ISOTOPE SHIFT IN THE Cd I

INTERCOMBINATION RESONANCE LINE λ 3261 A°

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ABSTRACT

The isotope shifts in the Cd I intercombination resonance line $\lambda 3261 \ A^0 \ (5s^{2} \ ^1S_0 - 5s5p \ ^3P_1)$ were measured for seven of the eight naturally occurring isotopes of cadmium using an atomic beam light source together with a Fabry-Perot interferometer. The measured shifts between the even isotopes were

 $\Delta \mathcal{V}(116,114) = 9.3 \times 10^{-3} \text{ cm}^{-1}$ $\Delta \mathcal{V}(114,112) = 13.5 \times 10^{-3} \text{ cm}^{-1}$ $\Delta \mathcal{V}(112,110) = 16.3 \times 10^{-3} \text{ cm}^{-1}$ $\Delta \mathcal{V}(110,106) = 35.4 \times 10^{-3} \text{ cm}^{-1}$

The position of 108 was not determined because of its low percentage abundance. The positions of the centres of gravity of the odd isotopes relative to the evens were

> $\Delta \vee (113,112) = 2.6 \times 10^{-3} \text{ cm}^{-1}$ $\Delta \vee (111,110) = 1.9 \times 10^{-3} \text{ cm}^{-1}$

The isotope shifts of the even isotopes decrease with increasing mass number while the odd isotopes are "staggered" lying closer to the next lighter even isotope.

The isotope shifts were corrected for the normal mass effect and their ratios were found to be in good agreement with the corresponding ratios determined by Kuhn and Ramsden for the Cd II line λ 4416 A^O. The agreement between the two sets of ratios indicates that any residual specific mass effect is probably quite small. The corrected shifts can then be interpreted as being due mainly to the nuclear field or volume effect. The general features

of the ratios indicate that for cadmium $\frac{SC_{exp}}{SN}$, the change of the isotope shift constant C_{exp} for a pair of isotopes with neutron number, N, is negative. The square of the nuclear deformation α^2 (N) then reaches a maximum in the neutron region 50 to 82. On the collective model, the "staggering" of the odd isotopes can be interpreted as even-odd nuclei being less deformed than even-even nuclei. In terms of the shell model the "staggering" of the odd isotopes of cadmium can be interpreted as a $3s_2^1$ neutron only slightly increasing the shift caused by the addition of a pair of $5g_7/2$ neutrons to the nucleus.

The isotope shift constant, $\beta C_{5s} \exp$, was estimated for the ground term of the single valence electron spectrum, Cd II 5s ${}^{2}S_{\frac{1}{2}}$, for the isotope pair 112,114 as

 $\beta C_{5s exp}$ (Cd 112,114) = 34 ± 4 x 10⁻³ cm⁻¹.

The accuracy of this experiment was checked by comparing the ratio of the nuclear magnetic moments of the odd isotopes with the ratio determined by the more accurate nuclear induction method by Proctor and Yu. The value determined in this experiment was $\mathcal{M}_{113}/\mathcal{M}_{111} = 1.041 \pm 0.021$ which is in good agreement with nuclear induction value $\mathcal{M}_{113}/\mathcal{M}_{111} = 1.0461 \pm 0.0001$.

The nuclear magnetic moments of the odd isotopes of cadmium were calculated using the appropriate intermediate coupling formula of Breit and Wills and were $\mathcal{M}_{113} = -0.52$ n.m. and $\mathcal{M}_{111} = -0.50$ n.m. These values are about 16% lower than the accepted values $\mathcal{M}_{113} = -0.619$ and $\mathcal{M}_{111} = -0.592$ determined by Proctor and Yu. This discrepancy can be accounted for by allowing 10% for the screening of the 5s electron by the 5p electron in the 5s5p ${}^{3}P_{1}$ level. This 10% allowance is justified as in similar electron configurations the s electron is screened by the p electron by this amount. The nuclear magnetic moments are then estimated as

 $\mathcal{U}_{113} = -0.58 \pm 0.03$ n.m. and $\mathcal{U}_{111} = -0.56 \pm 0.03$ n.m.

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CHAPTER I

INTRODUCTORY THEORY

1.1 Introduction

Under high resolution, many atomic spectral lines are found to consist of a number of closely spaced components. These spectral lines are said to exhibit hyperfine structure (hfs). Hyperfine structure can arise from isotope shift or from magnetic hyperfine structure or from a combination of both of these.

1.2 Isotope Shift

Isotope shift, which is caused by differential shifts in terms due to differences in nuclear properties of the isotopes of the same element, can be subdivided into the mass effect and the field or volume effect. Isotope shift in the lighter elements is completely accounted for by the mass effect while isotope shift in the heavier elements is completely accounted for by the field or volume effect.

(i) The mass effect

The mass effect can be subdivided into the normal mass effect and the specific mass effect.

The normal mass effect explains completely the isotope shift in one-electron hydrogenic spectra. In this case the finite mass of the nucleus is accounted for by replacing the

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mass of the electron with its reduced mass in the hydrogenic term value so that

$$T = \frac{R_{\infty} Z^{2}}{n^{2}} \left(1 - \frac{m}{m_{n}} \right) = T_{\infty} \left(1 - \frac{m}{m_{n}} \right)$$
(1.1)

where T is the term value for a nucleus with finite mass m_n T_{∞} is the term value for a nucleus with infinite mass m is the mass of the electron

 R_∞ is Rydberg's constant for an infinite nuclear mass Z is the atomic number

n is the principal quantum number

From this relationship it is obvious that the term value of the heaviest isotope lies "lowest" in the energy level diagram. The normal mass effect must be taken into account for every atomic energy level. The separation in wave numbers ΔY between the components of two isotopes is given by

$$\Delta \mathcal{V} \approx \frac{\mathrm{m}}{\mathrm{m}_{\mathrm{p}}} \frac{\mathrm{M}_{2} - \mathrm{M}_{1}}{\mathrm{M}_{2}\mathrm{M}_{1}} \mathcal{V}$$
^(1.2)

where m_p is the mass of the proton

 M_1 and M_2 are the mass numbers of the two isotopes with

 $m_n = m_pM$ where the mass defects have been ignored.

 ${\cal V}$ is the wave number of the spectral line

The specific mass effect occurs in atoms with several electrons and arises from the interaction of the electrons. It may operate in the same or in the opposite sense to the normal mass effect depending upon whether the electrons "move" predominantly in the same or in opposite directions resulting in an increase or decrease in the nuclear motion which is required to keep the centre of gravity of the whole atomic system at rest. While the calculation of the normal mass effect is easily performed, the calculation of the specific mass effect is very difficult as it involves the evaluation of integrals which are of the same form as those which arise in intensity calculations. Both mass effects decrease with increasing mass number and they become negligibly small for the heaviest elements.

(ii) The field or volume effect

The field or volume effect arises because the nucleus is not a point charge but has a finite volume within which there is a departure from the Coulomb potential experienced by the electrons. The departure from the Coulomb potential is least for the isotope with the smallest nuclear radius so that the term value of the smallest isotope lies "lowest" in the energy level diagram. Figure 1 shows the potential energy V between an electron and a nucleus as a function of their relative distance apart r, together with the corresponding energy level diagram. The figure shows the potential energies of two isotopes of mass numbers M and M + 1 with corresponding nuclear radii $r_{\rm M}$ and $r_{\rm M} + \frac{1}{2}$ where $r_{\rm M} \langle r_{\rm M} + \frac{1}{2}$. In general, if the nucleus is assumed to be spherical its radius r is given by

$$r = r_0 M^{1/3}$$
 (1.3)

where M is the mass number of the nucleus and

 $r_0 = 1.2$ to 1.6×10^{-13} cm.



The corresponding term values of the two isotopes are T_M and $T_M + 1$ while the term of a hypothetical point charge nucleus is $T_C \cdot \Delta T_M$ and ΔT_{M+1} , the deviations of the terms of the two isotopes from the term of a point charge nucleus, will be referred to as the "displacements" in the term due to the nuclear field or volume effect, while the difference in the displacements, **S** ΔT , will be called the isotope shift in the term due to the field or volume effect.

All the s electrons and to a much smaller extent all the $\mathtt{p}_{\overline{\mathtt{Z}}}$ electrons of the electron configuration contribute directly to the displacement, while all the electrons of the configuration affect the displacement indirectly through screening effects. However, this total displacement is not directly observable in practice. What is generally observed is the difference in energy between the line-components of two different isotopes of the same This will be referred to as the isotope shift in the element. spectral line. Since a spectral line involves a transition between two terms, the isotope shift in a spectral line corrected for the mass effect will be equal to the difference in SAT between the two terms. Under favorable conditions the corrected isotope shift may be very nearly equal to the field-dependent isotope shift due to a valence electron in only one of the terms. Thus in a transition of an electron from a p-state to an s-state the corrected isotope shift of the spectral line is very nearly equal to the field-dependent isotope shift due to the s valence

electron, where it is assumed that the electronic cores of the two states are identical and that the smaller field-dependent isotope shift of the p electron is negligible. Isotope shift studies are almost exclusively restricted to spectral lines involving a transition to or from a term having one or two s electrons in the outermost shell.

The information about the angular shape and size of atomic nuclei which is obtained from the field-dependent isotope shift can be summarized in one number C_{exp} , the experimental isotope shift constant. C_{exp} is defined for two isotopes of the same element for a single valence s electron as

$$C_{exp} = \frac{\delta \Delta T_s}{\Psi_s^2(o) \pi d_H^3/Z} = \frac{\delta \Delta T_s}{Z_o^2 (1 - \frac{ds}{dh})/N_o^3}$$
(1.4)

where $\delta\Delta T_s$ is the field-dependent isotope shift in the term for two isotopes due to a single valence s electron $\Psi_s(o)$ is the non-relativistic wave function of the s elec-

tron evaluated at the nucleus

- a_H is the Bohr radius
- Z is the atomic number of the element
- Z_o is the effective nuclear charge outside of closed electronic shells
- n_0 is the effective principal quantum number and is equal to $n - \sigma$ where n is the principal quantum number and σ is the quantum defect
- $(1 \frac{dG}{dn})$ is the Fermi-Segrè factor

If the screening of the s valence electron on the elec-

tronic core is taken into account equation (1.4) must be written as

$$\beta^{c}_{exp} = \frac{\delta \Delta T_{exp}}{Z_{o}^{2} \left(1 - \frac{de}{dn}\right) / n_{o}^{3}} = \frac{\beta \delta \Delta T_{o}}{Z_{o}^{2} \left(1 - \frac{de}{dn}\right) / n_{o}^{3}}$$
(1.5)

where β is a screening factor equal to $1 - \dot{\gamma}$ where $\delta \Delta T_{exp}$ is given by $(1 - \dot{\gamma}) \delta \Delta T_{exp}$

SATexp is the experimentally determined isotope shift in the term due to the valence s electron.

The actual calculations of C_{exp} involve many difficulties and where they have been performed the accuracy is of the order of about 20%. In contrast, relative isotope shifts, the ratios of the shifts, can be determined more accurately and give C_{exp} on a relative scale.^{5,12,13} Furthermore the changes in these relative isotope shifts between successive pairs of isotopes, occurring either gradually or in "jumps", must be due to corresponding changes in the nuclear charge distribution resulting from the addition of neutrons to the nucleus, and therefore must give $\frac{\delta C_{exp}}{\delta N}$ on a relative scale to a considerable accuracy.¹³

If $C_{\rm th}$ is the theoretical isotope shift constant for a pair of isotopes derived from a particular nuclear model, then a comparison of $C_{\rm exp}$ with $C_{\rm th}$ gives information about the validity of that particular nuclear model regarding the change of nuclear charge distribution due to the addition of neutrons to the nucleus.

If C_{th} is calculated on the basis of a standard nuclear

model of spherical, homogeneously charged, incompressible nuclei with radius r proportional to $\mathbb{M}^{1/3}$, it is found that the values of βC_{exp} are in general smaller than C_{th} by a factor of between l.5 and 7. Other evidence indicates that probably $\beta \approx 1$ so that this discrepancy cannot be accounted for by the screening effects of the electronic core.^{5,12} Of the other factors which could possibly influence the isotope shift are the non-Coulombic interactions between the electrons and the neutrons, and the polarization of the nucleus by the orbital electrons, but these have been ruled out for various reasons.^{12,21} Apart from this general discrepancy, a plot of $\beta C_{exp}/C_{th}$ against N brings out certain anomalies, and discontinuities at the "magic" neutron numbers, which cannot be explained on the basis of this standard model. Furthermore, the "staggering" of the even-odd nuclei cannot be explained on this model.

In general, the smallness of the observed isotope shifts can be accounted for by nuclear compressibility and nuclear surface phenomena.²¹

Brix and Kopfermann (1947) and Wilets, Hill and Ford (1953), have expressed the view that a large part of the field-dependent isotope shift, expecially most of its change with neutron number N and atomic number Z is related to an "intrinsic quadrupole" moment Q_0 resulting from a nuclear deformation \mathcal{A} . They assumed that even-even nuclei for which the spin I = 0 could have a charge distribution which deviates from spherical symmetry just like a

nucleus with $I \neq 0$. If I = 0 there is no preferred direction or "axis of quantization" so on averaging the charge distribution over all directions the deformation is detected as an increased volume effect rather than an observable quadrupole moment Q. On the basis of the dynamical model A. Bohr has derived the following relationship between Q and Q₀ for strong coupling

$$Q = \frac{I(2I-1)}{(I+1)(2I+3)} Q_0$$
 (1.6)

where Q is the quantum mechanical quadrupole moment

 ${\tt Q}_{{\scriptstyle {\scriptsize O}}}$ is the classical "intrinsic" quadrupole moment

I is the nuclear spin The "quadrupole" isotope shift can be calculated if the deformed nucleus is approximated by a uniformly charged ellipsoid of revolution with the generating ellipse given by

$$\mathbf{r}(\theta) = \mathbf{r}' \left[1 + \alpha \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right]$$
 (1.7)

where r' is the radius of the undeformed spherical nucleus of equal volume

 \propto is the deformation parameter and is equal to 2/3 ξ where ξ is the ellipticity

 Θ is the angle between the radius and the symmetry axis. For a prolate spheroid $\ll > 0$ and for an oblate spheroid $\ll < 0$. The calculation indicates that the shift in a term value as compared with its value for a spherical nucleus, ΔT_{\ll} , is proportional to \propto^2 . This relationship has been shown to hold by A. Bohr if \propto describes the root mean square of a deformation due to a surface vibration rather than a static deformation. Experimentally what is observed is not ΔT_{\propto} but the change $S\Delta T_{\propto}$ for a change in \propto

at constant Z so that $\mathbf{S} \Delta T_{\mathbf{x}}$ is proportional to $\mathbf{S}(\mathbf{x}^2)$. The "quadrupole" isotope shift constant $C_{\mathbf{x}}$ then has the following relationships

$$\frac{C_{\infty}}{C_{\rm th}} \propto \frac{\mathbf{s}(\alpha^2)}{\mathbf{s}N} \propto \frac{\mathbf{s}(Q_0^2)}{\mathbf{s}N}$$
(1.8)

and

$$\frac{\beta C_{exp}}{C_{th}} = \frac{C_{\alpha}}{C_{th}} + K$$
(1.9)

where the "quadrupole" effect has been added to the "normal" shift to give the total isotope shift $\beta C_{exp}/C_{th}$. On the standard model K = 1 but if the compressibility of the nucleus is also considered K \approx 0.7.

The change in the relative isotope shift from isotope pair to isotope pair, which gives $\frac{\&C_{exp}}{\&N}$ on a relative scale, is then proportional to $\frac{\&C_{\infty}}{\&N} \propto \frac{\&C_{\infty}^2(\swarrow^2)}{\&N^2}$ where the suggestion of Brix, Kopfermann, Wilets, Hill and Ford has been invoked.

While the nuclear deformation affords a satisfactory explanation of the fluctuations of the isotope shifts and the discontinuities in the isotope shifts at the "magic" neutron numbers, it provides only a qualitative explanation of evenodd "staggering". 21,12 According to the theory of the "quadrupole" effect, the addition of a single neutron to a nucleus of even mass number leads to a smaller Q_0^2 and, hence, to a smaller isotope shift than the addition of two equivalent neutrons.¹² Even-odd "staggering" still presents a challenging problem to nuclear theorists and it may be that several other effects, such as nuclear polarization contribute to it.^{21,12}

1.3 Magnetic Hyperfine Structure

Magnetic hyperfine structure is caused by the interaction of the nuclear magnetic moment with the valence electrons resulting in a splitting of the energy levels into a number of hyperfine structure states. The nuclear magnetic moment \mathcal{M}_{I} arises from the orbital motion of the protons and the magnetic moments of the nucleons. The angular momentum of the nucleus can be represented by a dimensionless vector \underline{I} which gives the angular momentum in units of \underline{K} . The maximum possible component of \underline{I} in a fixed direction gives the nuclear spin I. Then

$$\mathcal{M}_{I} = g_{I} \mathcal{M}_{N} \underline{I}$$
(1.10)

where g_I is the nuclear gyromagnetic ratio

 $\mathcal{M}_{\mathbb{N}}$ is the nuclear magneton which is \mathcal{M}_{0} where \mathcal{M}_{0} is the Bohr magneton.

Nuclear magnetic moments are usually expressed in units of nuclear magnetons in which case

 $\mathcal{U}_{I} = g_{I} I \tag{1.11}$

 \mathcal{M}_{I} is positive or negative depending upon whether \mathcal{M}_{I} and \underline{I} are parallel or antiparallel.

The magnetic field produced by an electron at the nucleus arises from the electron's orbital motion which is associated with its orbital angular momentum vector \mathcal{L} and its intrinsic magnetic moment which is associated with its spin angular momentum. The total angular momentum of the electron j is $\underline{l} + \underline{s}$. Where there are several electrons outside of closed electronic shells, there may be LS coupling, jj coupling or some intermediate form of coupling between the valence electrons. The total angular momentum of the atom \underline{F} is $\underline{I} + \underline{J}$. There are 2J + 1 or 2I + 1 hyperfine structure states depending upon whether $J \ge I$ or $I \ge J$. The statistical weight of a hyperfine structure state with quantum number F is 2F + 1 so that the sum rule can be used to determine the intensity ratios of the components. The sum rule states that the sum of the intensities of all transitions originating or ending on a hyperfine structure state is proportional to the statistical weight of that state.

The interaction energy between the nuclear magnetic moment and the field due to the valence electrons for a given J level is

W (I, J) = $\frac{1}{2}A_J \left[F(F+1) - I(I+1) - J(J+1)\right]$ (1.12) while the separation between two hyperfine structure states ΔW , of a given J level with quantum numbers F and F - 1 is the product of the interval factor A_J and the higher F value, that is

$$\Delta W = A_J F$$
 (1.13)
Equation (1.13) is a statement of the interval rule.

For electron configurations with one electron outside of closed shells, the interval factor as determined by Goudsmit, Fermi and Segre, Breit and Racah is for a non-s electron

$$a_{j} = g_{I} \frac{\Delta V_{p}}{Z_{i}} \frac{l(l+1)}{18^{36}(l+2)j(j+1)} \frac{F_{n}(j,Z_{i})}{H_{n}(l,Z_{i})}$$
(1.14)

and for an s electron

$$a_{s} = g_{I} \frac{8R\alpha^{2}Z_{i}Z_{o}^{2}}{3n_{o}^{3}} \frac{1836}{1836} \left(1 - \frac{de}{dn}\right) F_{n}(j, Z_{i})$$
(1.15)

where a_j and a_s are the interval factors of a non-s and s electron respectively in cm⁻¹

 \mathbf{g}_{T} is the nuclear gyromagnetic ratio

- no is the effective principal quantum number.
- Z_i is the effective nuclear charge in the inner region and is equal to Z for an s electron. For a p electron Z_i can be obtained from the doublet fine structure separation.
- Z₀ is the effective nuclear charge outside of closed shells and is 1 for a neutral atom and 2 for a singly ionized atom.
- R is the Rydberg constant, 109,737.31 cm⁻¹
- \propto is the Sommerfeld fine structure constant, $\frac{1}{137.04}$
- $F_{\rm r}$ and $H_{\rm r}$ are relativistic corrections tabulated by Kopfermann. 12
- n is the principal quantum number
- σ is the quantum defect and is equal to $n n_0$
- $\Delta V_{\rm p}$ is the interval, in cm⁻¹, between the two levels of

the doublet with the same n and $oldsymbol{\chi}$.

For electron configurations with more than one electron outside of closed shells, the various types of coupling must be taken into account in determining the interval factor. The vector model and the principle of energy sums enables explicit formulae

to be derived for LS and jj coupling. For the intermediate types of coupling quantum mechanics must be used. (See Kopfermann¹² and Breit and Wills⁴). The interval factor A for a triplet level ${}^{3}L_{l}$ by an intermediate coupling calculation for a two- electron configuration nsnl is

$$A({}^{3}L_{j}) = \frac{1}{2j(j+1)} \left\{ \left[(l+1)C_{2}^{2} - jC_{1}^{2} \right] a_{s} + (2l+3)C_{1}^{2}a' + (2l+3)C_{1}^{2}a' + 4C_{1}C_{2}\sqrt{j(l+1)} a''' \right\}$$
(1.16)
a is the interval factor of the selectron.

where a is the interval factor of the s electron.

a and a are two splitting factors for the l electron given by

$$a'_{a'} = a_{l} \pm \frac{1}{2} = \frac{l(l+1)}{j(j+1)} \frac{\Delta V_{l}}{Z_{i}} + \frac{1}{(l+\frac{1}{2})} \frac{g_{I}}{1836} + \frac{F_{r}(j,Z_{i})}{H_{r}(j,Z_{i})} \quad (1.17)$$
a splitting factor designated by $a_{l} \pm \frac{1}{2}, l = \frac{1}{2}$ given by

$$a''' = \frac{1}{2(2l+1)(l+\frac{1}{2})} \frac{\Delta V_{M}}{Z_{i}} \frac{g_{I}}{1836} \frac{G_{r}(l,Z_{i})}{H_{r}(l,Z_{i})}$$
(1.18)

where $G_r(l,Z_i)$ is a relativity correction tabulated by Kopfermann¹² In equation (1.16) C_1 and C_2 are coupling coefficients which are, for a ${}^{3}Lq$ level

$$C_1 = \sin \left(\mathbf{Q}_0 - \mathbf{Q} \right) \qquad C_2 = \cos \left(\mathbf{Q}_0 - \mathbf{Q} \right) \qquad (1.19)$$

where

S

$$Q_0 = \tan^{-1} \sqrt{\frac{l}{l+1}} \tag{1.20}$$

and where \mathbf{Q} is a measure of the deviation from Russell-Saunders coupling and is given by

$$in^2 \mathbf{Q} = \underline{\Delta} \tag{1.21}$$

where Δ is the deviation of the term ${}^{3}L_{\ell}$ from its position in Russell-Saunders coupling where the interval rule is strictly obeyed.

D is the separation ${}^{3}L_{l} - {}^{1}L_{l}$ M_{l} is the fine structure multiplet splitting ${}^{3}L_{l+1} - {}^{3}L_{l-1}$ (See Figure 2).



CHAPTER II

DISCUSSION OF THE PROBLEM

There are eight naturally occurring isotopes of cadmium, six even and two odd. Their relative abundances are given in Table 1 (from Bainbridge and Nier, 1950)².

Table 1.	Relative	Abundar	ices of	f the	Isotopes	of Nat	ural (Cadmium
Isotope	106	108	110	1 11	112	113	114	116
%	1.22	0.88	12.4	12.8	24.1	12,3	28.8	3 7.6

Isotope shifts in the intercombination resonance line $\lambda 3261 \ A^{\circ} (5s^{2} \ ^{1}S_{\circ} - 5s5p \ ^{3}P_{1})$ have been measured previously by Brix and Steudel⁶ who used the absorption of six atomic beams in series. However, they were only able to measure the isotope shifts between the three most abundant even isotopes 110, 112 and 114. They also reported that the odd isotopes showed a total splitting due to the ${}^{3}P_{1}$ level of 0.214 cm⁻¹ and that the odd isotopes lie unsymmetrically towards the even isotopes with smaller mass numbers but they were unable to determine the position of the centre of gravity of each odd isotope.

Isotope shifts in cadmium have also been measured by several authors in the spark line Cd II λ 4416 A° (4d¹⁰5p ²P_{3/2} - 4d⁹5s² ²D_{5/2}). The best results are those of Kuhn and Ramsden¹³ who used enriched isotopic samples in a hollow cathode cooled

with liquid hydrogen and the high resolution of a double etalon. They were able to measure the isotope shifts of all the stable isotopes.

The purpose of the present work was to redetermine the isotope shifts in the Cd I intercombination resonance line λ 3261 A^O reported by Brix and Steudel, using an atomic beam in emission in place of the generally inferior absorption technique, with the prospect of obtaining the isotope shifts of other even isotopes and the positions of the centres of gravity of the odd isotopes. Once the isotope shifts have been determined and corrected for the normal mass effect, their ratios can be compared with the corresponding ratios reported by Kuhn and Ramsden for Cd II λ 4416 A^O, to check the possible influence of a residual specific mass effect.

As each even isotope of cadmium has a zero nuclear spin, there will be no magnetic hyperfine structure due to the even isotopes so that the isotope shifts of the even isotopes will be determined directly in λ 3261 A^O. However, each odd isotope has a spin of $\frac{1}{2}$ and a negative nuclear magnetic moment.¹⁸ Therefore each odd isotope must give rise to two magnetic hyperfine structure components in the Cd I intercombination resonance line λ 3261 A^O (5s² ¹S₀ - 5s5p ³P₁), with the weaker component on the high frequency side of the stronger component. (See Figure 3). To determine the isotope shifts of the odd isotopes, it is then



necessary to calculate the positions of the centres of gravity of each pair of magnetic hyperfine structure components.

CHAPTER III

THE ATOMIC BEAM LIGHT SOURCE

3.l Theory

A major problem in atomic spectroscopy is to obtain spectral lines with sufficiently narrow line widths so that the desired structure is not obscured. Every spectral line has a natural line width due to the uncertainty in the energy ΔE which arises from the finite lifetime Δt of an excited state. From Heisenberg's Uncertainty Principle ΔE and Δt are related as follows

(3.1)

AE . At ≥ t

Under ordinary circumstances it is estimated that the natural line width of spectral lines is rarely larger than 0.001 cm⁻¹. In addition to natural line width, there are several other causes of line width which are summarized by Tolansky.²⁰ Among these are pressure broadening, resonance broadening, Zeeman and Stark broadening, and self-absorption broadening. However, the most important cause of line width in atomic spectroscopy is Doppler broadening which is due to the random thermal motion of the emitting atoms in the light source such that the atoms moving towards the observer have a higher frequency than those receding from him. The Doppler half-width of a spectral line $\Delta \vee$ is given by

$$\Delta Y = 2\sqrt{\log 2} \sqrt{\frac{2RT}{Mc^2}} V \text{ cm}^{-1}$$

= 0.71 x 10⁻⁶ $\sqrt{T/M} V \text{ cm}^{-1}$ (3.2)

where R is the gas constant

T is the absolute temperature

M is the molecular weight

c is the velocity of light

 γ is the wave number of the radiation

Doppler broadening can be reduced considerably by means of low temperature light sources but especially by means of an atomic beam light source. In an atomic beam light source the emitting atoms are made to travel perpendicularly to the direction of observation so that the average value of the component of velocity in the direction of observation is small. The atomic beam light source also reduces pressure broadening which is caused by collisions between the atoms.

The essential features of an atomic beam light source are given in Figure 4. An atomic beam light source consists of a high vacuum chamber dividend into three sections, a furnace section for the evaporation of the material under study, a water cooled central section in which are mounted collimating slits, and an upper section in which the atoms are excited and from which the radiation is emitted. In the atomic beam light source used in this experiment, the evaporated atoms of cadmium moved from the furnace through the collimating slits to the upper chamber where they condensed on the liquid nitrogen trap. The atomic beam was excited by means of an electron beam passing perpendicularly to the atomic beam. The emitted light was observed perpen-



SCHEMATIC DIAGRAM OF AN ATOMIC BEAM LIGHT SOURCE

FIGURE - 4

dicularly to both the electron and atomic beams. In Figure 4, if o is the diameter of the oven aperture, s is the collimating slit length in the direction parallel to the line of sight, his the distance between the oven slit and the trap, \mathcal{A} is the length of the spot collected on the liquid air trap, and d is the distance between the trap and collimating slit, then the largest deviation of the atomic paths from the axis of the beam is given by the angle \ll where

$$\alpha = \tan \alpha = \frac{l-s}{2d} = \frac{0+s}{2(k-d)}$$
(3.3)

The collimation of the beam C is defined by

$$C = \frac{1}{\alpha}$$
(3.4)

The collimation of the atomic beam is then given by the geometry of the source as

$$C_{geom} = \frac{2(h - d)}{o + s}$$
 (3.5)

This can be checked experimentally by

$$C_{exp} = \frac{2d}{l - s}$$
(3.6)

The ratio of the half-widths of the spectral line from the beam to that from vapor at the temperature of the oven is given by

$$\Delta V_{B} / \Delta V_{c} = 0.41 / C \qquad (3.7)$$

The effective collimation depends also on the lens system used to focus the image of the source onto the slit of the spectrograph. If C is the collimation of the light beam, then the effective collimation C_{eff} is given by

$$1/C_{eff} = 1/C + 1/C'$$
 (3.8)

3.2 Experimental Considerations

The main features of the atomic beam light source used in this experiment are shown in Figure 5 and Plate 1. It is similar in construction to that described by Crawford et al (1950).⁸,10,17

The furnace section was pumped by a MC 275 oil diffusion pump in series with a Cenco Hypervac rotary foregump while the excitation chamber was pumped through a side arm by a pumping system consisting of a MCF 300 oil diffusion pump in series with a Cenco Megavac rotary forepump. With this arrangement, pressures of~ 10^{-5} mm. of Hg were obtained.

The electrically heated furnace consisted of an iron core covered with "Sauereisen" cement in which was embedded the windings of #19 nickel-chrome wire. The furnace was fitted with an iron cover with a circular aperture. The furnace had a resistance of 8.5 ohms at room temperature. A plot of temperature against power input was obtained for the furnace with a chromelalumel thermocouple. The melting point of cadmium is 321° C. At 392° C its vapor pressure is 1 mm. of Hg and at 455° C its vapor pressure is 5 mm. of Hg. A satifactory beam was obtained when the furnace was operated at ~23 volts and ~3 amperes corresponding to an operating temperature of 380° to 430° C.

The best operating conditions for the electron gun were

	Current (amperes)	Potential (volts)
Anode	0.010	25
Grid	0.290	200
Filament	6.0	

These conditions were arrived at by comparing the intensities of photographic exposures of $\lambda 3261 \ A^{O}$ made under various operating conditions. Higher filament and grid currents would have given darker exposures but as the grid was not water-cooled there was no way of dissipating the extra heat produced at the grid. The values given above were found to be quite satisfactory.

The anode was water-cooled. The darkest exposures were obtained with low anode voltages. This arises from the fact that the probability of excitation of a triplet state by electron collision has a fairly narrow peak at low potentials.

The cadmium beam was collimated sharply by the system of slits. This was evident from the clearly defined image on the nitrogen cold trap and from the cadmium beam itself which appeared bluish in the region of the space charge.

Using T = 430 + 273 = 703 °A and M = 106, the maximum temperature and the minimum atomic mass number in equation (3.2), the maximum possible oven half-width of a hyperfine structure component of $\lambda 3261$ A° is

$\Delta V_{a} = 0.066 \text{ cm}^{-1}$

For the atomic beam light source used in this experiment the following values were obtained, l = 1.339, 0 = 0.154, s = 0.867,

d = 3.8, and h - d = 9.5 inches. From equations (3.5) and (3.6)

 $C_{geom} = 18.6$ and $C_{exp} = 16.1$

The value of C_{exp} is smaller than C_{geom} . This can be explained by the scattering of the cadmium atoms from the walls of the source, the lips of the slit and from the gun. The scattering of the cadmium atoms causes a slightly larger \pounds in equation (3.6) than would be expected on theoretical grounds and consequently a smaller C_{exp} .

The half-width of a hyperfine structure component of λ 3261 A^O emitted from the source, from equation (3.7) is

 $\Delta Y_{\rm B} = 0.0017 \text{ cm}^{-1}.$





PLATE 1. ATOMIC BEAM LIGHT SOURCE



PLATE 2. OPTICAL APPARATUS

CHAPTER IV

THE OPTICAL SYSTEM

4.1 Theory

The Fabry-Perot interferometer is a high resolution instrument consisting of two p**arallel** optical flats separated by a fixed spacer. The theory of the Fabry-Perot interferometer is discussed by Tolansky, Williams, and Kopfermann. The essential results are summarized here.

Concentric interference fringes are formed at infinity and are given by the formula

$$n\lambda = 2\mu t \cos \Theta \qquad (4.1)$$

where t is the separation of the partially reflecting coatings

- of the optical flats
- n is the order of the interference
- λ is the wavelength of the incident light
- Mis the refractive index of the medium between the optical flats
- e is the semi-angle of the cone along whose surface the incident light travels

If $d\nu$ is the wave-number change corresponding to the change in order dn, then at or near the centre of the fringe system when moving from one fringe to the next in the adjacent order

$$\Delta V = \frac{1}{2\mu t}$$
(4.2)

where equation (4.1) has been differentiated and dn = 1 and

cos $\theta = 1$, and $d \mathbf{V} \approx \Delta \mathbf{V}$ have been substituted. By varying t the interorder separation can be varied at will. In air the interorder separation $\Delta \mathbf{V}$ is given by $\frac{1}{2t}$.

The intensity distribution in the fringes of a Fabry-Perot interferometer is given by Airy's formula

$$I = I_{0} \frac{T^{2}}{(1 - R)^{2}} \frac{1}{1 + \frac{4R}{(1 - R)^{2}}} \sin^{2} \frac{5}{2}$$
(4.3)

where I is the intensity

I is the intensity in the absence of the interferometer

S is the phase difference between successive beams

R is the reflection coefficient

T is the transmission coefficient

A is the absorption coefficient

Furthermore

$$\mathbf{8} = \left(\frac{2\pi}{\lambda}\right) 2 \,\mu t \cos \theta \tag{4.4}$$

1 1 1

and

$$R+T+A=1 \tag{4.5}$$

The "half-width" b of the fringe is

$$b = \frac{2}{\pi} \sin^{-1} \frac{1}{2} \frac{R}{\sqrt{R}} \approx \frac{1-R}{\pi\sqrt{R}}$$
(4.6)

The theoretical "instrumental width" $\delta \gamma$ of the interferometer is

$$SY=bAV\approx \frac{1-R}{2\pi t \sqrt{R}}$$
 (4.7)

The theoretical resolving power A of the interferometer is

$$A = \frac{\gamma}{s\gamma} = \frac{n}{b} \approx \frac{2t}{\lambda b}$$
(4.8)

As the theoretical resolving power contains λ it is usual to speak of the theoretical resolving limit $\underline{d\gamma}$ of the Fabry-Perot interferometer which is defined as

 $\frac{\mathrm{d} \mathcal{V}}{\mathrm{d} \mathcal{V}} \approx \frac{1}{2 + \frac{1}{N}}$

where N is the "effective number of interfering component beams" and is equal to 1/b, i.e. $\pi\sqrt{R}/1 - R$

(4.9)

It is clear from equations (4.7) and (4.9) that \mathbf{SV} and \underline{dV} are equal.

Airy's formula was derived assuming a monochromatic light source; reflecting planes infinite in extent, exactly parallel, and perfectly plane; and neglecting the small influence of the optical flats on the reflection and absorption coefficients. As these conditions are not met in practice, the theoretical "instrumental width" and hence the theoretical resolving limit can only serve as a lower limit. To find the actual "instrumental halfwidth", the fringes must be photometered. Kuhn¹⁴ reports that the smallest fraction of an order which has been resolved in the red region with silver films is 1/50, while the smallest fraction of an order which has been resolved in the near ultra-violet region with aluminum films is 1/15.

4.2 Experimental Considerations

As the Cd I intercombination resonance line λ 3261 A^o is in the ultra-violet region of the spectrum, all optical apparatus must be of quartz. A Hilger Medium Quartz Spectrograph (*f*/10) was used to isolate λ 3261 A^o from the other spectral lines. The high resolution was supplied by a Fabry-Perot interferometer with crystalline quartz plates. The plates were separated with quartz spacers. The plates were coated with spectroscopically pure aluminum by vacuum evaporation. The Fabry-Perot interferometer was

mounted externally to the spectrograph. (See Plate 2)

Two quartz lenses were also used in the optical arrangement. The focal lengths of the two lenses were 107.5 cm. and 53.5 cm. in the visible. Using the "lensmaker's equation" for a thin lens in air,

$$1/f = (n - 1) K$$
 (4.10)

where f is the focal length of the lens

n is the refractive index of the material of the lens K is a constant depending upon the radii of curvature of the lens

and $n_{5500} = 1.547$ and $n_{3200} = 1.570$, the focal lengths of the lenses at $\lambda 3261 \ A^{\circ}$ were estimated to be 103 cm. and 51.3 cm. The 103 cm. lens was placed so that the excited part of the atomic beam was at the focal point of the lens so that parallel light beams entered the interferometer. The Fabry-Perot fringes were focused on the slit of the spectrograph by the high quality 51.3 cm. lens. The final focussing of the 51.3 cm. lens was made by photographing the very fine off-centre fringes for a series of 1 mm. positionings of the lens, and then selecting the lens position which corresponded to the exposure with the sharpest fringes.

The atomic beam source was carefully positioned on the axis of the spectrograph. The 103 cm. and 51.3 cm. lenses were then properly positioned. Finally the axis of the interferometer was aligned by viewing the fringe system through the spectrograph.

The interferometer plates were adjusted for parallelism by observing the fringes of the mercury green line. The light source was a water-cooled Hg198 discharge tube which produces lines with a small half-width. The green line was isolated with a Wratten No. 77 filter.

The crystalline quartz plates of the interferometer were coated with a film of spectroscopically pure aluminum in the evaporator constructed for this purpose and described by Sutherland¹⁹. Initially several evaporation trials were conducted with glass plates to obtain a plot of transmission in the blue against the time of evaporation t. Evaporator pressures of the order of 10⁻⁵ mm. of Hg were obtained. The transmissions in the blue were measured with a commercial light meter and a blue filter in conjunction with a white light source. After a selection of an appropriate evaporation time, an evaporation was performed for the quartz plates with $p\sim40$ (in units of 10^{-5} mm. of Hg.) and t~0.06 (in minutes) giving pt~2.5. The average transmission of the two films in the blue was measured to be 0.031. From the curves of Burridge et al⁷ $T_{3261} = 0.060$ and $R_{3261} + T_{3261} = 0.916$ giving $R_{3261} = 0.86$. With this reflection coefficient it was estimated that about 1/18 of an order could be resolved. The quantity pt is a measure of the optical quality of the films. The lower the value of pt, the lower is the probability of an impurity atom striking the plates during the evaporation. However, in order to evaporate in a shorter time a higher current must be used

thus increasing the probability of releasing absorbed gases from the vacuum chamber. Films of optimum quality are produced if a proper balance is obtained between these two effects. It has been shown that if $pt\langle 3$ the films are of good optical quality.⁷ The value of pt = 2.5 indicates that the films produced in this experiment are of good optical quality.

Temperature and pressure variations cause displacements of the fringe system through variations of \mathcal{A} in equation (4.1). The interferometer and spectrograph were accordingly housed in a separate room where the temperature variation was controlled to about 0.01°C. by means of an ether-mercury thermostat with an electronic relay connected to several small electric heaters mounted on the walls of the room.⁹ The refractive index of ordinary air is about 1.0003 and \mathcal{A} - 1 is proportional to the density of the air, so that a change in pressure Δp causes a shift in the interference pattern $\Delta \gamma$ given by

$$\Delta Y = 0.0003 \ (\underline{\Delta p})_{p} \ \gamma \ cm^{-1}$$
(4.11)

A rise in pressure of 1 mm. has the same effect as a drop of 0.36° C in the temperature.²⁰ The pressure and temperature must be so controlled that any broadening does not mask the structure which is sought nor introduce an appreciable error through broadening. The temperature in the room was so controlled that the change in temperature of the interferometer was 0.01° C (which corresponds to a change in pressure of less than 0.03 mm.) while the exposures were taken so that the pressure did not fluctuate by more than 0.1 mm. of Hg. Taking p~70 cm. in equation (4.11)

the shift of the fringes in wave numbers is

 $NV = 0.0013 \text{ cm}.^{-1}$

If the temperature effect is taken into account the total shift could not be greater than 0.002 cm.⁻¹ which is much smaller than any of the separations measured.

The Cd I intercombination resonance line λ 3261 A^o was photographed on Eastman 103a - 0 spectroscopic plates with exposure times varying from 10 to 60 minutes.

The collimation of the light beam from the source to the spectrograph depends upon the 51.3 cm. lens. The aperature of the lens system was controlled by a mask placed behind the interferometer. The diameter of the opening in the mask was 4 cm. so that the largest deviation \measuredangle of the light rays from the optical axis is

Then the collimation of the light beam C is

$$C' = \frac{1}{\alpha} \approx 25.6$$

The effective collimation C_{eff} from equation (3.8) is then

$$1/c_{eff} = \frac{1}{16.1} + \frac{1}{25.6}$$

AN)

The half-width of a hyperfine structure component of λ 3261 A^O from the source is then, from equation (3.7),

$$\Delta Y_{\rm B} / 0.066 = 0.41 / 10$$

 $\Delta V_{\rm B} \approx 0.003 \ {\rm cm}^{-1}$

The theoretical "instrumental half-width" of the interferometer is calculated from equation (4.7) for a 5 cm. spacer to be

$$8V \approx 1 - 0.86$$

 $2 \times 5 \times 3.14 \times \sqrt{0.86}$

$$SY \approx 0.005 \text{ cm}^{-1}$$

The half-width of a hyperfine structure component of λ 3261 A^O was estimated by taking the sum of the instrumental half-width and the line-width from the source and was found to be 0.008 cm⁻¹. The actual line widths of the hyperfine structure components of λ 3261 A^O can only be determined from a microphotometer trace of the photographic exposures. These traces could also provide an objective check on the visual measurements of the photographic exposures. However, a microphotometer was not available for this experiment.

CHAPTER V

RESULTS

5.1 Experimental Observations

The hyperfine structure of the Cd I intercombination resonancelline $\lambda 3261 \text{ A}^{\circ}$ was studied with a 5 cm. (4.999 cm.) and a 3 cm. (3.010) spacer. The patterns obtained with the 5 and 3 cm. spaces are shown in Figure 6. The interorder separations for the 5 and 3 cm. spacers are 0.100 cm⁻¹ and 0.166 cm⁻¹ respectively. Since the average magnetic splitting of the strong (s) and weak (w) components of the odd isotopes is 0.214 cm⁻¹ (from Brix and Steudel⁶), these components are overlapped one order in the patterns. Thus the weak components are properly associated with the evens in the next order on the low frequency side while the strong components are properly associated with the evens in the next order on the high frequency side.

The components due to 116, 114, 112 and 110 were clearly resolved with the 5 cm. spacer. The positions of 1135, 111w and 1115 + 113w were determined with the 5 cm. spacer. The position of 111s relative to 113s was determined with the 3 cm. spacer so that the position of 113w can be determined by a centre of gravity calculation. The measurements for 110, 112, 114, and 116 for the 3 cm. spacer were rejected as these components were not clearly resolved and because 111w and 113 w were superimposed on the even components. The relative position of 106 was determined with the





√ XIO⁻³ CM⁻¹

3000

POSITION OF THE ODD ISOTOPES IN C dI 入 3261A°

FIGURE - 7

3 cm. spacer. It was thought that 108 was observed with the 3 cm. spacer but because of its low percentage abundance no conclusive evidence was obtained as to its position.

Some twenty exposures with each spacer were measured five times with a comparator by each of two observers and the results averaged. The relative separations of the components were calculated from these measurements by the on-centre "rectangular array" method of reduction described by Tolansky.²⁰ The average values of these relative separations together with their probable errors are listed in column 4 of Table 2.

Table 2. Relative Separations of the H. F. S. Components of λ 3261 A^O (5s² 1S₀ - 5s5p ³P₁)

Isotope Pair	Number of Fringes Measured	Etalon Spacer (cm.)	Separation (x10 ⁻³ cm ⁻¹)	Overlap Correction (xlo cm)	Corrected Separation (x10 ⁻³ cm ⁻¹)
116,114	81	5	9.1±0.3	+0.2	9.3 ± 0.3
114,112	301	5	13.5±0.4		13.5 ± 0.4
112,110	98	5	16.3 ± 0.5		16.3 ± 0.5
112,113s	88	5	26.0±0.4	+ 0.1	26.1 ± 0.4
112,111w	69	5	51.3 ± 0.4	+0.2	51.5 ± 0.4
112,113w+111s	69	5	44.0±0.4		44.0 ±0.4
112,106	24	3	51.7±1.7		51.7 ± 1.7
113s,111s	164	3	19.8±0.3		19.8±0.3

Theoretical intensity curves were plotted so that the pulls of the closely spaced components could be estimated. The corrections are given in column 5 of Table 2 while the corrected separations are listed in column 6.

5.2 Isotope Shift In λ 3261 A^o

The isotope shifts of the even isotopes in λ 3261 A^o are given directly in column 6, Table 2, and are indicated in Figure 8.



The isotope shifts of the odd isotopes in $\lambda 3261 \text{ A}^{\circ}$ are given by their centres of gravity which can be calculated using the data of column 6, Table 2. As the strong and weak components of the odd isotopes in the patterns (see Figure 6) are properly associated with the evens in the adjacent orders, the positions of the components which are properly associated with these evens must be calculated first. Thus

	$\Delta \gamma$ (112,111w) = 100 + 51.5 = 151.5 ± 0.4
and	$\Delta\gamma$ (112,111s) = $\Delta\gamma$ (112,113s) - $\Delta\gamma$ (113s,111s)
SO	ΔV (112,111s) = (100 - 26.1) - 19.8 = 54.1±0.7
Therefore	$\Delta \gamma$ (111w,111s) = 205.6±1.1 x 10 ⁻³ cm ⁻¹
Furthermore	ΔV (112,113s) = 100 - 26.1 = 73.9 ± 0.4
And	$\Delta \gamma$ (112,113w + 111s) = 44.0 ± 0.4
Also	$\Delta \gamma$ (112,111s) = $\Delta \gamma$ (112,113s) + $\Delta \gamma$ (111s,113s)
So	$\Delta \gamma$ (112,111s) = 26.1 + 19.8 = 45.9 ± 0.7

Therefore llls is 1.9 ± 1.1 on the high frequency side of the centre of gravity of ll3w + llls. The position x of ll3w is obtained by a centre of gravity calculation, weighting llls and ll3w according to the known relative abundances and statistical weights,

$2/3 \times 12.8 \times 1.9 = 1/3 \times 12.3 \times X$

Therefore $X = 3.9 \pm 2.3$ on the low frequency side of the centre of gravity of $113w \pm 111s$ and so 113w is 40.1 on the high frequency side of 112. Then $\Delta Y (112,113w) = 140.1 \pm 2.7$ and finally

 $\Delta \gamma$ (113w,113s) = 214.0 ± 3.1 x 10⁻³ cm⁻¹

The two separations $\Delta \gamma$ (lllw,llls) and $\Delta \gamma$ (ll3w,ll3s) give the magnetic hyperfine structure splittings of the two odd isotopes of cadmium. (See Figure 7).

The po	sitions of the centres of gravity of the odd iso-
topes can now	be determined using equation (1.13). Thus the
interval facto	rs are $A_{113} = 142.7 \pm 2.1$ and $A_{111} = 137.1 \pm 0.7$
Then $\Delta \mathcal{V}(c.$	g. 113,113s) = ¹ 2A ₁₁₃ = 71.3±1.1
But ΔY (11	2,113s) = 73.9±0.4
So <u>AY(11</u>	2, c. of g. 113) = $2.6 \pm 1.5 \times 10^{-3} \text{ cm}^{-1}$
Furthermore	ΔV(c.g. 111,111w) = 137.1±0.7
And	$\Delta \gamma$ (112,111w) = 151.5 ± 0.4
Therefore	Δγ(c. of g. 111,112) = 14.4±1.1
Or	$\Delta \gamma$ (110, c. of g. 111) = 1.9 \pm 1.6 x 10 ⁻³ cm ⁻¹

Figure 8 shows the isotope shifts in Cd I λ 326l A^O. It is clear from Figure 8 that the isotope shifts of the even isotopes decrease with increasing mass number while the odd isotopes show a pronounced even-odd staggering (the atomic number of cadmium is 48), that is the centroids of the odd isotopes lie closer to the next even isotope with the smaller mass number.

5.3 Relative Isotope Shifts

The isotope shift in λ 3261 A^O is due to the mass effect and the field or volume effect. The shifts can be corrected for the normal mass effect with equation (1.2). The corrected shifts are given in column 4, Table 3.

Table of	•				
Isotope	Shifts	<u>In λ3261 A</u>	Corrected Fo	or The Norma.	L Mass Effect.
Isotope	Pair	Uncorrecte Shift (x 10 ⁻³ cm ⁻	d Normal Effect (x 10	Mass C cm ^{-l}) (x	orrected Isotope nift ₃ cm ⁻¹)
116,114		9.3±0.4	+ 2.5	5	11.8±0.4
114,112		13.5 ± 0.4	+ 2.6	5	16.1±0.4
112.110		16.3 ± 0.5	+ 2.7	, .	19.0±0.5
110,106		35,4±2,2	+ 5.4	<u> </u>	40.8±2.2
113,111		17.0 + 2.6	+2.7		19.7 ± 2.6

The corrected isotope shifts are then due to any residual specific mass effect and the field or volume effect. The relative isotope shifts corrected for the normal mass effect in λ 3261 A^O are compared with the corresponding ratios determined by Kuhn and Ramsden¹³ for λ 4416Åin Table 4 and Figure 9. The isotope shift of the pair 110,112 has been taken as unity in both cases.

Table 4.	Comparison of Rel	ative Isotope Shifts
Isotope Pair	Re	elative Isotope Shift
	In 23261 A	In λ4416Å
(106,110) <u>늘</u> 106,1 08 108,110	1.07	1.04 1.07 1.00
110,112 1 11,113 112,114 114,116	1.00 1.04 0.85 0.62	1.00 1.03 0.93 0.65

A comparison of the relative isotope shifts corrected for the normal mass effect for two different spectral lines having different electron configurations should give an indication of the effect of any residual specific mass effect on the relative isotope shifts since the field or volume effect should be

44

Doblo 3





RELATIVE ISOTOPE SHIFTS FOR CdII λ4416A° (KUHN AND RAMSDEN)



the same for both sets of ratios. The agreement between the two sets of ratios in Table 4 indicates that the effect of any residual specific mass effect on the relative isotope shifts is probably quite small as all the ratios agree within the experimental error except for the isotope pair 112,114. Here the difference in the ratios is 9% whereas the sum of the errors in the two experiments is 7%. This discrepancy may be due to some systematic error in the visual measurements. A systematic error of this sort can sometimes be eliminated using microphotometer traces of the interference patterns rather than visual measurements. However, no microphotometer was available for this experiment.

The main portion of the corrected isotope shifts (see column 4, Table 3) can then be interpreted as a nuclear field or volume effect and can be fitted into the picture of the collective model. The relative isotope shifts in Table 4 and Figure 9 give $C_{exp} \propto \frac{S \alpha'}{SN}^2$ on a relative scale. Much of the change in the isotope shift with neutron number N at constant Z is due to a nuclear deformation α . The change in the relative isotope shift from isotope pair to isotope pair gives $\frac{SC_{exp}}{SN} \propto \frac{SC_{\alpha}}{SN} \propto \frac{S^2(\alpha^2)}{SN^2}$ on a relative scale. From Table 4 and the general features of Figure 9 it is clear that $\frac{SC_{exp}}{SN} \propto \frac{S^2(\alpha^2)}{SN^2}$ is negative in the neutron region N = 58 to N = 68. If a zero deformation is assumed at the "magic" neutron numbers 50 and 82 the negative value of $\frac{S^2(\alpha^2)}{SN^2}$ indicates that the square of the deformation, $\alpha'^2(N)$, reaches a maximum.

Figure 8 shows that the even-odd "staggering" is extremely large in cadmium. The "staggering" effect has been ascribed to a tendency of odd-neutron nuclei (even-odd nuclei) to be less deformed than even-neutron nuclei (even-even nuclei). In terms of the shell model, the even-odd "staggering" in cadmium can be interpreted as a $3s_{\frac{1}{2}}$ neutron only slightly increasing the isotope shift caused by the addition of a pair of $5g_{7/2}$ neutrons.¹³

5.4 Estimation Of The Isotope Shift Constant

Equation (1.5), which is defined for a single s valence electron, is not directly applicable to the $5s^2 \, {}^1S_0$ or $5s5p \, {}^3P_1$ levels because of the screening of the valence electrons. However, if it is assumed that calculations on spectra similar to that of cadmium are transferrable to the spectrum of cadmium, then an estimation of βC_{5s} exp for the ground term of the single valence electron spectrum, Cd II 5s ${}^2S_{\frac{1}{2}}$, can be made.

Following Brix and Steudel⁶, the normal mass effect for the cadmium isotope pair 112,114 from equation (1.1), is 0.0062 cm⁻¹ for the ${}^{1}S_{0}$ level and 0.0036 cm⁻¹ for the ${}^{3}P_{1}$ level of cadmium. In the HeI and Li II spectra, there is no specific mass effect in the ${}^{1}S_{0}$ level but a specific mass effect in the ${}^{3}P_{1}$ term which is roughly one half the magnitude of the normal mass effect and is in the opposite sense to the n.m. effect. Assuming an analogous situation for the corresponding cadmium levels, the total mass effect which is to be applied to the isotope shift for the isotope pair 112,114 in the Cd I λ 3261 A⁰ line is 0.0044

cm⁻¹. The isotope shift for the isotope pair 112,114 is 13.5 x 10^{-3} cm⁻¹ and the corrected shift is 0.0179 cm⁻¹. In the mercury spectrum, which cadmium resembles, the ratio of the corrected isotope shift in the analogous transition (${}^{1}S_{0} - {}^{3}P_{1}$), to β Δ T_s in the ground term of the one electron spectrum, is 0.65.⁶,12 Applying this ratio to the cadmium spectrum, β Δ T_s is 0.0275 cm⁻¹. Using Z₀ = 2, n₀ = 1.794 and $(1 - \frac{dc}{dn}) = 1.16^{-6,19}$ in equation (1.5)

 $\beta c_{5s exp}$ (Cd 112,114) = 34±4 x 10⁻³ cm⁻¹. The error is estimated by allowing an error in the estimated specific mass effect of the same order of magnitude as the estimated specific mass effect in the ³P₁ level of cadmium.

The isotope shift constants of the other isotope pairs are related to $\beta C_{5s exp}$ (Cd 112,114) as the relative isotope shifts.

5.5 Ratio Of The Nuclear Magnetic Moments

The calculation of the actual value of a nuclear magnetic moment from spectroscopic measurements involves theoretical difficulaties. The ratios of the nuclear magnetic moments of the isotopes of an element, however, can be determined much more accurately from the direct measurements of the magnetic hyperfine structure splittings. From equations (1.11) and (1.13) and the fact that the interval factor is proportional to the nuclear gyromagnetic ratio (See equation (1.16)), the ratio of the nuclear

magnetic moments are proportional to the ratio of the magnetic hyperfine structure splittings.

In section 5.2 the magnetic hyperfine structure splittings of the odd isotopes of cadmium were calculated to be

 $\Delta \gamma (113 \text{w}, 113 \text{s}) = 214.0 \pm 3.1 \times 10^{-3} \text{ cm}^{-1}$ $\Delta \gamma (111 \text{w}, 111 \text{s}) = 205.6 \pm 1.1 \times 10^{-3} \text{ cm}^{-1}.$

Consequently,

 $\mathcal{M}_{113}/\mathcal{M}_{111} = 1.041 \pm 0.021$

The accuaracy of this experiment can be checked by a comparison of the ratio of the nuclear magnetic moments as determined optically in this experiment with the ratio determined by the more accurate nuclear induction method. The ratio $\mathcal{M}_{113}/\mathcal{M}_{111} = 1.041 \pm 0.021$ determined in this experiment is in good agreement with Proctor and Yu's¹⁶ nuclear induction value of $\mathcal{M}_{113}/\mathcal{M}_{111} = 1.0461 \pm 0.0001$.

5.6 Estimation Of The Nuclear Magnetic Moments

The interval factor for the ${}^{3}P_{1}$ level can be calculated from the intermediate coupling equation (1.16).

The relevant term values for cadmium as given by Bacher and Goudsmit¹ are

5s5p		28846.6	cm ⁻¹
əsəp	2 ⁴ 2	40711.5	
	³ P ₁	41882.6	
	Sp- o	42424.5	

From equation (1.21) (ψ , the deviation from Russell-Saunders coupling is 2° 42. From equation (1.20), $\psi_0 = 35^{\circ} 16$. Therefore

 $C_1 = 0.5383$ and $C_2 = 0.8428$ from equation (1.19). Thus equation (1.16) becomes

 $A({}^{3}P_{1}) = \frac{1}{4}(1.130 a_{s} + 1.450 a + 1.420 a' + 2.566 a'')$ $a_{5s} = 0.4186 g_{I}$ from Sutherland.¹⁹ $a' = 0.00686 g_{I}$ and $a'' = 0.04171 g_{I}$ from equation (1.17) $a''' = 0.00216 g_{I}$ from equation (1.18)

Consequently

 $A(^{3}P_{1}) = 0.131 g_{1}$

Using the magnetic hyperfine structure splittings from section 5.2 in equation (1.11) and (1.13)

 $\mathcal{M}_{113} = -0.52 \text{ n.m.}$ $\mathcal{M}_{111} = -0.50 \text{ n.m.}$

These values are about 16% lower than the values given by Proctor and Yu, $^{16} \mathcal{M}_{113} = -0.619$ and $\mathcal{M}_{111} = -0.592$. However, the values of \mathcal{M}_{113} and \mathcal{M}_{111} determined by the intermediate coupling calculation are subject to a number of possible errors. The value of a_{5s} was determined from Cd II data whereas in fact the 5s electron is screened by the 5p electron. For the similar configuration in the Hg I spectrum which resembles the Cd I spectrum, the p electron screens the s electron by about 10%. ¹² Reducing a_{5s} by 10%,

 $\mathcal{U}_{113} = -0.57 \text{ n.m.}$

 $M_{111} = -0.55 \text{ n.m.}$

Allowing 2% for the finite size of the nucleus

 $\mathcal{M}_{113} = -0.58 \pm 0.03$ n.m.

 $\mathcal{U}_{111} = -0.56 \pm 0.03 \text{ n.m.}$

The experimental errors in \mathcal{U}_{113} and \mathcal{U}_{111} were estimated by allowing

a 50% error in the estimate of the screening of the 5s electron by the 5p in addition to the errors in the magnetic hyperfine structure splitting.

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