus, we assign the first two bands (at 7.53 and 8.94 eV respectively) separated by 1.4 eV and each with a width of $\sim 0.27\text{ eV}$ to the two $^2\Pi$ partners. The sharp line at 9.30 eV is assigned to the $(\sigma_g 6p)^{-1}$ state and the weak line at 14.87 eV to the $(\sigma_u 6s)^{-1}$ state. As pointed out in Section III, the identification of the latter state is only tentative. We note the $^2\Sigma_u^+$ state at 14.87 eV falls in the expected energy region, as the binding energy of the atomic 6s shell is about 16.8 eV and the binding energy of $(\sigma_u 6s)$ is expected to be lower than this value because of its slightly antibonding nature. The $(\sigma_g 6s)^{-1}$ state is however not definitely observed presumably

to its small cross section (cf. the weak intensity of $^2\Sigma_u^+$), and/or its binding energy being higher than 21.21 eV.

In view of the large s-o interaction in bismuth, it is interesting to compare the spectrum of Bi_2^+ with those of the iso-valent molecules N_2^+ , $^{24}\text{PN}^+$, 25 and P_2^+ . 26 For this purpose, we have collected the relevant data in Table III. We note the general appearance of the corresponding bands in every spectrum is strikingly similar in that only the $^2\Pi_{3/2,1/2}$ bands show appreciable width due to vibrational structure while the rest are relatively sharp peaks. This indicates that only the $(\pi_u np)$ molecular orbital is bonding while the other orbitals are relatively nonbonding. While the general resemblance of the spectra is usually expected from chemical similarity, the gradual crossover in energy between the ionic states $^2\Sigma_g^+$ and $^2\Pi_u$ from N_2^+ , PN^+ , P_2^+ , to Bi_2^+ (Table III) requires comment.

The photoionization of N_2 to N_2^+ , in which $^2\Sigma_g^+$ comes lower than $^2\Pi_u$ state, is the classical example of the breakdown of molecular orbital ordering by Koopmans' theorem, 27 since Hartree-Fock MO calculations of N_2 28 invariably predicts $(\pi_u 2p)$ as the highest occupied MO. Various elaborate theoretical attempts 29 have been made to elucidate the cause of the discrepancy, while Price 30 has given a simple physical explanation. Price pointed out that the internuclear distance in N_2 is so short as a result of its 'triple' bond that the two nuclei have been pulled through some of the $(\sigma_g 2p)^2$ cloud and this orbital therefore supplies no bonding energy at this separation. Consequently, for N_2 it takes less energy to remove a $(\sigma_g 2p)$ than a $(\pi_u 2p)$ electron. However, going down the periodic table, the atomic valence orbitals become larger, increasing the internuclear separation; therefore, the $(\sigma_g np)$ MO will be expected to become

increasingly more stable with respect to $(\pi_{\text{u}}\text{np})$. The latter will eventually become the highest occupied MO and the $^2\Pi$ state the ground ionic state, as observed (Table III). In Fig. 3, the difference between the vertical binding energies of the $(\sigma_{\text{g}}\text{np})$ and $(\pi_{\text{u}}\text{np})$ MO's (the mean of the $^2\Pi$ energies is taken for the Bi_2^+ of $\pi_{\text{u}}\text{np}$ orbital) is plotted against the internuclear distances of the diatomics. An approximate linear relation is obtained. From Fig. 3, it is seen that the crossover occurs at $r_{\text{e}} \sim 1.9 \text{ \AA}$. Therefore, for AsN^+ with $r_{\text{e}} = 1.618 \text{ \AA}$,³¹ the $^2\Sigma_{\text{g}}^+$ would be the ground ionic state whereas for As_2^+ and Sb_2^+ , with r_{e} expected to be larger than that of P_2^+ , the reverse would be true.

In spite of the large error in estimating the intensities of molecular lines, the reported $^2\Pi_{1/2}/^2\Pi_{3/2}$ ratio of ~ 1.5 is significantly different from 1, the expected statistical ratio. This value contrasts sharply with the value of 10 for the intensity ratio $X^2\Pi_{\text{g},1/2}/X^2\Pi_{\text{g},3/2}$ in Te_2 , which Berkowitz^{22,23} attributed to the photoelectron leaving predominantly in an np_{σ} channel. Recently, we³² have advocated an alternative explanation based upon unequal population of the $\pi_{\text{g},1/2}$ and $\pi_{\text{g},3/2}$ MO's. In other words, the ground state of the π^2 configuration is better described as $\Psi = a(\pi_{\text{g},1/2})^2 + b(\pi_{\text{g},3/2})^2$ with $a^2 > b^2$, as a result of large s-o coupling. In our picture, the ratio of the $^2\Pi$ partners should be 1 as long as the molecule has a closed shell configuration, whereas there is no a priori reason why the ratio for Bi_2 should be so much different from Te_2 according to Berkowitz's interpretation. On the other hand, the slight deviation of the ratio from 1 in Bi_2 may arise from a difference in the wavefunctions of the $\pi_{\text{u},1/2}$ and $\pi_{\text{u},3/2}$ MO's due to relativistic effects; a similar effect has been observed in Hg .¹²

Finally, we note the intensity of the $^2\Sigma_g^+$ line relative to the $^2\Pi$ appears to be proportional to their statistical weights, while the extremely weak intensity of the $(\sigma_u 6s)^{-1}$ state is consistent with the intensity of the atomic $(6s)^{-1}$ peak.

E. Conclusions

The principal conclusion of this work can be stated as follows:

1. The HeI photoelectron spectrum of Bi was satisfactorily interpreted by describing the ground state of Bi in the j-j coupling scheme.
2. Within experimental accuracy, relativistic effects did not seem to have caused sufficient difference in the initial state wave function to affect the statistical intensity ratio, i.e., 1 : 3 : 5 of the $^3P_{0,1,2}$ lines.
3. The configuration-interaction satellite peaks 1D_2 at 11.49 eV and possibly $^3D_{2,1}$ at 17.12 and $^3F_{2,3}$ at 17.47 eV were observed.
4. An autoionization process occurring at the energy of HeI γ radiation (23.74 eV) was suggested by the spectra.
5. Despite the large s-o coupling, the photoelectron spectrum of Bi_2 followed the general trend of those of other lighter Group VA diatomics.
6. The difference in the binding energies of the $(\sigma_g np)$ and $(\pi_u np)$ MO's was found to vary linearly with the internuclear distances.

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Table I. Observed States of Bi^+ and Bi_2^+ .

Ion	Final State	Apparent Relative Intensity	Experimental FWHM(a) (eV)	Vertical Binding Energy(a) (eV)	Apparent Adiabatic Binding Energy(eV)	Energy from Other Data (eV)
Bi^+	$6s^2 6p^2$ 3P_0	100	0.075	7.29(3)		7.289 ^(c)
	3P_1	320(50)	0.08	8.94(3)		8.942
	3P_2	510(40)	0.08	9.40(3)		9.401
	$6s^2 6p^2$ 1D_2	16(3)	0.07	11.49(3)		11.495
	$6s 6p^3$ 5S_2	26(5)	0.07	16.73(3)		16.730
	$6s^2 6p_{1/2} 6d_{3/2}$ 3D_2	54(10)	0.08	17.12(4)		17.090
	3D_1		—	—		17.274
	$6s^2 6p_{1/2} 6d_{5/2}$ 3F_2		0.07	17.47(4)		17.457
	3F_3		—	—		17.483
Bi_2^+	$(\sigma_u 6s)^2 (\sigma_g 6p)^2 (\pi_u 6p)^3$ $^2\Pi_{u,3/2}$	220(20)	0.27	7.53(3)	7.35(5)	7.1(3) ^(d)
	$^2\Pi_{u,1/2}$	340(50)	0.26	8.94(5)	8.65(5)	8.9
	$(\sigma_u 6s)^2 (\sigma_g 6p) (\pi_u 6p)^4$ $^2\Sigma_g^+$	240(30)	0.09	9.30(3)	9.30(3)	—
	$(\sigma_u 6s) (\sigma_g 6p)^2 (\pi_u 6p)^4$ $^2\Sigma_u^+$	4(2)	0.07	14.87(3)	14.87(3)	—

a) This work, areas corrected for $\Delta E/E = \text{Constant}$, Xe and Ar used for calibration. Experimental errors are given parenthetically.

b) No correction for thermal population of vibrational levels in the ground state have been employed.

c) Optical data from Ref. 13.

d) Electron impact data from Ref. 9.

Table II. Relative Intensities^a of 3P_0 , 3P_1 , and 3P_2 with Different HeI Lines.

Ion State	HeI α (21.22 eV)	HeI β (23.09 eV)	HeI γ ^c (23.74 eV)	
3P_0	100	3.0 (.5)	6.7 (1)	[1.0]
3P_1	320 (50)	~ 2 (1)	7.3 (1)	[1.1 (.1)]
3P_2	510 (40)	b —	7.9 (1)	[1.2 (.1)]

a) Areas corrected for $\Delta E/E = \text{constant}$ and normalized to 3P_0 (HeI α).

b) This peak is overlapped by the $^2\Pi_{u,3/2}$ line of Bi_2^+ , thus no estimate is possible.

c) Values in square brackets are normalized to 3P_0 .

Table III. Electronic Structure Data on the Diatomics of Group VA Element.

Molecule	States	Vertical Binding Energy from PES (eV)	ω_e (cm ⁻¹)	Internuclear distance, r_e (Å)	Remarks
N ₂	^a 1 Σ_g^+	—	2359.61	1.094	—
	^b 2 $\Sigma_g^+(\sigma_g)^{-1}$	15.60	2340		Sharp, very little change in ω_e (Non-Bonding)
	2 $\Pi_u(\pi_u)^{-1}$	16.98	1810		Shows vibrational structure, large decrease in ω_e (Bonding)
PN	^a 1 $\Sigma_{(g)}^+$	—	1337.24	1.491	—
	^c 2 $\Sigma_{(g)}^+(\sigma_{(g)})^{-1}$	11.85	1200		Sharp (Non-Bonding)
	2 $\Pi_{(u)}(\pi_{(u)})^{-1}$	12.52	1050		Shows vibrational structure (Bonding)
P ₂	^a 1 Σ_g^+	—	780.43	1.894	—
	^d 2 $\Pi_u(\pi_u)^{-1}$	10.65			Shows a vibrational structure large decrease in ω_e (Bonding)
	2 $\Sigma_g^+(\sigma_g)^{-1}$	10.84			Sharp (Non-Bonding)
Bi ₂	1 Σ_g^+	—	172.71 ^g	2.85 ^h	—
	2 $\Pi_u(\pi_u)^{-1}$	7.53 ^f 8.94			Shows unresolved vibrational structure (Bonding)
	2 $\Sigma_g^+(\sigma_g)^{-1}$	9.30			Sharp (Non-Bonding)

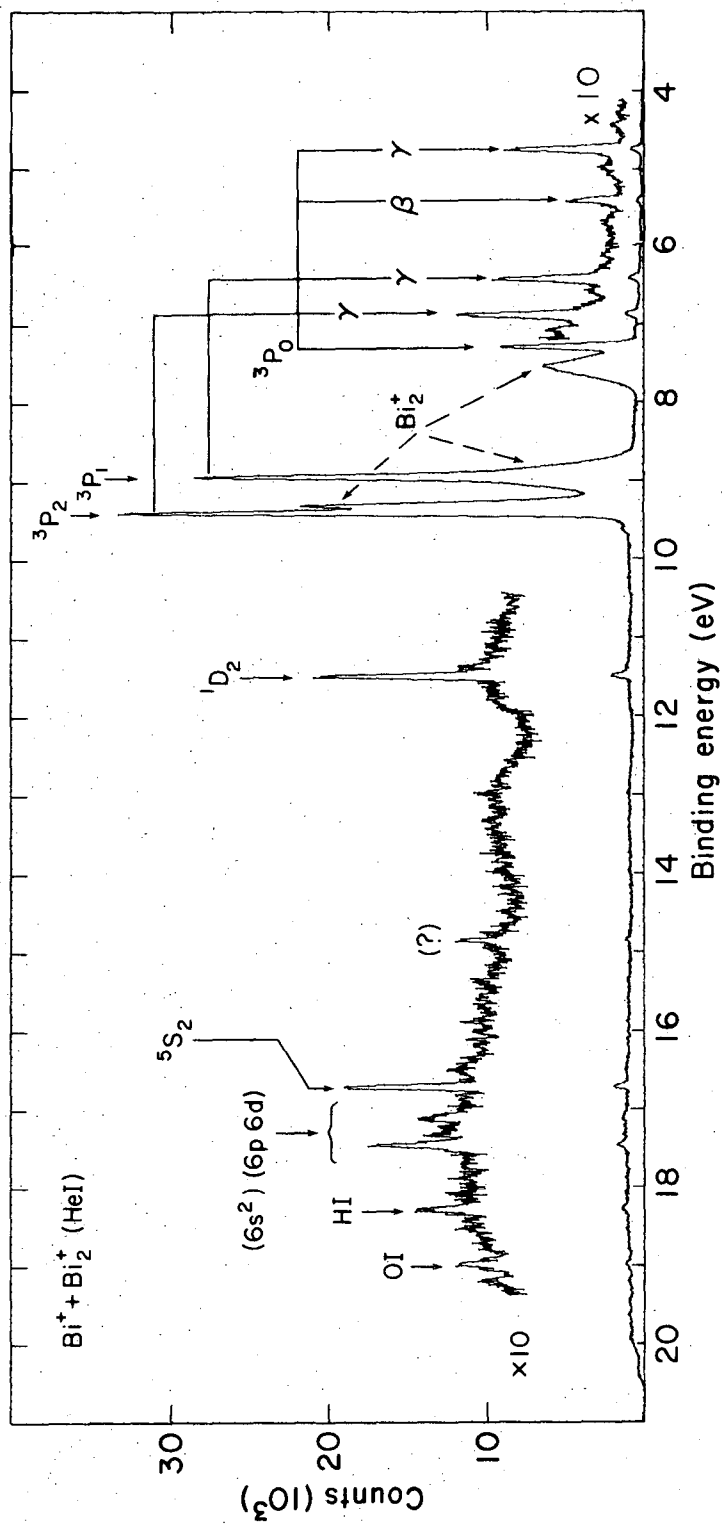
- a) Ref. 33 e) This work
 b) Ref. 24 f) Spin-orbit partners
 c) Ref. 25 g) Ref. 17
 d) Ref. 26 h) Ref. 16

FIGURE CAPTIONS

Fig. 1 The HeI photoelectron spectrum of atomic and diatomic bismuth.

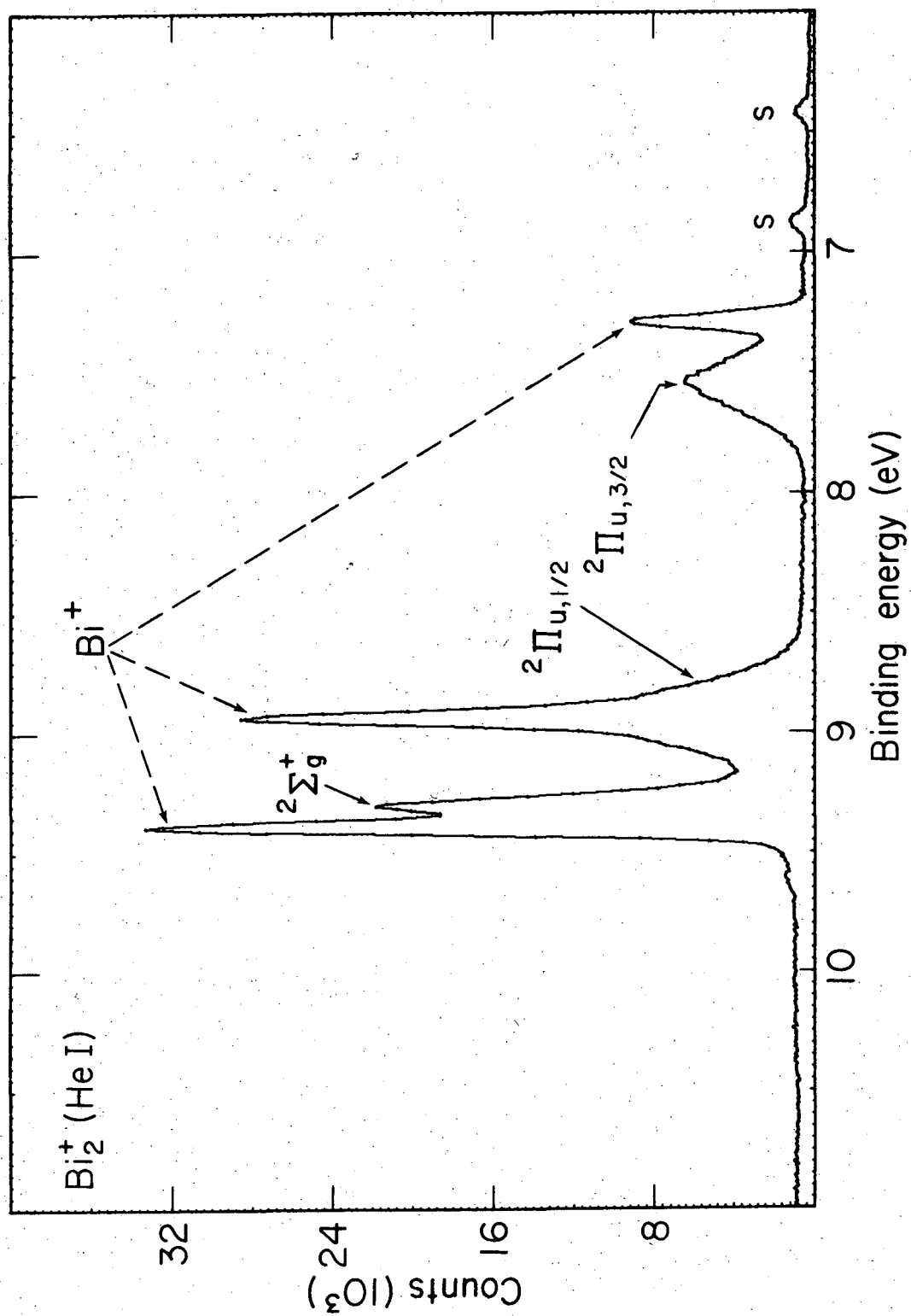
Fig. 2 The expanded portion of Fig. 1 from 6 to 11 eV, showing the molecular lines of Bi_2 .

Fig. 3 The plot of internuclear distances (r_e) vs the differences in the binding energies ($\Delta E_{\text{B.E.}}$) of the two lowest occupied MO's, $\sigma_g(p)$ and $\pi_u(p)$.



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Figure 1



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Figure 2

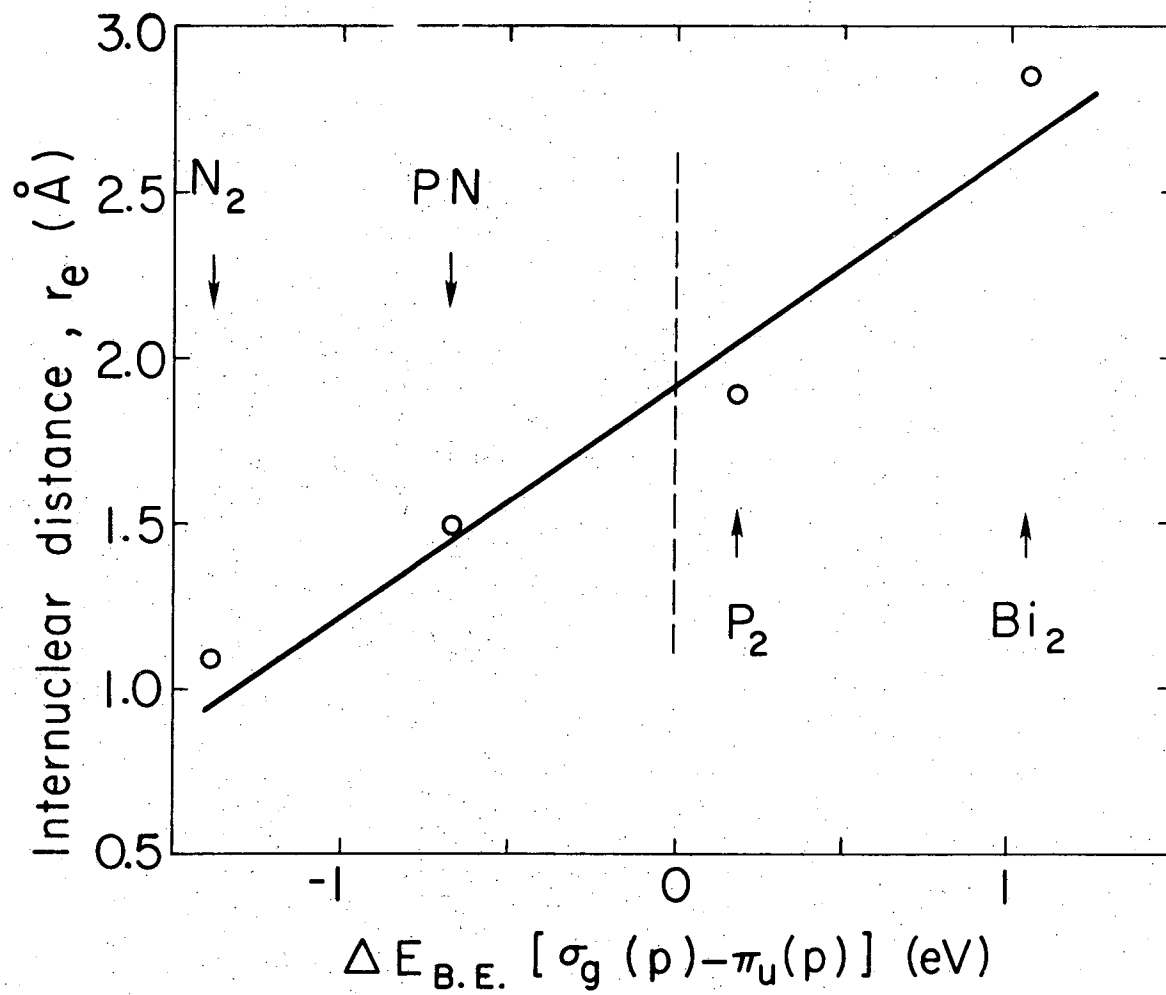


Figure 3

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