A SPECTROSCOPIC DETERMINATION OF
THE NUCLEAR MOMENTS OF BISMUTH

by

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ABSTRACT

The nuclear magnetic moment μ , and the nuclear electrostatic quadrupole moment Q , were determined from the optical hyperfine structures of Bi. The magnetic moment was calculated for 8 configurations and 14 levels. The quadrupole moment was calculated for 4 configurations and 6 levels. The values of μ that were obtained from one-electron spectra showed good agreement with more precise resonance measurements. The agreement for Q was not quite so good. Good measurements were made for the $5d^96p$ configuration, but there is no readily-available theory from which to calculate Q for this configuration. The light source used in this investigation was a "condensed" electrodeless discharge, and the spectrograms were taken on a 9.1 metre concave grating spectrograph. Q was found to be $-.5(1)$ barns. Using values of μ that employed information from one-electron spectra, μ was found to be $4.1(1)$ nuclear magnetons.

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INTRODUCTION

If the nucleus of a free atom has a magnetic moment, the nucleus can exist only in a finite number of orientations with respect to the orbital electrons' magnetic field. The energy of interaction is $W = -\mu H \cos(\underline{\mu}, \underline{H})$, where μ is the nuclear magnetic moment, and H is the magnetic field at the nucleus, produced by the electrons. Since the nuclear orientation is quantized, $\cos(\underline{\mu}, \underline{H})$ has a finite number of values. For each electronic energy level, a group of closely spaced energy levels exists. This group is called an hfm (hyperfine multiplet). When electronic transitions occur, an hfs (hyperfine structure) is emitted. From both an analysis of the hfm and also information about the electronic configuration that includes the hfm, the nuclear magnetic moment can be obtained.

Hyperfine refers to electron-nuclear interactions. Historically, hyperfine meant the energies involved were much smaller than fine-structure energies. Fine structure energies are on the order of 1000cm^{-1} ; hyperfine energies are seldom greater than a few cm^{-1} . An hfs will also be observed if there is more than one isotope in a sample. So if one uses a sample of say, naturally occurring indium, the hyperfine structures would result from two effects. The isotopic spectrum and nuclear moment spectrum would overlap, and the resulting hyperfine structures would be difficult to analyze.

The spectrum of bismuth is well suited to analysis. It has a large magnetic moment, and there is only one stable

isotope. Therefore, the hyperfine structures are large and one does not have to be troubled with separated-isotope samples. When doing hfs experiments, Q , the nuclear electrostatic quadrupole moment, can also be determined from the hfs data. Considering the nucleus to be an ellipsoid, the physical significance of Q is illustrated as

The reference axis is the spin vector $\underline{I}$, and the shape indicates the charge distribution.

The energy of interaction, W_Q , is proportional to $\overline{\varphi_{JJ}(0)}Q$, where $\overline{\varphi_{JJ}(0)}$ is the time average of the gradient of the electrostatic field of the electrons; the gradient is evaluated at the nucleus. In Bi, W_Q is $\approx .01W_\mu$.

The nucleus of ${}_{83}\text{Bi}^{209}$ has a magic number of neutrons and one more than a magic number of protons. A magic number of nucleons constitutes a closed shell, or core, that has zero spin. When $I \neq 0$, $\mu = 0$ and $Q = 0$. Therefore, in Bi μ and Q are produced by a single proton outside a closed shell.

In this thesis, the nuclear moments of bismuth were obtained from the optical spectrum. Optical spectroscopy is not the only method of obtaining nuclear moments. Resonance techniques,

namely radio frequency and atomic beam techniques, yield more precise measurements than optical spectroscopy. However, atomic beams give information only on the ground state of the atom. Radio frequency techniques are usually limited to states which belong to the neutral atom. A discussion of radio frequency techniques is given by Kastler (1967). Kopfermann (1958) discusses atomic beam studies.

Optical spectroscopy makes available for study many more states than do the resonance techniques. The results from atomic spectroscopy are more accurate than much of the theory from which nuclear moments are calculated.

The purpose of these experiments then, was to provide a test of the theories that deal with nuclear moments. In some cases, the theory applied to the spectrum of Bi yields moments that are in agreement with each other and with the results of resonance experiments. In other cases, the calculations yield moments that do not agree at all with accepted values.

In this thesis, the notation and treatment of nuclear moments follows that given by Kopfermann (1958).

CHAPTER I

THEORY

In the following, the direction of the magnetic moment is assumed to be that of the nuclear spin vector $\underline{I}$, and $\underline{H}$ to be antiparallel to $\underline{J}$. Vectorially, $\underline{I} + \underline{J} = \underline{F}$, and $\cos(\underline{I}, \underline{J}) = -\cos(\underline{\mu}, \underline{H}) = (F^2 - I^2 - J^2)/2IJ$. Quantum mechanically, F^2 is replaced by $F(F+1)$, J^2 is replaced by $J(J+1)$, and I^2 is replaced by $I(I+1)$, so

$$W_{\mu} = \mu H (F(F+1) - I(I+1) - J(J+1)) / 2IJ.$$

For convenience, let

$$A = \mu H / IJ$$

and

$$C = F(F+1) - I(I+1) - J(J+1),$$

so W_{μ} becomes

$$W_{\mu} = AC/2.$$

Experimentally, $\Delta W = W_{\mu}(F) - W_{\mu}(F-1)$ is needed. ΔW_{μ} is given by the Landé interval rule,

$$\Delta W_{\mu} = AF$$

Since we have assumed $\underline{H}$ is antiparallel to $\underline{J}$, $\cos(\underline{\mu}, \underline{H}) = -\cos(\underline{I}, \underline{J})$. In some cases, $\underline{H}$ is parallel to $\underline{J}$, then the A factor is negative, and the multiplet is said to be inverted. This parallelism arises, for example, when two electrons have their spin parallel, but oppositely directed to the orbital angular momentum vector $\underline{L}$. For example, in a two electron, $s\ell$ configuration, $A(^3L_{\ell-1})$ is negative.

In describing the quadrupole interaction, the following

assumptions are involved. The electronic cloud distribution is cylindrically symmetrical about the J axis, and the nuclear charge is cylindrically symmetrical about the I axis. $\phi_{JJ}(0)$ is the gradient of the electrons' electric field, evaluated at the nucleus. $\overline{\phi_{JJ}(0)}$ is the time average of $\phi_{JJ}(0)$. The energy of interaction, from a vector model, is equal to $eQ\overline{\phi_{JJ}(0)} (3/2 \cos^2(I,J) - 1/2)$. Quantum mechanically, this becomes

$$W_Q = \frac{1}{4}eQ\overline{\phi_{JJ}(0)} \left\{ \frac{3/2C(C+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)} \right\}.$$

As before, $C = F(F+1) - I(I+1) - J(J+1)$. For convenience, W_Q will be shortened to

$$W_Q = \frac{1}{4}BG, \text{ where } B = eQ\overline{\phi_{JJ}(0)},$$

and G is the expression in curly brackets.

In many of the earlier papers, (including Brix (1952)), W_Q was given by $W_Q = B'(C(C+1) - 4I(I+1)J(J+1))/3$, where $B' = 3B/8I(2I-1)J(2J-1)$. To compare my work with the values in Brix (1952), I was set equal to 9/2, and the following table used.

J	1	2	3	4	$1\frac{1}{2}$	$2\frac{1}{2}$
B/B'	96	576	1440	2688	288	960

Whenever values of B_{Brix} have been used or quoted in this thesis, they have been converted using the above table.

The Hyperfine Multiplet

The energy of each level in an hfm is given by $W = W_\mu + W_Q$, or $W = AC/2 + BG/4$. A and B are constant for each electronic energy level, and C and G depend on the quantum numbers I, J, and F.

If $I=0$, then $\mu=0$ and there would be only one energy level for each electronic energy level, i.e. W_μ and W_Q would always be zero. For Bi, $I=9/2$. When $J=0$, W_μ and W_Q still equal zero. But for example, when $J=1$, the following energy scheme results.

$$\begin{array}{llll}
 F=11/2 & \text{-----} & 10A-.2083B & \\
 & & & 11/2A+.9167B \\
 F=9/2 & \text{-----} & 9/2A-1.1250B & \\
 & & & 9/2A-1.1250B \\
 F=7/2 & \text{-----} & 0 &
 \end{array}$$

The first values on the right hand side of the above energy diagram are calculated from $W=AC/2+BG/4$. Experimentally, the energy differences are wanted, and these are given by the second set of values.

When transitions between two hyperfine multiplets occur, the selection rules governing the transitions are $\Delta J=0, \pm 1$; $\Delta(\sum \ell_i) = \pm 1$, i.e. the transitions must be from an even to odd (or vice versa) electronic state; and $\Delta F=0, \pm 1$, and $F=0 \rightarrow F=0$ is forbidden.

For example, if the transition is from a $J=1$ to a $J=1$ state, the description of the resulting hfs could be drawn as follows.

In this diagram, the lower A value is negative, or inverted, and is greater than the A of the upper level; the upper A is positive. Below the transition scheme are shown what the hfs would look like on a spectrogram, and the theoretical intensities; the heights of the lines are proportional to the intensities. These values of intensity are taken from Table 2 of Kopfermann(1958). Wavelengths are shown increasing to the right. The intensities can be very helpful when analyzing an hfs; almost all of the Bi hyperfine structures studied followed the theoretical intensities.

Departures From the Interval Rule

If, in some nucleus, $Q=0$, the difference in energy between one level and the next is proportional to the upper F value. So in the diagram on p.6 , the ratio of the energy differences would be 11:9. When the experimental differences form ratios that equal the ratios of the F values, the hfm is said to satisfy the interval rule.

The interval rule will not be satisfied if 1) there is a non-zero quadrupole moment or 2) if the hfm is perturbed by a neighbouring multiplet. The only way to tell for sure if the departure is due to 1) is to calculate Q from different multiplets. In practice, Q can be calculated for very few multiplets, because theoretical expressions have been derived only for a few configurations; furthermore, the electronic configuration must be unperturbed. Also, the only hfs components

that can be used are ones that are completely resolved.

If the electronic energy levels are unperturbed, μ can be obtained from A, and Q from B. When dealing with two-electron configurations, A and B will be used to denote the interaction constants; a and b will be used for one-electron configurations. Following the notation of Kopfermann (1958), the interaction constants are:

Single Electron Levels

s electrons

$$a_s = \frac{8hcR_\infty \alpha^2 Z_i^2 Z_a^2 (1-d\sigma/dn) (1-\delta) (1-\epsilon) F_r m_e \mu}{3n_a^3 m_p I} \quad 1.$$

μ is in nuclear magnetons.

$b=0$; there is no interaction between a spherical electron cloud and Q.

p,d electrons

$$a_j = \frac{2K_m \mu_B^2 \overline{r^{-3}} \ell (\ell+1) F_r \mu}{m_p I j (j+1)} \quad 2.$$

$$b_{j > \frac{1}{2}} = \frac{e^2 Q (2j-1) R_r \overline{r^{-3}}}{K_e 2(j+1)} \quad 3.$$

$\overline{r^{-3}}$ is given by

$$\overline{r^{-3}} = \frac{\delta W^0}{2K_m \mu_B (\ell + \frac{1}{2}) Z_i H_r} \quad 4.$$

σ = the quantum defect

n = principal quantum number

$n_a = n - \sigma$, n_a is the effective quantum number

$Z_i = Z$ for s electrons, $Z-4$ for p electrons, and $Z-11$ for d electrons.

$Z_a = 1$ for neutral atoms, 2 for singly-charged ions, etc.

δW^0 = fine structure splitting, e.g. the difference between
 $^2P_{1/2}$ and $^2P_{1/2}$

F_r, R_r = relativity corrections tabulated in Kopfermann(1958)

δ = correction for the distribution of nuclear charge

ϵ = correction for the distribution of the magnetic moment

$k_e = 1.11264 \times 10^{-10}$ coulomb/volt metre

$k_m = \mu_0 / 4\pi = 10^{-7}$ volt sec./amp metre

μ_B = Bohr magneton

Two Electron, $s\ell$ Configuration

In the following, an ℓ electron is defined to be one with orbital angular momentum greater than zero. It has been found that the influence of the s and the ℓ electrons can be considered independently. This is reasonable since the s orbit is far more penetrating than the ℓ orbit.

The interaction constants are:

$$A(^3L_{\ell+1}) = a_s / (2(\ell+1)) + (2\ell+1)a_{\ell+1/2} / (2(\ell+1)) \quad 5$$

$$A(^3L_{\ell-1}) = -a_s / 2 + (2\ell+1)a_{\ell-1/2} / 2\ell \quad 6$$

$$A(^3L_{\ell}) = \left\{ [(\ell+1)c_2^2 - c_1^2] a_s + (2\ell+3)c_1^2 a' + (2\ell-1)(\ell+1)c_2^2 a'' + 4c_1c_2(\ell(\ell+1))^{1/2} a''' \right\} / (2\ell(\ell+1)) \quad 7$$

For $A(^1L_{\ell})$, c_1 is replaced by c_2 , c_2 is replaced by $-c_1$. c_1 and c_2 are defined on p.32. In equations 5, 6, and 7,

$a_s = a_s$ of eq. 1.

$\left. \begin{matrix} a' \\ a'' \end{matrix} \right\} = a_{\ell \pm 1/2} = a_j$ of eq. 2.

a''' is given in Kopfermann(1958) on p. 151.

To obtain Q from an s configuration,

$$B(^3L_{\ell+1}) = \frac{e^2 Q_2 R'_r \overline{r^{-3}}}{k_e (2\ell+3)} \quad 8$$

$$B(^3L_{\ell-1}) = \frac{e^2 Q_2 (\ell^2-1)(2\ell-3) R'_r \overline{r^{-3}}}{k_e \ell (4\ell^2-1)} \quad 9$$

$$B(^3L_{\ell}) = \frac{e^2 Q}{k_e (\ell+\frac{1}{2})} \left\{ \frac{\ell(\ell+2)(2\ell-1) R'_r c_1^2}{(\ell+1)(2\ell+3)} + \right. \\ \left. (\ell-1) R''_r c_2^2 - \frac{6(\ell(\ell+1))^{\frac{1}{2}} c_1 c_2 S_r}{(2\ell+3)} \right\} \overline{r^{-3}} \quad 10$$

R'_r , R''_r , and S_r are relativistic corrections, and are tabulated in Kopfermann(1958). $\overline{r^{-3}}$ is given by eq. 4, but now δW^0 is the energy difference, $^3L_{\ell+1} - ^3L_{\ell-1}$. For $B(^1L_{\ell})$, in eq. 10, c_1 and c_2 are replaced by c_2 and $-c_1$.

A and B, or for the one electron spectra, a and b, are calculated from the experimental data by the method described on p.26. For a one electron configuration, μ and Q are calculated from eq. 1 or 2, and 3.

Perturbations

Calculations for perturbations of a hf multiplet have been made for only a few special cases. Kopfermann(1958) on page 29, discusses the case that applies to Hg^{201} ; his treatment is taken from Goudsmit and Bacher (1933). McLay and Crawford (1933) applied the same idea to the 6s7p configuration of Bi IV. Kopfermann, on page 137, also discusses perturbations by states with the same J; this

discussion is qualitative.

Lurio et al (1956) have given expressions for second order, intra-configuration perturbations, for an sp configuration. Based on this paper, a sample calculation was made for 6p7s of Bi II. This calculation was the correction to the hf levels of 3P_2 , due to the influence of 3P_1 , 3P_0 , and 1P_1 . These corrections, along with the quadrupole contributions, are shown below.

Pert. $\neq 0$		3P_2 6p7s, Bi II		Pert. = 0
Q = 0		Q = 0, Perturbation = 0		B = -.04 cm ⁻¹ .
F				
6.5		.009	.018	
5.5	.006			
4.5	.004			
3.5	.002		.013	
2.5	.0006		.016	

The ζ and η that appear in Lurio's paper was taken = 1. (Calculations by Schwarz (1955), page 389, show 1 to be a good approximation.) $b_{1\frac{1}{2}}$ was taken equal to .1 B(3P_2). Lurio's calculations require c_1 and c_2 , therefore the configuration needs to be unperturbed. Since these second-order perturbation calculations can not always be made, and are small compared to the quadrupole interaction, only this one calculation was done.

CHAPTER II

EXPERIMENTAL

Light Sources

1. Hollow Cathode

A few pictures were taken using a hollow cathode discharge tube. The cathode was of molybdenum. A hole approximately $\frac{1}{2}$ " deep and $\frac{1}{2}$ " in diameter was drilled in the molybdenum, and a piece of bismuth placed in the hole. The anode was a ring of stainless steel.

Several exposures were made with a Fabry-Perot interferometer. The interferometer was crossed with a large, Littrow-mount, prism spectrograph. Helium at a pressure of approximately 7 torr was slowly circulated through the tube. With a d.c. voltage of 350 volts and .180 amps, a good exposure was obtained in 15 minutes.

The full width at half maximum (FWHM) under these conditions was estimated to be at most $.03 \text{ cm}^{-1}$, or $.01\text{\AA}$ for the $5719\text{\AA}$ Bi II line. This value was obtained by calculating the dispersion between successive interference fringes, measuring the FWHM as displayed by the comparator, and then multiplying the dispersion by the displayed FWHM.

2. Pulsed Hollow Cathode

Since the hfs spectrum of Bi I and II had already been studied by Schuler and Schmidt (1936), Fisher and Goudsmit (1931) and Mrowzowski (1942), it was desirable to obtain a source that would produce sharp lines of the doubly and

triply ionized atom. For this purpose, the hollow cathode was pulsed. A schema is shown in Fig. 1. The external gap was set to break down at approximately 3500 volts. This method is similar to that described by Gartlein and Gibbs (1931). In the present work, the gap broke down approximately five times per second. Each breakdown was a sinusoid of 20 μ sec period. The oscillations were heavily damped and lasted only 2 or 3 periods. A faint spectrum of the material of the anode was produced, and heating of the anode also occurred. The hollow cathode operated in this manner produced most of the classified III and IV lines, and many of the I and II lines were absent that in the d.c. mode were present. A Fabry-Perot picture was taken, and the lines showed poorly-resolved hfs.

3. Condensed Electrodeless Discharge.

A schema of this source is shown in Fig. 2. The gap was set to break down at approximately 50,000 volts. To produce a discharge, the vapour pressure of the material in the quartz tube has to be approximately 0.1 torr. For bismuth, this required a temperature of 800°C. The quartz tube was 2.5 cm. in diameter, 60 cm. long, and had a quartz window at each end. The coils surrounding the tube had 9 turns in 10 cm., and was of 4 mm. diameter copper wire. A discussion of this source is given by Minnhagen (1964).

A Fabry-Perot picture with 1 cm. etalons, was made with the condensed electrodeless discharge. All three components of the 5719 Bi II line were resolved, and the

PULSED HOLLOW CATHODE

GL 8020

Fig. 1.

"CONDENSED" ELECTRODELESS DISCHARGE

Fig. 2.

FWHM estimated to be $.05 \text{ cm}^{-1}$ or $.015\text{\AA}$. The FWHM due to Doppler broadening is given by $\Delta\nu = 7 \times 10^{-7} \nu_0 (T/M)^{1/2}$. See, e.g. Kuhn (1962), page 386. The molecular weight of Bi is 209, the temperature was approximately 1000°K . Then $\Delta\nu = 16 \times 10^{-7} \nu_0$. For $5719\text{\AA}$, $\nu_0 = 17,500 \text{ cm}^{-1}$, so $\Delta\nu = .03 \text{ cm}^{-1}$. If we attribute the total width to Doppler broadening, the effective temperature would be $\approx 3000^\circ\text{K}$. Or, if the pressure increased considerably during operation, the line width might be explained by pressure broadening.

4. Microwave Electrodeless Discharge.

This source consisted of a small, sealed quartz tube into which Bi had been distilled. Neon, to a few torr pressure, was included as a carrier gas. The tube was placed in a resonant cavity, and the cavity was powered by a 2450 Megacycle diathermy unit. On the Argonne spectrograph, the Zeeman spectra in a field of 24 K gauss was taken, but only the zero-field spectrum was measured in this work.

The Bi I spectrum was very strong, Bi II was weak, and the higher ionized spectra were absent altogether.

Spectrographs

1. Prism.

A large prism spectrograph was used for several different kinds of exposures. In preparation for the Argonne pictures, "survey" exposures were made with the prism spectrograph. To identify the wavelength and ionization of some of the unclassified hfs that appeared on the Argonne plates, spark-in-helium pictures were made with the prism instrument. And the Fabry-Perot interferometer was crossed with the prism spectrograph.

This instrument was made by Hilger, was a Littrow mount, and had easily interchanged glass and quartz optics. The focal length was 1.5m, and the f/number was 18.

2. Fabry-Perot Interferometer.

The flats were from Zeiss, and coated with a multilayer dielectric sandwich. The useful range of the plates was from about $4000\text{\AA}$ to at least $8500\text{\AA}$. This instrument provided a measure of the FWHM of the light sources, and also a good spectrogram of the $5719\text{\AA}$ hfs of Bi II. This hfs was analyzed according to the procedure described by Meissner (1941).

3. Argonne Grating Spectrograph

The majority of the information presented in this thesis was obtained with a grating spectrograph at the Argonne National Laboratory. This spectrograph is a 9.1 metre Rowland mount. The grating used for this work was designated by Tomkins and Fred "G5", and is an original. It is ruled with 15,000 lines/inch, or $8333\text{\AA}/\text{line}$. The dispersion ranged from about $.8\text{\AA}/\text{mm}$, in the first order to about $.15\text{\AA}/\text{mm}$ in the fifth order.

Thorium, in the form of thorium iodide and placed in a 2450 Mc/s cavity, was used as the standard. The wavelengths of the thorium lines used as standards were obtained from the compilation of Giachetti (1966).

The exposure times were: 1) condensed electrodeless discharge, 2 hours; 2) microwave electrodeless discharge (zero-field), 4 minutes; 3) Th standards, $2\frac{1}{2}$ to 10 minutes,

depending on the filter used. When the exposures were taken, the Th spectrum was projected through, i.e., along the axis of, the Bi discharge tube.

All the plates were 18" x 2". The emulsions used depended on the wavelength covered. The Ilford emulsions used were Q2 and HP3; on Kodak plates, the 103-0 emulsion was used.

A discussion of the Argonne spectrograph is given by Tomkins and Fred (1963).

Comparator

The comparator used in this work was built by Grant and used the display device invented by Tomkins and Fred (1951). This device displays, on an oscilloscope screen, the density trace of a line, as well as the mirror image of the line. If a line is perfectly symmetrical, the center of the line is reached when there appears to be only one profile. If a line is asymmetrical, the maximum density of the line can quite reproducibly be measured. It was found that the centre of strong, symmetrical lines could be reproducibly set to $\pm .005$ of the FWHM.

The position and transmission of the plate are stored in digital form. By pressing a switch, the information is transferred to, and punched onto cards by an IBM card punch. The position characters go from .000 to 252.000 millimetres; the transmission goes from 000 to 999.

A motor and gear train was connected, via a clutch, to the drive of the comparator. The output of the transmission

photomultiplier was fed into a pen recorder. When line profiles were traced, the motorized drive and pen recorder were used. The resulting trace was very nearly the same size as the profile that appeared on the oscilloscope, and was approximately a 50x magnification of what appeared on the photographic plate.

The measurement of lines was done manually; the gear train was disengaged, and the stage advanced by hand.

CHAPTER III

DATA REDUCTION

Dispersion Tables

For the Argonne plates, a table of dispersion as a function of wavelength was found to be very useful. The dispersion formula is derived from the following figure and formulae.

R = radius of the grating, $\frac{1}{2}R$ = radius of the Rowland circle.

$n = b (\sin i + \sin \theta)$; n = order; θ is positive if on the same side of the normal as i , negative if on the opposite side.

s = distance along the Rowland circle.

The plate factor (sometimes referred to as the dispersion)

$$\text{is } D = \frac{\partial \lambda}{\partial s} = \frac{\partial \lambda}{\partial \theta} \frac{\partial \theta}{\partial s} = \frac{b}{Rn} \left\{ 1 - \left(\frac{n\lambda}{b} - \sin i \right)^2 \right\}^{\frac{1}{2}}$$

At Argonne, R , b , and i were measured to be $R = 9143.3$ mm., $b = 8333.679^{\circ}\text{\AA}$ and $i = 52^{\circ} 59'$. (Empirically, it was found that $b = 8333.700^{\circ}\text{\AA}$ gave a better fit.)

A computer programme was written that calculated D in increments of $10^{\circ}\text{\AA}$ and printed the results in table form. This was done for $n = 1, 2, 3, 4$ and 5 .

Identification Cards

When taking the exposures of Bi, filters were not used. To aid in the identification of overlapping orders, cards with the following appearance were made. When a photographic plate was placed on its card, the possible wavelengths of a line were easily seen.

<u>5528.5</u>	<u>11057.0</u>	<u>3685.7</u>
2764.3		2211.4	
<u>65532.4</u>	<u>11064.7</u>	<u>3688.2</u>	
2766.2		2212.9	
<u>5536.2</u>	<u>11072.5</u>	<u>3690.8</u>	
2768.1		2214.5	

Using the dispersion formula, the computer calculated the wavelengths for each centimetre.

Energy Differences in an HFS

The energy differences between members of an hfs are more important than the energies of the individual members. The differences between non-adjacent components was often needed. A programme was written that 1) allowed several scanning measurements to be taken of a single hfs, 2) for

each scan, calculated the differences between all members of the hfs, 3) calculated the average energy differences and standard deviation from all the measurements and 4) printed the average difference and standard deviation in a format that made it easy to tell which components the values belonged to.

First, all the lines on a plate, Bi and Th, were measured. To measure an hfs, the comparator stage was shifted perpendicular to the long dimension of the plate. A measuring scan was made. The stage was shifted again and another scan was made. The average differences and standard deviation of the differences were found to be the same for ten scans as for three scans. Therefore three scans were usually made.

The Th lines that were used as standards are those tabulated by Giachetti (1967). These were interferometrically determined, and are accurate to a few ten-thousandths of an angstrom. The wavelength and comparator readings of all the standard Th lines were fitted by a least squares procedure to a fourth degree polynomial. From the positions of the standards and the quartic polynomial, a derived set of wavelengths was calculated. The difference between the true and derived wavelength was taken, and the standard deviation of all these differences calculated. If the difference of any one line was more than twice the standard deviation, that line was omitted and a new polynomial

calculated. A new standard deviation was found, and the individual differences were found. This process was repeated until all the differences were less than twice the standard deviation. These calculations were all done on the computer. Standard deviations ranged from $2 \times 10^{-3} \text{ \AA}$ to $5 \times 10^{-4} \text{ \AA}$.

On the low - $n\lambda$ plates, as many as 20 standards occurred in 25 cm; on the high - $n\lambda$ plates, as few as 8 standards were available. The lines from only one order were used, but the wavelengths were converted to $n\lambda$. This was often a nine-digit number, and single precision often yields unacceptable round-off errors. Therefore, double-precision format was used in all the calculations, but for output that was less than 9 digits, the double precision was changed to single precision. This allowed more room for output, and the results were easier to read.

Calculations for the wave numbers included Edlén's dispersion for air. No correction was made for non-standard air. As Tomkins and Fred (1963) stated, these corrections would amount to a few parts in 10^8 ; for energy differences covering an hfs, i.e. less than 10 cm^{-1} , the correction would not be detectable.

To illustrate the method of analysis, the well-resolved $3012\text{\AA}^0$ hfs of Bi IV will be explained. A print of this hfs is shown on the next page.

← Scan 1

← Scan 2

See Page 28.

← Scan 3

3012 Å hfs of Bi IV

The classification of the 3012 Å hfs states that the upper level is $J = 2$ and the lower level $J = 1$. From the appearance of the hfs, the $J = 1$ level has the larger A factor. Brix (1952) states both A 's are positive. We can now draw the following diagram.

Diagram for the 3012 Å hfs of Bi IV.

The numbers at the bottom are intensities, and are from Table 2 of Kopfermann (1958). The numbers at the top indicate the order in which the components would appear on a spectrogram. A densitometer trace of the observed hfs is on page 27. When the separations, direction of increasing wavelength, and intensities are compared with the densitometer trace, we see that both A's are indeed positive.

If the interval rule were followed, the difference in energy between components 1 and 5 would equal $(9/2)A_{\text{lower}}$. For this hfs, 2 differences determine both $9A_{\ell}/2$ and $11A_{\ell}/2$, and one difference $13A_{\ell}/2$ and $7A_{\ell}/2$.

Since the effect of the quadrupole moment is to be taken into account, the interval rule is not exactly obeyed. The energy differences, from the table on page 28, are

F = 13/2	_____	13A/2 + .5417B
11/2	_____	11A/2
9/2	_____	9A/2 - .3125B
7/2	_____	7A/2 - .4375B
5/2	_____	
11/2	_____	11A/2 + .9167B
9/2	_____	9/2A - 1.1250B
7/2	_____	

To see how the experimental energy differences were determined, look at page 28. On the first scan, the nine components were measured. Their positions and transmission are printed on the first line. The measurements from the second and third scans are printed on the second and third lines. For each scan, the computer calculated the 36 possible differences, averaged each of the 36 differences, and found the standard deviation of each of the 36 differences. These averages and standard deviations are printed in the triangular array. For example, the difference between the first and second component is $.8404 \text{ cm}^{-1}$, and the standard deviation of three measurements is $.0019 \text{ cm}^{-1}$.

From the diagram on the previous page, the difference between the first and second component is $9A_0/2$. Similarly, the difference between the 4th and 8th component is $11A_0/2$. All these pertinent energy differences are identified on the triangular array.

The width of the output sheet limited the hfs to 14 components. Hfs with more members had to be done in two groups. Resolved hfs components are essential for quantitative results. Therefore, a microphotometer trace was made of each hfs. When energy differences were selected from the computer output, the trace was consulted to check that the components were indeed resolved.

To obtain A and B for an hf multiplet, two differences have to be known. Then two equations are solved for the two unknowns, A and B. For example, the $3012A^0$ line of Bi IV

HFS WL=3012, B14, FROM PLATE C131

213.755	436	3011.4552	33196.864
214.191	213	3011.5312	33196.025
214.527	171	3011.5898	33195.379
216.844	148	3011.9941	33190.924
217.387	158	3012.0888	33189.880
217.824	337	3012.1651	33189.040
220.641	092	3012.6566	33183.626
221.296	214	3012.7709	33182.367
221.839	740	3012.8656	33181.324

HFS WL=3012, BI4, FROM PLATE C131

COMP 1	COMP 2	COMP 3	COMP 4	COMP 5	COMP 6	COMP 7	COMP 8	COMP 9	COMP	
213.755	214.191	214.527	216.844	217.387	217.824	220.641	221.296	221.839		Position
436	213	171	148	158	337	092	214	740		Transmission } First Scan
213.766	214.203	214.539	216.858	217.401	217.839	220.657	221.312	221.860		Second Scan
445	213	172	149	161	345	091	218	732		
213.769	214.207	214.542	216.862	217.405	217.844	220.661	221.317	221.862		Third Scan
445	217	172	148	161	342	092	218	747		
$9/2 A_v$	$7/2 A_v$		$11/2 A_v$	$9/2 A_v$		$13/2 A_v$	$11/2 A_v$			
0.8404	0.6455	4.4583	1.0439	0.8420	5.4150	1.2593	1.0479			
0.0019	0.0011	0.0029	0.0000	0.0019	0.0011	0.0011	0.0048			
	1.4859	5.1039	5.5023	1.8859	6.2571	6.6744	2.3072			
	0.0011	0.0022	0.0029	0.0019	0.0022	0.0011	0.0048			
	5.9443	6.1478	6.3443	7.3010	7.5164	7.7223				
	0.0040	0.0022	0.0048	0.0022	0.0029	0.0058				
	$9/2 A_s$	$9/2 A_s$		$11/2 A_s$	$11/2 A_s$					
	6.9882	6.9898	11.7593	8.5603	8.5643					
	0.0040	0.0040	0.0051	0.0029	0.0069					
	7.8302	12.4048	13.0187	9.6082						
	0.0059	0.0044	0.0059	0.0069						
	13.2453	13.6642	14.0665							
	0.0062	0.0051	0.0095							
	14.5046	14.7121								
	0.0069	0.0091								
	15.5525									
	0.0106									

shows intervals for 6_1 of 6.9856 and 8.5702 cm^{-1} . From the figure on page 6, the two equations are

$$4.5A - 1.1250B = 6.9890$$

$$5.5A + .9167B = 8.5603.$$

(The $9/2$ interval value is an average of the two values, 6.9882 and 6.9898 cm^{-1} . The $11/2$ interval is from the strong transition only; component 9 is weak, and measurements involving this component have a relatively large uncertainty.) From these, $A = 1.5559 \text{ cm}^{-1}$, $B = .014 \text{ cm}^{-1}$.

When analyzing the data, it was essential to know

$$\Delta W \equiv W(F) - W(F-1) = \Delta W_\mu - \Delta W_Q. \Delta W_\mu = FA, \text{ and}$$

$$\Delta W_Q = \frac{1}{4}B(G(F+1) - G(F)) = \frac{1}{4}B\Delta G; G \text{ is given on page 3.}$$

A short table of $\Delta G/4$ is given below.

$J \backslash F$	8	7	6	5	4	3	2	1
$1\frac{1}{2}$			.6667	-.2083	-.6667			
$2\frac{1}{2}$		.4667	.0750	-.1667	-.2833	-.3000		
$3\frac{1}{2}$	.3810	.1250	-.0476	-.1488	-.1905	-.1845	-.1429	

$J \backslash F$	$8\frac{1}{2}$	$7\frac{1}{2}$	$6\frac{1}{2}$	$5\frac{1}{2}$	$4\frac{1}{2}$	$3\frac{1}{2}$	$2\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$
1				.9167	-1.1250				
2			.5417	0	-.3125	-.4375			
3		.4167	.1083	-.0917	-.2000	-.2333	-.2083		
4	.3542	.1339	-.0193	-.1146	-.1607	-.1667	.1414	-.0938	

From each hfs that was used, A and B for each level was calculated. For each level, if components from several levels were resolved, more than one value of A and B were calculated; e.g. 12 pairs of measured energy differences were used to calculate A and B for the $14\frac{0}{2}$ level of Bi IV. Three pairs were from the 3rd order line of $3012\frac{0}{2}$, three from the 4th order of $3012\frac{0}{2}$.

For each level, all the A's and B's were averaged, and the standard deviations calculated. If an individual value differed from the average by more than twice the standard deviation, that value was thrown out and a new average and standard deviation calculated.

If the sign of B was not the same for the calculations involving energy differences of one hfm, then the deviation from the interval rule, in that multiplet, was not due to the quadrupole moment. Obviously, no B could be assigned in cases like this.

Intensities

A step wedge was not used when making the Bi exposures. An effort was made to calibrate the Argonne plates by using a step wedge on different plates of the same emulsion. The results were not reproducible, and were practically useless for obtaining hfs intensities.

It was noted that a log-log plot of the measured transmission vs. the theoretical intensities of the hfs components gave a straight line with negative slope. Assigning intensity $I = 100$ to the component of minimum transmission, $T_{\min}$, meant $I = 100 (T_{\min}/T)^x$, and x is the γ of the emulsion. For each resolved hfs, the strongest component was assigned intensity 100, and the intensity of the other components calculated from the above equation for I . x was varied from 1.0 to 2.1, in increments of 0.1. A programme was written to do the calculations. The calculated intensities were compared with the theoretical values, and

the values of x that gave the best agreement appear with the wavelengths in Appendix I.

CHAPTER IV

RESULTS

Nuclear Moments From Bi II

complete, classified

There is only one Λ 's configuration in Bi II, 6p7s.

Before the magnetic and quadrupole moments are calculated, the coupling constants c_1 and c_2 will be evaluated. These constants are defined below. These constants are necessary for the evaluation of nuclear moments from the terms that are dependent on coupling, $^3L_\ell$, and $^1L_\ell$.

In the above diagram, $d = ^1L_\ell - ^3L_\ell$, and δ = the fine structure splitting, $^3L_{\ell+1} - ^3L_{\ell-1}$. If the triplet terms obeyed the Landé interval rule, the 3P_1 term would be at the dashed line. The "Landé position" is given by

$$(^3L_{\ell+1} - ^3L_{\ell-1}) / (2\ell + 1); \text{ for 6p7s of Bi II, this } = 6545.$$

Δ is the difference between the "Landé position" and the actual position of $^3L_{\ell-1}$. For this configuration,

$\Delta = 6545 - 465 = 6080$. Following Kopfermann's notation,

$c_1 = \sin(\theta_0 - \theta)$, $c_2 = \cos(\theta_0 - \theta)$, where $\theta_0 = \arctan(\ell/(\ell+1))^{1/2} = 35^\circ 16'$. $\theta = \arcsin(\Delta/d)^{1/2} = 33^\circ 11'$. $c'_2 = -c_1$, and $c'_1 = c_2$;

thus

$${}^3P_1 \begin{cases} c_1 = .0363 \\ c_2 = .9993 \end{cases} \quad {}^1P_1 \begin{cases} c'_1 = .9993 \\ c'_2 = -.0363 \end{cases}$$

Magnetic Moment

Before using equations 5, 6 and 7 to obtain a_s , eq. 2 is used to obtain $a''' = .033a''$, $a' = .1943a''$. For $\ell = 1$, $A({}^3P_0) = 0$, so $a'' = a_s/3$. Then using the measured A's we have

$$A({}^3P_2) = .2761a_s = .1057 \quad a_s = .3828$$

$$A({}^3P_1) = .6633a_s = .3905 \quad a_s = .5887$$

$$A({}^1P_1) = -.1704a_s = -.0607 \quad a_s = .3562$$

To obtain μ from a_s , eq. 1 is used. However, the factors in eq. 1, and especially n_a , refer to the s electron alone. Therefore data from the ns sequence were needed, i.e. values of n_a , Za , and $d\sigma/dn$ from Bi III. For the 7s term of Bi III, $n_a = 3.981$, and $d\sigma/dn = -.07$. The right hand side of eq. 1 is $.113\mu$. The average value of a_s from 6p7s is $a_s = .44$. Thus, $.44 = .113\mu$, or

$$\mu = 3.9 \text{ nuclear magnetons.}$$

The value 3.9 n.m. is not too reliable; the uncertainty is 27% or ± 1 n.m. It is not known what causes the large spread in values. The closest classified level that could perturb any of the 6p7s levels is 6000 cm^{-1} away. Therefore, strong mixing from other states is not expected. Another fact that argues against significant mixing is that the whole configuration is unperturbed.

Quadrupole Moment

For ease of calculating Q from equations 8, 9 and 10, we note that $e^2 / (k_e k_m \mu_B^2) = 2.675 \times 10^{21} \text{ cm}^{-2}$. Eq. 8 gives $B = .099Q$; $B = -.038$, therefore

$$Q = -.38 \text{ barns. } {}^3P_2$$

For the 3P_0 term, the quadrupole interaction is zero. For 3P_1 , eq. 10 gives $B = Q(62.6 \times 10^{21}) (.0005 - .1011) = -Q(6.3 \times 10^{21})$. $B = .0035 \text{ cm}^{-1}$, so

$$Q = -.55 \text{ barns } {}^3P_1$$

For 1P_1 , Schuler and Schmidt (1936) obtained $B = -.022 \text{ cm}^{-1}$, This gives

$$Q = -.36 \text{ barns. } {}^1P_1$$

The average of these values is

$$Q = -.43 \text{ barns.}$$

Before the hfs were analyzed, they were identified according to the classified line lists. The spectra were described by the following people: Bi I Mrozowski (1942); Bi II Crawford and McLay (1934); and Fisher and Goudsmit (1931); Bi III Crawford and McLay; Bi IV McLay and Crawford (1933). A summary of the A's and B's up to 1952 was published by Brix (1952). In the following tables, the level designation is from Moore (1958). Values for A and B are in cm^{-1} .

Bi II

Level	A_{Brix}	B_{Brix}	A	B	Lines
$4_2 {}^1D_2 (6p^2)$	-		.025		2368, 2803

Level	A_{Brix}	B_{Brix}	A	B	Lines
$2_1^{\text{O}} 3P_1$ (6p7s)	.39090	.0028	.3905(3)	.003(2)	2530, 5209, 5270, 5719
$4_2^{\text{O}} 5S_2$ (6s6p ³)	.410		.404(3)		2503, 3411
$5_2^{\text{O}} 3D_2$ (6p6d)	.127		.14(1)		3654, 3815, 3845
$6_1^{\text{O}} 3D_1$ (6p6d)	-.165		-.1736(3)		2746, 3408, 3648
$7_2^{\text{O}} 3F_2$ (6p6d)	.099		.091		4301
8_3^{O} (6p6d)	.080		.0845(4)		4259
6_1 (6p7p)	.2697		.268(1)		4476, 5818
$8_1 3D_1$ (6p7p)	-.10210	-.00077	-.1021(3)		5144, 5270
$9_2^{\text{O}} 3P_2$ (6p7s)	.10599	-.035	.1057(3)	-.04(1)	4916, 5091
$9_2 3D_2$ (6p7p)	.1232	-.0029	.1234(1)	-.007(3)	5209
$10_1^{\text{O}} 1P_1$ (6p7s)	-.06068	-.022			
10_2 (6p5f)	-.008				
12_3 (6p5f)	-.018		-.028(1)		3430, 3815
13_3 (6p5f)	.065		.056(1)		3411
20_2^{O}	.124				
14_4 (6p5f)	.056				
15_1 (6p8p)	-.036				
or (6p7p)					

Level		A_{Brix}	B_{Brix}	A	B	Lines
21_1^0	(6p7d)	-.085		-.0793(2)	.003(1)	4476
or (6s6p ³)						
16_3	(6p7p)	.012				
17_1	(6p7p)	-.014				
or (6p8p)						
22_2	3D_2 (6p8p)	-		.102(1)		2544
18_1	3S_1 (6p7p)	-		-.068(1)		2501, 2530 4916
19_2	(6p7p)	.03699	-.0013	.0351	-.0064	3408
or (6p8p)						

Nuclear Moments From Bi III

Magnetic Moment

For the 7s and 8s levels, eq. 2 was used to calculate μ ; eq. 3 was used for the 7p levels. The following table was obtained.

	n_a	$1-d\sigma/dn$	δW^o	a_s	μ
7s	2.981	1.07		.472	4.18
8s	4.025	1.009		.185	4.27
$7p_{1/2}$			5135	.105	4.26
$7p_{1\frac{1}{2}}$			5135	.017	6.62

Neglecting the last value,

$$\mu = 4.24(.05) \text{ n.m.}$$

Kelly et al (1950) discuss the perturbation affecting $7p_{1\frac{1}{2}}$.

Quadrupole Moment

From the $7p\ ^2P_{1\frac{1}{2}}$ level, Schuler and Schmidt (1936) obtained $Q = -.44$ barns. In the present work, the only level of Bi III from which it was possible to calculate B was $6s6p\ ^2P_{1\frac{1}{2}}$; $B = -.038(3)$. Q was not calculated for this term.

Bi III

Level	A_{Brix}	B_{Brix}	A	B	Lines
$2\ ^0P_{1\frac{1}{2}}\ ^2P_{1\frac{1}{2}} (6p)$	small				
$4\ ^1P_{1\frac{1}{2}} (6s6p^2)$	2.00				
$1\ ^1P_{1\frac{1}{2}} (6s6p^2)$	.50		.5160(2)	-.038(3)	2944
$2\ ^2P_{1\frac{1}{2}} (6s6p^2)$	.50		.503		3039
$9\ ^1S_{1\frac{1}{2}}\ ^2S_{1\frac{1}{2}} (7s)$	.472		.4704(2)		4561
$10\ ^1D_{1\frac{1}{2}}\ ^2D_{1\frac{1}{2}} (6d)$	-.082	-.0043			
$11\ ^1D_{2\frac{1}{2}}\ ^2D_{2\frac{1}{2}} (6d)$	.10		.140(2)		2855, 5079
$5\ ^1P_{1\frac{1}{2}} (6s6p^2)$	.80				
$6\ ^1P_{1\frac{1}{2}} (6s6p^2)$	.17		.076		3450
$3\ ^2P_{1\frac{1}{2}} (6s6p^2)$	.37		.370(2)		2499, 4752
$3\ ^0P_{1\frac{1}{2}}\ ^2P_{1\frac{1}{2}} (7p)$	.106		.106(1)		2944, 4561 3540
$4\ ^0P_{1\frac{1}{2}}\ ^2P_{1\frac{1}{2}} (7p)$	.0167	-.0011	.017		3848

Level		A _{Brix}	B _{Brix}	A	B	Lines
7 _{1½}	(6s6p ²)	-.33				
8 _½	(6s6p ²)	2.062		2.030		3930
12 _½	² S _½ (8s)	.182		.185		3540

Nuclear Moments From Bi IV

Magnetic Moment

a_{6s} will be obtained from the data of Bi IV, but to calculate μ , data from Bi V were needed. The right hand side of eq. 2, applied to Bi V, yields $a_{6s} = .591\mu$. (For 5d¹⁰6s of Bi V, $n_a = 2.464$, and $(1-d\sigma/dn) = 1.14$.)

6s6d

This configuration is perturbed, but the two levels that are independent of coupling yield a value that is consistent with the values from Bi II and III. Using $a' = .4018a''$,

$$A(^3D_3) = .1667a_s + .3348a'' = .422 \text{ cm}^{-1}$$

$$A(^3D_1) = -.2500a_s + 1.250a'' = -.587 \text{ cm}^{-1};$$

from these, $a_s = 2.471$. This = $.591\mu$, or

$$\mu = 4.18 \text{ n.m.}$$

6s7p

This configuration has two terms whose separation is the same order of magnitude as the hf energies. These terms have been discussed by Crawford and McLay (1933). The configuration has the following appearance.

6s7p configuration of Bi IV

From the results of Bi II, $A(^3P_2) = .2761a_s = .517 \text{ cm}^{-1}$.

$a_{6s} = 1.87$, and $\mu = 1.87/.591$,

$$\mu = 3.12 \text{ n.m.}$$

This value is considerably lower than the average of 4.1 n.m., but that is not too surprising. The 3P_2 term lies above 1P_1 , so one of the two terms is strongly perturbed.

6s5f

For the terms independent of coupling, $a' = .555 a''$,
thus

$$A(^3F_4) = .125a_s + .486a'' = .30$$

$$A(^3F_2) = -.167a + 1.167a'' = -.32,$$

$$a_s = 2.22 \text{ cm}^{-1}, \mu = 2.22/.591, \text{ or}$$

$$\mu = 3.76 \text{ n.m.}$$

Even though the 6s6d and 6s5f configurations are perturbed, the terms independent of coupling gave consistent results for μ . If these two terms are unperturbed, they should give good values of μ . A look at $(^3L_{l+1} - ^3L_{l-1})$ in the isoelectronic sequence, Hg I, Tl II, Pb III, and Bi IV shows the differences in Bi IV are in line with the other members

in the isoelectronic sequence, therefore the terms probably are not perturbed.

Quadrupole Moment

6s6d

The two terms independent of coupling, 3D_3 and 3D_1 , are considered. For 3D_3 , calculations of B gave an inconsistent sign. For 3D_1 , $B = -.002 \text{ cm}^{-1}$. Using $\delta W^0 = 2618 \text{ cm}^{-1}$, and eq. 8, $Q = 395 B$ barns, or

$$Q = -.70 \text{ barns.} \quad ^3D_1$$

This value of Q should be treated a little suspiciously, because the value of B came from only one pair of energy differences, while 11 pairs of energy differences were used to calculate $B(^3D_3)$. Obviously more measurements for 3D_1 are desirable.

6s7p

$\delta W^0 \approx 8000 \text{ cm}^{-1}$, and for 3P_2 , eq. 8 gives $Q = 50B$ barns. $B = -.03$, so

$$Q = -1.5 \text{ barns.} \quad ^3P_2$$

B was obtained from two intervals of the $2842 \text{ \AA}^0$ hfs, in two orders. Again, more measurements of B would be desirable. Considering the perturbations involved in this configuration, an inconsistent value of Q would not be surprising.

6s5f

$\delta W^0 = 485 \text{ cm}^{-1}$, and application of eq. 9 yields $Q = 67.0B$. For 3F_2 , $B = -.03$, so

$$Q = -20 \text{ barns.} \quad ^3F_2$$

This is more than 10 times as great as Q from any other configuration, and will be ignored in the final averaging.

Bi IV

In Bi IV, there are 6 levels that have lines only in the vacuum u.v. The following tabulation excludes only those 6 levels.

Level	A_{Brix}	A	B	Line
$5_1 \ ^3D_1 (6s6d)$	-.589(1)	-.591(4)	-.002	2629*, 3683
$6_1 \ ^3S_1 (6s7s)$	1.556(2)	1.5556(3)	.011(2)	2842, 3012
$7_2 \ ^3D_2 (6s6d)$	.413(2)	.410(2)	-.04(1)	2677, 2823
$8_3 \ ^3D_3 (6s6d)$	.421(5)	.422(1)		3239, 3868
$10_2 (6p_{1/2} 6p_{1/2})$	-.127(1)	-.129		3171
$11_2 (6p_{1/2} 6p_{1/2})$	small	.05		5029*
$7_2^o (5d^9 6p)$	.150	.150		3683
$8_0^o - 11_0^o (6s7p) \ ^3P_{0,1}$				
12_4^o	.091(2)	.095(7)		3868
$13_1^o (5d^9 6p)$	.178(1)	.178(1)		3766
$14_2^o (5d^9 6p)$	.190(2)	.190(1)	.052(5)	3012, 3239
$15_1^o \ ^1P_1 (6s7p)$	-.414	-.413		2756

* These hfs are odd; analysis of the hfm is somewhat uncertain.

Level	A_{Brix}	A	B	Line
$16_2 \ ^3P_2$ (6s7p)	.516(1)	.5174(2)	-.03(1)	2842
17_3^0 ($5d^9 6p$), or (6s5f)	.063	.060(1)	.06(1)	2823
18_3^0 ($5d^9 6p$) or (6s5f)	.053	.049		3171
21_3^0 ($5d^9 6p$) or (6s5f)	.044	.041		2933**
$19_2^0 \ ^3F_2$ (6s5f)	-.322(2)	-.319(1)	-.03(2)	2677
$20_4^0 \ ^3F_4$ (6s5f)	.30			
22_1^0 ($5d^9 6p$)	-.124	-.125	-.004	2768
13_1 (6s8s)	1.429 &			
$14_1 \ ^3D_1$ (6s7d)	-.646 &			
$15_2 \ ^3D_2$ (6s7d)	.50			
$17_3 \ ^3D_3$ (6s7d)	.433 &			
$18_2 \ ^1D_2$ (6s7d)	- .325			2641

18_2 is strongly perturbed; see the following page.

** 2933 Å is also classified as the $7_2-15_1^0$ transition of Bi IV. However, the intervals of neither 7_2 nor 15_1^0 showed up in this hfs in the present work.

& These hfs have not been resolved by any of the workers describing the spectra of Bi. Brix (1952) claims the values listed above are from Richmond (1937), but a description of these levels are absent from Richmond's work.

On the next two pages are the measurements of the $2641\text{\AA}^{\circ}$ hfs of Bi IV. The upper level of the line, 1D_2 of $6s7d$, is very strongly perturbed. This level is of special interest because the $6s7d$ configuration is unperturbed; Kelly et al (1950) used this level to calculate μ .

The only mention in the literature of this hfm is by McLay and Crawford (1931). They list the total hyperfine interval of 1D_2 only as -6.5 cm^{-1} , and describe the $2641\text{\AA}^{\circ}$ hfs as one broad line.

In this work, the $2641\text{\AA}^{\circ}$ hfs was observed in two orders, and the level was deduced to have the following appearance.

F = 13/2	_____	
		2.16 cm^{-1}
11/2	_____	
		1.10
9/2	_____	
7/2	_____	.45
		1.35
5/2	_____	

1D_2 (6s7d) Level of Bi IV

HFS WL=2642, BI4, FROM PLATE C115

89.499	406	2641.4373	37846.900
89.654	396	2641.4685	37846.453
89.794	285	2641.4967	37846.049
89.902	283	2641.5184	37845.738
90.125	297	2641.5633	37845.095
90.275	134	2641.5935	37844.663
90.437	219	2641.6261	37844.195
90.541	351	2641.6470	37843.896
90.930	802	2641.7253	37842.774

HFS WL=2642, BI4, FROM PLATE C115

COMP 1	COMP 2	COMP 3	COMP 4	COMP 5	COMP 6	COMP 7	COMP 8	COMP 9	COMP
89.499 406	89.654 396	89.794 285	89.902 283	90.125 297	90.275 134	90.437 219	90.541 351	90.930 802	
89.497 408	89.654 399	89.794 288	89.903 293	90.122 293	90.275 139	90.438 226	90.540 355	90.928 805	
89.495 401	89.654 395	89.794 294	89.902 298	90.121 289	90.275 143	90.440 233	90.537 348	90.930 813	
$\frac{1}{2} A_u$ 0.4528 0.0058	0.4037 0.0000	0.3124 0.0017	0.6354 0.0067	0.4393 0.0060	$\frac{1}{2} A_u$ 0.4710 0.0044	0.2912 0.0104	$\frac{9}{2} A_u$ 1.1245 0.0076		
	0.8565 0.0058	0.7161 0.0017	0.9478 0.0060	$\frac{9}{2} A_u$ 1.0746 0.0017	0.9102 0.0101	0.7622 0.0060	1.4157 0.0050		
	1.1689 0.0060	$\frac{13}{2} A_u$ 1.3515 0.0060	1.3870 0.0000	1.5456 0.0050	1.2014 0.0033	$\frac{9}{2} A_u$ 1.8866 0.0033			
	1.8043 0.0017	1.7908 0.0000	1.8580 0.0044	$\frac{9}{2} A_u$ 1.8368 0.0058	2.3259 0.0060				
	$\frac{1}{2} A_u$ 2.2435 0.0058	$\frac{1}{2} A_u$ 2.2617 0.0044	$\frac{7}{2} A_u$ 2.1492 0.0060	2.9613 0.0050					
		2.7145 0.0101	2.5530 0.0060	3.2737 0.0033					
		3.0057 0.0017	3.6774 0.0033						
			4.1302 0.0067						

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The numbers on the densitometer trace are the calculated intensities. The γ of this particular plate was assumed to be 1.5, i.e. x was set equal to 1.5 (see page 30). Therefore the intensities are only approximate.

Magnetic Moment From Bi V

For completeness, data for Bi V are included. All V lines are in the vacuum u.v.; the values Kelly et al (1950) give are:

	a_s	μ
6s	2.6	4.2
7s	.773	4.11

Summary of Results

My results are summarized in the following table. μ_k refers to the value quoted by Kelly et al (1950), Q_{ss} refers to values from Schuler and Schmidt (1936), μ and Q refer to my results.

Level	μ_k	μ
	Q_{ss}	Q
Bi II		
$2_1^o (6p7s \ ^3P_1)$	-.43	3.9 -.55
$9_2^o (6p7s \ ^3P_2)$	-.36	3.9 -.38
$10_1^o (6p7s \ ^1P_1)$	-.39	3.9 -.36

Level	μ_k Q_{ss}	μ Q
Bi III		
$7s \ 2S_{1/2}$	4.03	4.18
$7p \ 2P_{1/2}$	3.81	4.26
$7p \ 2P_{1/2}$	6 - .44	6.6
$6s6p^2$	4.06	
8s	4.09	4.27
Bi IV		
$5_1 \ (6s6d \ 3D_1)$	3.91	4.18 - .79
$6_1 \ (6s7s \ 3S_1)$	4.12	
$8_3 \ (6s6d \ 3D_3)$	4.09	4.18
$15_1^O \ (6s7p \ 1P_1)$		3.12
$16_2^O \ (6s7p \ 3P_2)$		3.12 -1.5
$19_2^O \ (6s5f \ 3F_2)$		3.76 -20
$20_4^O \ (6s6f \ 3F_4)$		3.76
$13_1 \ (6s8s)$	4.09	
$14_1 \ (6s7d \ 3D_1)$	4.24	-
$17_3 \ (6s7d \ 3D_3)$	4.22	

In addition to the above values, work by the following people should be noted. Dickie and Kelly (1966) found $Q = -.37(4)$ barns. This was from the spectrum of Bi I, produced by a hollow cathode discharge tube and photographed with a Fabry-Perot interferometer. Title and Smith (1960), using atomic beam resonance techniques, found $Q = -.35$ barns. Proctor and Yu (1950), with nuclear magnetic resonance apparatus, found $\mu = 4.0820(5)$ n.m.

The average nuclear moments, calculated from my data are

$$\mu = 4.1(1) \text{ n.m.}$$

and

$$Q = -.5(1) \text{ barns}$$

These averages do not include μ from $^2P_{1\frac{1}{2}}$ of Bi III or 6s7p of Bi IV; nor do they include Q from the 6s7p and 6s5f configurations of Bi IV.

CONCLUSION AND COMMENTS

When calculating μ from two electron spectra, a_s was always used. Eq. 1 requires spectroscopic information about the s electron, i.e. n_a , Z_i , Z_a , and $d\sigma/dn$. Therefore, information from the appropriate one-electron spectrum must be used.

In principle, the two electron spectrum contains enough information to determine μ . Eq. 2 requires only the fine-structure splitting of an $s\ell$ configuration, δW^0 . In practice, a_j from eq. 2 gives poor values of μ . The following table illustrates this. (The data for the 6s6p configuration were taken from the paper by Crawford and McLay (1933).)

Configuration	Ion	δW^0	$a_{\ell-1/2}$	μ
6p7s	II		.15	1.4
6s7p	IV	8000	.62	5.6
6s6p	IV	25460	.43	.013
6s6d	IV	2618	.024	.12
6s5f	IV	485	.046	120

The poor agreement for the above values of μ arise, either from perturbations or from the way in which $\overline{r^{-3}}$ is calculated. Eq. 4 states that $\overline{r^{-3}}$ is proportional to δW^0 . If significant perturbations are absent, then this is obviously not a satisfactory way to estimate $\overline{r^{-3}}$. Values of μ calculated from Bi III and V (one electron configurations) are more consistent with each other and with the resonance value of μ .

In this thesis, μ was calculated for 8 configurations

and 14 levels. Q was calculated for 4 configurations and 6 levels, and all the configurations were two electron configurations. For the levels of the $6p7s$ configuration of Bi II, Q showed good agreement both amongst the levels and with atomic beam measurements. Experimentally, the most reliable Q from Bi IV was -20 barns. The large discrepancy between this and the accepted value of -.4 barns might be explained by an "anti-shielding" of the outer electrons by the inner core. Sternheimer (1967) states this effect can be very large in ions.

From the data in this thesis, the most reliable levels from which to calculate the quadrupole moment belong to the $6s7s$ and $5d^9 6p$ configurations of Bi IV. These levels have the smallest uncertainty in B . However, these levels were not used, as there is no readily available theory to indicate how to do the calculations.

Additional experimental work could be done. It is known that a metallic halide is much more volatile than the metal. It is suspected that in the case of Bi, instead of an oven at 800°C , bismuth iodide would give a discharge in the condensed electrodeless discharge tube at room temperature or less. If the line widths are really proportional to $T^{\frac{1}{2}}$, using bismuth iodide should reduce the line widths by a factor of two. The instrument width of the Argonne spectrograph was considerably less than the natural line width of the spectral lines. So, if the natural line width could be decreased, more hyperfine structures would be resolved, and the measuring accuracy would increase.

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APPENDIX I

LINE LIST

In the following line list, the wavelengths and wave numbers are as measured in the highest order in which the line was found. For sharp, well-resolved lines, the wavelength in another order differs by as much as $-.001\text{\AA}$. Therefore, the number of significant figures indicates the sharpness of the line as it appears on the plate.

Bi II

			I_{exp}	I_{theo}	$\times$ (see p.30)	
2368	$4_2 - 4_2^0$	2368.195	44213.36			
		.334	10.87			
		.443	08.93			
		.458	.67			
		.539	07.22			
		.551	.01			
		.620	05.78			
2501	$1_0^0 - 18_1$	2501.0045	39971.886			
		.0232	.586			
		.0462	.219			
2503	$4_2^0 - 25_3$	2502.5319	39947.491			
		.55	.3			
		.6259	45.990			
		.6366	.820			
		.6524	.567			
		.7538	43.949			
		.7678	.726			
		.7866	.426			
		.9023	41.579			
		.9265	.192			
		.9485	40.843			
		3.0899	38.586			
		.1141	.200			
		.1387	37.808			
2530	$2_1^0 - 18_1$	2530.2788	39509.458	46	44	1.0
		.2976	.164	68	69	
		.3907	7.711	66	69	
		.41	.4			
		.4347	.025	69	69	
		.5486	5.245	69	69	
		.5725	4.873	100	100	

Bi II

				I _{exp}	I _{theo}	x
2544	$2_1^0 - 22_2$	2544.2912	39291.878	18	22	1.2
		.3207	.423	35	35	
		.3438	.067	43	43	
		.3691	90.675	60	51	
		.4047	.126	47	46	
		.4343	89.668	25	22	
		.4655	.188	100	100	
		.5082	88.527	36	35	
		.5457	87.950	16	51	
2746	$5_0 - 6_1^0$	2746.1235	36404.201	65	67	2.1
		.1808	3.442	88	83	
		.2538	2.473	100	100	
2803	$4_2 - 2_1^0$	2803.3401	35661.223			
		.47	59.5			
		.4848	.383			
		.4914	.300			
		.4961	.239			
3408	$6_1^0 - 19_2$	3408.4979	29330.021			
		.5240	29.797			
		.55	.6			
		.6382	28.814			
		.6608	.620			
		.68	.5			
		.76	27.8			
		.77	.6			
		.78	.5			
3411	$4_2^0 - 13_3$	3411.282	29306.09			
		.3	5.9			
		.316	.79			
		.4129	4.960			
		.4423	.708			
		.4640	.521			
		.5867	3.468			
		.6226	.159			
		.6523	2.904			
		.8002	1.634			
		.8430	.266			
		11.8792	300.955			
		12.0532	299.461			
		.0988	.070			
		.1493	8.636			
3430	$4_2^0 - 12_3$	3430.0	29145.7			
		3430.23	4.2			
		.25	4.1			
		.4	2.4			
		.4593	2.260			
		.4766	42.113			
		.7377	39.895			
		30.7586	9.717			
		31.07	7.10			
		.0908	6.896			

Bi II				I _{exp}	I _{theo}	x
3648	$6_1^0 - 21_0$	3648.5437 .6714 .7750	27400.388 399.429 8.650	100 89 66	100 83 67	2.1
3654	$5_2^0 - 15_1$	3653.9559 54.0150 .0968 .1995 .3163	27359.803 9.361 8.749 7.980 7.106			
3815	$5_2^0 - 12_3$	3815.66 .74 .84 .86 .94 .96 15.98 16.08 .10 .13	26200.3 199.8 .1 9.0 8.4 .3 8.1 7.5 .3 .1			
3845	$5_2^0 - 10_2$	3845.68 .75 .83 5.94 6.07	25995.8 5.4 4.8 4.1 3.2			
3863	$6_1^0 - 15_1$	3863.9173 3.9392 4.0409 .0585 .1	25873.134 2.989 .308 2.190 1.7			
4301	$7_2^0 - 12_3$	4301. .53 .56 .6320 .6603 .7529 .7880 .8970 .9387	23241. 40.99 .8 .453 40.300 39.799 .610 39.021 38.796			
4476	$6_1^0 - 21_1$	4476.4722 .5431 .7148 6.8743 7.0833 7.1714	22332.753 2.399 1.542 0.746 29.704 .265	48 71 69 70 70 100	44 69 69 69 69 100	2.1

Bi II				I _{exp}	I _{theo}	x
4916	$9_2^0 - 18_1$	4916.1171	20335.579	42	43	1.5
		.2106	5.192	37	35	
		.2882	4.871	23	17	
		.3282	.706	21	22	
		.4045	4.390	54	46	
		.5	4.	11	8	
		.5457	3.806	59	51	
		.6367	.430	38	35	
		.7972	2.766	100	100	
4993	$10_1^0 - 19_2$	4993.382	20020.92			
		.437	.70			
		.527	.34			
		.577	20.14			
		.626	19.94			
		.696	.66			
5091	$9_2^0 - 17_1$	5091.104	19636.63			
		.232	6.14			
		.346	5.70			
		.481	5.18			
		.638	4.57			
		.826	3.85			
5124	$9_2^0 - 16_3$	5124.087	19510.23			
		.172	9.91			
		.280	9.50			
		.413	8.99			
		.57	.40			
5144	$1_0^0 - 8_1$	5144.3562	19433.364	62	67	1.0
		.4777	2.905	86	83	
		.6262	.344	100	100	
5209	$2_1^0 - 9_2$	5208.8455	19192.768			
		8.9968	2.210			
		9.1196	1.758			
		.1351	.701			
		.3209	1.016			
		.4755	0.447			
		.5043	.340			
		.7216	89.541			
		.9058	8.862			
5270	$2_1^0 - 8_1$	5269.7668	18970.892	40	44	2.4
		69.8947	70.431	79	69	
		70.2552	69.134	70	69	
		.5388	8.113	70	69	
		70.9799	6.526	69	69	
		1.1371	5.960	100	100	

Bi II

I_{exp} I_{theo} x

5719	$2_1^0 - 7_0$	5718.4318	17482.461			
		9.0058	80.707			
		.7092	78.557			
5818	$6_1 - 17_0^0$	5817.5991	17184.457	68	67	1.6
		8.0078	3.250	83	83	
		8.5104	1.765	100	100	

Bi III

2499 $3_{2\frac{1}{2}} - 8p \ ^2P_{1\frac{1}{2}}^o$	2498.498	40011.98
	.568	10.85
	.661	9.37
	.776	7.53
	.913	5.33
	.057	3.03
	.725	2.78
2855 $6d \ ^2D_{2\frac{1}{2}} - 5f \ ^2F_{3\frac{1}{2}}^o$	2855.403	35011.04
	.437	10.61
	.484	10.04
	.543	9.32
	.613	8.46
	.696	7.45
2944 $1_{1\frac{1}{2}} - 7p \ ^2P_{1\frac{1}{2}}^o$	2943.8206	33959.532
	.9560	7.970
	.0016	7.444
	.1802	5.384
	.2262	4.854
	.4465	2.314
3451 $6_{1\frac{1}{2}} - 5f \ ^2F_{2\frac{1}{2}}^o$	3450.830	28970.24
	.886	69.76
	.932	.38
	.965	.10
3540 $7p \ ^2P_{1\frac{1}{2}}^o - 8s \ ^2S_{1\frac{1}{2}}$	3540.6308	28235.486
	.6976	4.953
	.7457	.569
	.8130	.032
3848 $6d \ ^2D_{1\frac{1}{2}} - 7p \ ^2P_{1\frac{1}{2}}^o$	3848.82	25974.6
	.899	4.09
	.918	3.96
	.971	.60
	8.994	.45
	9.0	.2
3930 $8_{1\frac{1}{2}} - 8p \ ^2P_{1\frac{1}{2}}^o$	Energy difference between the two components = 10.150 cm ⁻¹ .	
4561 $7s \ ^2S_{1\frac{1}{2}} - 7p \ ^2P_{1\frac{1}{2}}^o$	4561.0640	21918.565
	.1754	8.029
	.5533	6.213
	.6644	5.680

Bi III

59

4752 $3_{2\frac{1}{2}}$ - $5f \overset{2}{\underset{3\frac{1}{2}}{F}}$ $\overset{0}{\underset{3\frac{1}{2}}{F}}$

4749.9
50.175
.515
0.937
1.440
2.022

21047.0
5.9
4.4
2.6
40.4
37.8

5079 $6d \overset{2}{\underset{2\frac{1}{2}}{D}}$ - $6p \overset{2}{\underset{1\frac{1}{2}}{P}}$ $\overset{0}{\underset{1\frac{1}{2}}{P}}$

5078.760
8.866
9.007
.185
.403
.650

19684.36
3.95
3.40
2.71
1.86
80.91

Bi IV

				I_{exp}	I_{theo}	x
2627	$14_2^{\text{O}} - 17_3$	2626.714	38059.03			
		.853	7.02			
		.941	5.73			
		.974	.25			
		7.048	4.20			
		.080	4.00			
		.139	2.86			
		.214	1.78			
		.273	50.92			
		.3	.6			
		.316	.58			
		.348	.15			
2629	$5_1 - 19_2^{\text{O}}$	2629.15	38023.8			
		.27	22.0			
		.37	20.5			
		.41	20.0			
		.45	19.3			
		.49	8.8			
		.55	7.9			
2641	$15_1^{\text{O}} - 18_2$	2641.437	37846.90	19	8	Assuming
		.468	.45	21	35	$x = 1.5$
		.496	6.05	32	43	
		.518	5.74	32	22	
		.563	5.09	33	100	
		.594	4.66	100	46	
		.626	4.19	47	51	
		.647	3.90	25	35	
		.725	2.77	7	17	
2677	$7_2 - 19_2^{\text{O}}$	2676.5580	37350.317	28	27	1.1
		.6389	49.188	31	29	
		.6626	8.858	33	29	
		.8463	6.294	44	43	
		.8772	5.864	48	43	
		6.9815	4.409			
		7.1058	2.674	44	48	
		.1424	2.164	46	44	
		.2686	40.404	40	38	
		.4145	38.369	30	30	
		.4577	7.768	32	30	
		.6057	5.703	100	100	
2756	$15_1^{\text{O}} - 16_{\text{O}}$	2755.502	36280.30			
		.675	78.03			
		.816	6.17			

Bi IV

I_{exp} I_{theo} x

2768	$7_2 - 18_3^0$	2766.918	36130.62			
		7.011	29.41			
		.122	7.96			
		.140	7.72			
		.268	6.05			
		.293	5.73			
		.440	3.80			
		.469	3.43			
		.495	3.10			
2823	$7_2 - 17_3^0$	2822.98	35413.1			
		23.00	2.9			
		.08	1.9			
		.10	1.6			
		.1987	10.392			
		.2236	10.080			
		.24	9.8			
		.3470	8.532			
		.3779	8.146			
		.40	7.9			
		.5196	6.368			
		.5564	5.907			
		.589	5.49			
2842	$6_1 - 16_2^0$	2840.9406	35189.262			
		41.1300	6.917			
		.27	5.1			
		.5051	82.272			
		.69	79.9			
		1.9673	6.550			
		2.1970	3.708			
2933	$10_2 - 21_3^0$	2932.8585	34086.456			
		.88	6.2			
		.9569	5.313			
		2.98	5.1			
		3.042	4.32			
		.059	4.12			
		.07	3.9			
		.11	.5			
		.13	3.3			
		.2	3.			
3012	$6_1 - 14_2^0$	3011.4473	33196.951	16	17	1.2
		.5231	6.115	36	35	
		.5815	5.471	48	43	
		11.9843	91.031	56	51	
		12.0787	89.993	52	46	
		.1546	9.156	21	22	
		.6441	3.764	100	100	
		.7579	2.510	36	35	
		.8522	1.472	8	8	

Bi IV

				I_{exp}	I_{theo}	$\times$
3171	$10_2 - 18_3^0$	3171.3071	31523.618	100	100	1.1
		.345	3.24	27B	23	
		.4281	2.415	66	67	
		.460	2.09	34B	37	
		.5326	1.377	41	41	
		.559	1.11	39B	46	
		.624	0.47	38	22	
		.64	20.3	39B	49	
		.71	19.6	41B	53	
3239	$8_3 - 14_2^0$	3238.3187	30871.312	21	25	1.6
		.3616	70.903	15	18	
		.429	70.26	30	32	
		.5171	69.421	36	30	
		.5836	8.787	8	8	
		.6275	8.369	37	34	
		.7150	7.534	19	22	
		.7610	7.096	31	31	
		.8703	6.055	44	41	
		8.9161	5.618	19	20	
		9.0484	4.357	70	67	
		.2471	2.465	100	100	
3643	$5_1 - (8^0 - 11^0)$	3640.1137	27463.842			
		.5423	60.608			
		0.7604	58.963			
		1.1895	5.723			
		1.5390	53.093			
		2.0703	49.088			
		2.4220	6.437			
		3.7100	6.736			
		4.1390	3.506			
		4.4908	0.858			
3681	$6_1 - (8^0 - 11^0)$	3679.7754	27167.836			
		80.0624	5.717			This hfs overlaps
		.6758	61.190			the following
		1.2221	57.159			hfs.
		.6235	4.198			
		.8819	2.293			
		2.776	45.69			
		3.79	38.2			
		4.8996	30.057			

"B" in the intensity column means that the line was a Blend of more than one component. The printed intensity is the sum of the intensities of the individual components.

Bi IV

 I_{exp} I_{theo} x

3683	$5_1 - 7_2^0$	3682.776	27145.69
		.8881	4.875
		2.9966	4.075
		3.3258	1.649
		.4348	0.846
		.5225	40.200
		.79	38.2
		.8812	7.558
		.9465	7.076
3766	$9_0 - 13_1^0$	3765.8734	26546.722
		6.0125	5.741
		.1268	4.936
3868	$8_3 - 12_4^0$	3866.23	25857.6
		.4409	6.249
		.8929	3.226
		.9414	2.902
		6.9742	2.683
		7.0160	2.403
		.0517	2.164
		.1136	1.750
		.1614	.431
		.2228	1.021
		.2617	0.760
		.3368	50.259
		.3968	49.858
		.5203	9.032
		.6106	8.428
		.6830	7.945
		.8289	6.970
		.9316	6.283
		8.1868	4.579
		.303	3.80

APPENDIX II

UNCLASSIFIED LINES

A number of unclassified hyperfine structures were photographed, but the only one that was definitely resolved was the $3255\text{\AA}$ hfs. This line appeared in one order on the Argonne plates, with wavelength either $3255\text{\AA}$ or $4882\text{\AA}$. A subsequent spark-in-Helium exposure on our prism spectrograph showed it was a II line, and wavelength of $3255\text{\AA}$.

The intensities and measurements indicated the transition was either

	J	A	J	A
Upper level	2	.058	1	-.267
Lower level	1	.267	2	-.058

A description of the hfs follows.

Wavelength	Wavenumber	I_{exp}	I_{theo}
3254.9503	30713.576	13	17
.978	.31	35	35
4.997	3.14	46	43
5.0431	2.701	51	51
.0775	.377	53	46
.1042	2.124	23	22
.1581	1.616	100	100
.1987	1.233	38	35
5.2331	0.909	8	8

ENERGY DIFFERENCES

Bi II

Level	λ	Plate	$7\frac{1}{2}$	$6\frac{1}{2}$	$5\frac{1}{2}$	$4\frac{1}{2}$	$3\frac{1}{2}$
4_2	2368	c131	$(5\frac{1}{2}+4\frac{1}{2})A=.256\text{cm}^{-1}, (4\frac{1}{2}+3\frac{1}{2})A=.209\text{cm}^{-1}$				
	2803	a95	.1379				
	A=.025						
2_1^0	5209	a115	2.1528 1.7527				
	5270	a115	2.1504 1.7551				
	5270	b115	2.1510 1.7556				
	5719	b127	2.1498 1.7562				
	2530	c111	2.1517 1.7476				
	A=.3905(3), B=.003(2)						
4_2^0	2503	c111	2.6471	2.2326	1.8540		
	3411	c111	2.2015	1.8003	1.3675		
	A=.404(3)						
5_2^0	3845	c127	20A=2.81				
	$2A=.14$						
6_1^0	2746	c91	.969 .759				
	3408	c111	.98 .83				
	3648	c83	.962 .779				
	A=-.174(1)						
7_2^0	4301	a95	.5914	.4993			
	A=.091						
8_3^0	4259	b95	.6362	.5521	.4615	These values are averages	
		b143	from the two orders.				
	A=.0845(4)						
6_1	4476	b99	1.4816 1.2101				
	5818	b127	1.480 1.212				
	A=.268(1)						

Bi II

Level	λ	Plate	$7\frac{1}{2}$	$6\frac{1}{2}$	$5\frac{1}{2}$	$4\frac{1}{2}$	$3\frac{1}{2}$	$2\frac{1}{2}$
8 ₁	5144 b111				.5590	.4578		
	5270 a115				.5654	.4583		
	5270 b115				.5629	.4588		
	A=-.1021(3)							
9 ₂ ⁰	4916 c107			.6640	.5827	.4848	.3881	
	A=.1057(3), B=-.04(1)							
9 ₂	5209 a115			.7990	.6781	.5580		
	A=.1234(1), B=-.007(3)							
12 ₃	3430 a79	.2070	.1799	.1471				
	3815 c127		.18	.134				
	A=-.028(1)							
13 ₃	3411 c111		.368	.309	.252	.18	.093	
	A=.056(1)							
21 ₁ ⁰	4476 b99			.4385	.3534			
	A=-.0793, B=.003							
22 ₂	2544 c143		.657	.57	.457	.354		
	A=.102(1)							
18 ₁	2501 c111			.3290	.2750			
	2501 c139			.300	.367			
	2530 c111			.3100	.3740			
	4916 c107			.3699	.2956			
	A=-.068(1)							
19 ₂	3408 c111		.2245	.1929				
	A=.0351, B=-.0064							

Bi III

Level	λ	Plate	7	6	5	4	3	
$1_{1\frac{1}{2}}$	2944	c131		3.0725	2.5874	2.0906		
	A=.5160(2), B=-.038(3)							
$2_{2\frac{1}{2}}$	3039	c99	3.5488	3.0311	2.5140	2.0092	1.4968	The $4_{1\frac{1}{2}}$ level is not resolved.
	3039	c135	3.5381	3.0327	2.5132	2.0026	1.5021	
	A=.503							
$9_{1\frac{1}{2}}$	4561	b99			{ 2.3514 2.3529			
	A=.4704(2)							
$11_{2\frac{1}{2}}$	2855	b127	1.009	.861	.718	.574	.424	
	5079	b111	.957	.844	.693	.545	.409	
	A=.140(2)							
$6_{1\frac{1}{2}}$	3450	b115		.476	.381	.279		
	A=.076							
$3_{2\frac{1}{2}}$	2499	c111	2.551	2.193	1.845	1.484	1.123	
	4752	c103	2.575	2.224	1.873	1.497	1.141	
	A=.370(2)							
$3_{1\frac{1}{2}}^O$	2944	c99			.521			
	2944	c131			.5303			
	3540	b115			.5340			
	4561	b99			.5335			
	A=.106(1)							
$4_{1\frac{1}{2}}^O$	3848	b127			.153			
	A=.017							
$8_{1\frac{1}{2}}$	3930	c131			10.150			
	A=2.030							
$12_{1\frac{1}{2}}$	3540	b115			.535			
	A=.107							

Bi IV

Level	λ	Plate	$8\frac{1}{2}$	$7\frac{1}{2}$	$6\frac{1}{2}$	$5\frac{1}{2}$	$4\frac{1}{2}$	$3\frac{1}{2}$	$2\frac{1}{2}$
5_1	3683	c83				3.2281	2.6643		
	A=-.591(4), B=-.002								
6_1	2842	c95				8.5702	6.9856		
	2842	c123				8.5664	6.9889		
	3012	c99				8.5645	6.9806		
	3012	c131				8.5603	6.9890		
	A=1.5556(3), B=.011(2)								
7_2	2677	c91			2.650	2.270		1.459	
	2823	c123			2.6391	2.2532			
	A=.410(2), B=-.04(1)								
8_3	3239	c107		3.1650	2.7417	2.3236	1.9000		
	3239	c143		3.1545	2.7376	2.3129	1.8899	1.4754	
	3868	c127		3.1661	2.7479	2.3305	1.9040	1.4759	
	A=.422(1)								
10_2	3171	c103	$(5\frac{1}{2}+6\frac{1}{2})A = 1.547\text{cm}^{-1}$.						
	A=-.129								
11_2	5029	c111	$20A - 1.0\text{ cm}^{-1}$.						
	A=.05								
7_2^O	3683	c83			.8183	$\left\{ \begin{array}{l} .7998 \\ .8013 \end{array} \right.$	.6457	.4833	
	A=.141(8), B=-.16(9)								
12_4^O	3868	c127	.7746	.6861	.6018	.5021	.4133 .4113	.3219	.2220
	A=.095(7)								
13_1^O	3766	c123				.9805	.7985	These values are averages.	
	A=.178(1)								
14_2^O	3012	c99			1.2623	1.0427	.8397	.6355	
	3012	c131			1.2593	1.0439	.8412	.6455	
	3239	c107			1.2577	1.0450	.8449	.6457	
	3239	c143			1.2583	1.0428	.8354	.6375	
	A=.190(1), B=.052(5)								
15_1^O	2756	c91				2.268	1.860		
	A=-.413								
16_2^O	2842	c95				2.8469	2.3358		
	2842	c123				2.8450	2.3420		
	A=.5174(2), B=-.03(1)								

Bi IV

Level	λ	Plate	$7\frac{1}{2}$	$6\frac{1}{2}$	$5\frac{1}{2}$	$4\frac{1}{2}$
17_3^0	2823	c123 A=.06(1)	.4749	.3974	.3223	
18_3^0	3171	c103 A=.049	.3783	.321	.719	
21_3^0	2933	c127 A=.041		.267		
19_2^0	2677	c91 A=-.319(1), B=-.03(2)	2.050	1.760	1.129	
22_1^0	2768	c91 A=-.125, B=-.004		.6815	.5650	

Levels 8^0 - 11^0 3643 c83
3681 c83 11^0 10^0 9^0 8^0 15.582
15.5716.647
6.6454.883
4.865