HYPERFINE STRUCTURE OF ATOMIC COPPER

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C. D. Hause
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HYPERFINE STRUCTURE OF ATOMIC COPPER

By

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A THESIS

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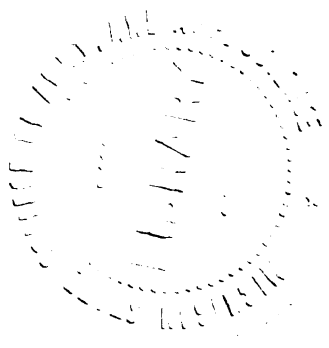

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INTRODUCTION

Since the development of high resolution interferometers of various types by Michelson, Fabry and Perot, and Lummer and Gehrcke it has been found by these original investigators and others that many spectral lines are not single but are made up of a number of components.

It is now known that this hyperfine structure arises either to the presence of isotopes or from elements whose nuclei possess a nuclear spin. Thus investigation of this structure yields valuable information about the nuclei giving rise to the effects.

In this report a brief review of the theory necessary to account for the hyperfine structure of radiation from elements whose nuclei possess spin and quadropole moments will be given. This will be applied specially to copper. Using copper in a hollow-cathode discharge tube in conjunction with a Fabry-Perot interferometer and a constant deviation spectroscope the hyperfine structure of the copper triplet ^2D-^2P has been photographed. The data so obtained will be compared with that of previous investigators.

In addition a technique suitable to allow the use of enriched Cu^{63} in the hollow cathode will be described. The hyperfine structure

patterns of Cu^{63} have been observed visually but not photographed.

GENERAL THEORY OF HYPERFINE STRUCTURE

The hyperfine structure observed when atomic radiation from an appropriate source is examined with high resolution equipment is known to arise from one of two causes: (1) small shifts in the term values due to the presence of isotopes; or (2) splitting of the terms due to the presence of a nuclear spin and moment which interact with the extra nuclear electrons. The first effect is largely due to the mass difference of the isotopes in light elements. In heavier elements nuclear volume effects seem necessary to explain the large shifts observed. Shifts of the order of 0.08 $cm.^{-1}$ are (Ref.)[7] observed in the radiation from Cu^{63} and Cu^{65}.

The second effect is of primary concern here. In general hyperfine structure may be due to four types of interaction.

a. Interaction of electron orbit and nuclear spin (orbit spin interaction).

$$V_{oi} = a \vec{L} \cdot \vec{I} \qquad (1)$$

where a is a constant, L and I are orbit and nuclear quantum numbers, with the magnitude of $\sqrt{L(L+1)}\,\frac{h}{2\pi}$ and $\sqrt{I(I+1)}\,\frac{h}{2\pi}$. L takes zero and integral numbers, but I may be integral or half integral.

In order to derive (1) one can consider a field H at the nucleus, produced by the motion of the orbital electron, about which the nuclear magnetic moment precess.

$$\vec{E} = \frac{e}{r^3}\vec{r} \tag{2}$$

$$\vec{H} = \frac{\vec{E}\times\vec{V}}{c} \tag{3}$$

$$\vec{H} = \frac{e}{c}\frac{\vec{r}\times\vec{V}}{r^3} \tag{4}$$

where E is the electric field and r is the distance of electron from nucleus.

From Bohr's relationship

$$m\vec{r}\times\vec{V} = \vec{L}\frac{h}{2\pi} \tag{5}$$

thus

$$\vec{H}_{ar} = \frac{e}{mc}\vec{L}\frac{h}{2\pi}\left(\frac{1}{r^3}\right) \tag{6}$$

where m and e are the mass and charge of the valence electron.

If one represent the magnetic moment of the nucleus by μ the ratio of the magnetic to the mechanical moment will be

$$\frac{\mu_I}{I\frac{h}{2\pi}} = g_I \frac{e}{Mc} \tag{7}$$

where g_I is the nuclear g factor, and M is the proton mass.

From (7)

$$\mu_I = g_I \frac{eh}{4\pi Mc} \vec{I} \tag{8}$$

The potential energy of this nuclear magnetic moment, in the magnetic field which is produced by the electron orbital motion is

$$V_{a1} = \vec{H} \cdot \vec{\mu_I} \tag{9}$$

$$V_{a1} = g_I \left(\frac{eh}{4\pi Mc}\right) 2 \left(\frac{eh}{4\pi mc}\right) \frac{1}{r^3} \vec{L} \cdot \vec{I} \tag{10}$$

According to the definition of nuclear and Bohr magnetons,

$$\mu_N = \frac{eh}{4\pi Mc} \quad , \quad \mu_B = \frac{eh}{4\pi mc}$$

$$V_{a1} = 2 g_I \frac{\mu_N \mu_B}{r^3} \vec{L} \cdot \vec{I}$$

$$\therefore \quad V_{a1} = a \vec{L} \cdot \vec{I} \tag{11}$$

b. Electron spin-nuclear spin interaction.

$$V_{dip} = a\left[\frac{3\vec{I}\cdot\vec{r}\,\vec{S}\cdot\vec{r}}{r^2} - \vec{I}\cdot\vec{S}\right] \tag{12}$$

This term arises because both the electron and the nucleus are like little magnets.

The interaction between two dipoles of magnetic moment μ_I and μ_S is[4]

$$V_{dip} = -\left[\frac{3\vec{\mu_I}\cdot\vec{r}\,\vec{\mu_S}\cdot\vec{r}}{r^5} - \vec{\mu_I}\cdot\vec{\mu_S}\right] \tag{13}$$

The magnetic moment in terms of nuclear and Bohr magnetons are

$$\vec{\mu_I} = g_I \mu_N \vec{I}$$

$$\vec{\mu_S} = -2\mu_B \vec{S}$$

Then (12) becomes

$$V = 2 g_I \frac{\mu_N \mu_B}{r^3}\left[\frac{3\vec{I}\cdot\vec{r}\,\vec{S}\cdot\vec{r}}{r^2} - \vec{I}\cdot\vec{S}\right]$$

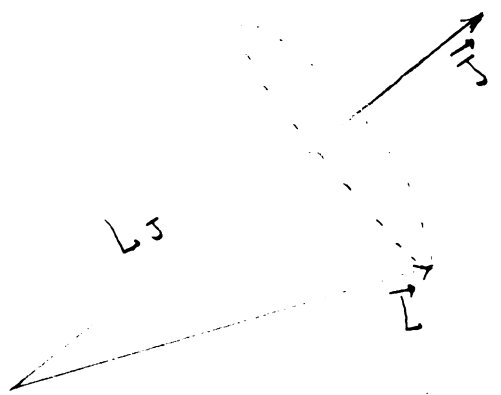
or $$V_{dip} = a\left[\frac{3\vec{I}\cdot\vec{r}\,\vec{S}\cdot\vec{r}}{r^2} - \vec{I}\cdot\vec{S}\right] \tag{14}$$

These interactions (a) and (b) may be combined and written in the following simplified form:

$$V = a_J \vec{I} \cdot \vec{J}$$

where J is a good quantum number.

This equation can be obtained as follows: It is known that the quantum mechanical average of a vector L in the direction of another vector suppose J is just the component of L along J if L precesses about J.



From the diagram, the magnetude of the component of L along J is $\vec{L}_J = \frac{\vec{L} \cdot \vec{J}}{|J|}$ and since the unit vector along J is $\frac{\vec{J}}{|J|}$ then $\langle \vec{L} \rangle_{av} = \frac{\vec{L} \cdot \vec{J}}{J(J+1)} \vec{J}$ where J^2 has been replaced by $J(J+1)$; i.e.,

$$\langle \vec{L} \rangle_{av} = \frac{\vec{L} \cdot \vec{J}}{J^2} \vec{J}$$

$$\therefore \quad a\vec{L}\cdot\vec{I} = \frac{\vec{L}\cdot\vec{J}}{J(J+1)}\,\vec{J}\cdot\vec{I}$$

This reduced to:

$$aL\cdot I = \frac{a}{2J(J+1)}\left[J(J+1) + L(L+1) - S(S+1)\right] I\cdot J \tag{15}$$

Bethe (Ref.) shows that (12) reduces to the form:

$$V_{dix} = \frac{-1}{(2L+3)(2L-1)J(J+1)}\left[\frac{3}{2}\left\{J(J+1) - L(L+1) - S(S+1)\right\}\right.$$

$$\left.\left\{J(J+1) + L(L+1) - S(S+1)\right\} - L(L+1)\left\{J(J+1) + S(S+1) - L(L+1)\right\}\right]\vec{I}\cdot\vec{J} \tag{16}$$

and hence the total interaction, V_{total}, is

$$V_{Tot} = a_J\,\vec{I}\cdot\vec{J} \tag{17}$$

where

$$a_J = \frac{a}{2J(J+1)}\left[J(J+1) + L(L+1) - S(S+1)\right] - \frac{a}{(2L+3)(2L-1)J(J+1)}$$

$$\left[\frac{3}{2}\left\{J(J+1) - L(L+1) - S(S+1)\right\}\left\{J(J+1) + L(L+1) - S(S+1)\right\} - L(L+1)\right.$$

$$\left.\left\{J(J+1) + S(S+1) - L(L+1)\right\}\right]$$

c. There is another term in the interaction potential which was discovered by Abrahm (Ref.) and Carr independently. It is of the form

$$V_3 = a_3 \vec{I} \cdot \vec{S}$$

It is of importance if the state concerned is an S state or contains an appreciable admixture of an S state. Following the previous method:

$$\vec{S}_{av} = \frac{\vec{S} \cdot \vec{J}}{J(J+1)} \vec{J}$$

$$a_3 = \vec{I} \cdot \vec{S} = \frac{a_3}{2J(J+1)} \left[J(J+1) + S(S+1) - L(L+1) \right] \vec{J} \cdot \vec{I} \qquad (18)$$

d. In addition to the above interaction some nuclei possess an electric quadripole moment which gives rise to an unsymmetrical shift of term values. The equation for this effect is (Ref. 7):

$$\Delta V = -e^2 \mathcal{Q}_K \frac{\frac{3}{8} C_{ij} \theta_e - 1}{2^3_e} \qquad \frac{\left[\frac{3}{8} K(K+1) - \frac{1}{2} I J(J+1)(J+1) \right]}{I(2I-1)(2J-1)} \qquad (19)$$

where $K = F(F+1) - I(I+1) - J(J+1)$; = quadripole moment.

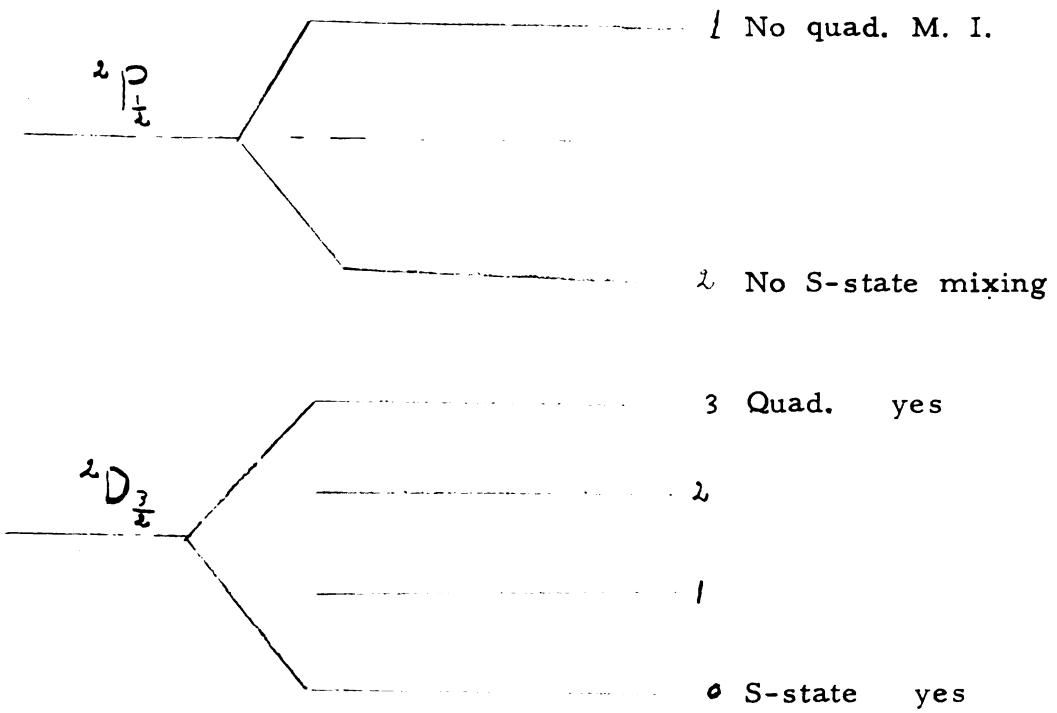
TABLE I

for	$J = \ell + \frac{1}{2}$	$J = \ell - \frac{1}{2}$
$3\overline{\cos^2\theta_e} - 1$	$-\frac{2\ell}{2\ell+3}$	$\frac{2(\ell-1)}{2\ell+1}$

Now if one calculate $3\overline{\cos^2\theta_e} - 1$ for $^2P_{\frac{1}{2}}$ where $\ell = 1$

$$3\overline{\cos^2\theta_e} - 1 = -\frac{2(\ell-1)}{2\ell+1} = 0$$

There is no quadripole moment interaction term in $^2P_{\frac{1}{2}}$. This interaction might exist in some other case. Suppose it does exist in case of $^2D_{\frac{3}{2}}$.



HYPERFINE STRUCTURE OF Cu^{63}

As an example of the above interactions the term values and resultant Hfs patterns for the ^2P-^2D transition in Cu^{63} will be calculated.

Cu^{63} is known to have a spin $I = \frac{3}{2}$ and a quadripole moment. The possibility of configuration mixing will be considered later. That is interaction (c) will be omitted.

The term values may be obtained from the equation

$$T_F = T_J + \frac{a}{2} K + bK(K+1)$$

where b is the quadripole term $b = -\frac{3}{8} e^2 \frac{3\cos^2\theta_e - 1}{z_e^3} \frac{Q_K}{I(2I-1)J(2J-1)}$

$$K = F(F+1) - I(I+1) - J(J+1)$$

The quadripole term is zero for the $^2P_{\frac{1}{2}}$ term and negligible for $^2P_{\frac{3}{2}}$ The term values are listed in Table II.

In hyperfine structure I takes only one value. It is either half or whole integral. F takes values differing by unity from each other. If $I \geq J$ the variation of F is between $I - J$ to $I + J$ and if $J \geq I$ the variation will be from $J - I$ to $J + I$. Selection rule for the transition is

$$\Delta F = \pm 1, 0$$

$0 \not\rightarrow 0$

forbidden.

The relative intensities of the hyperfine structure multiples may be obtained from White (Ref.). The energy levels, transitions, and resultant patterns for copper 63 are shown in Figure 1. The ^2P and ^2D levels are drawn to different scales. The line patterns were obtained by using data for the "a's" and "b" taken from the work of Schuler and Schmitt.

TABLE II

Terms	F	K	K(K + 1)	(a/2)K + bK(K + 1)
$^2P_{1/2}$	2	3/2	15/4	$3a_1/4 + 15b_1/4$
	1	-5/2	15/4	$-5a_1/4 + 15b_1/4$
$^2P_{3/2}$	3	9/2	99/4	$9a_2/4 + 99b_2/4$
	2	-3/2	3/4	$-3a_2/4 + 3b_2/4$
	1	-1/2	99/4	$-11a_2/4 + 99b_2/4$
	0	-15/2	195/4	$-15a_2/4 + 195b_2/4$
$^2D_{3/2}$	3	9/2	99/4	$9a_3/4 + 99b_3/4$
	2	-3/2	3/4	$-3a_3/4 + 3b_3/4$
	1	-11/2	99/4	$-11a_3/4 + 99b_3/4$
	0	-15/2	195/4	$-15a_3/4 + 195b_3/4$
$^2D_{5/2}$	4	15/2	255/4	$15a_4/4 + 255b_4/4$
	3	-1/2	-1/4	$-1a_4/4 - 1b_4/4$
	2	-13/2	143/4	$-13a_4/4 + 143b_4/4$
	1	-21/2	399/4	$-21a_4/4 + 399b_4/4$

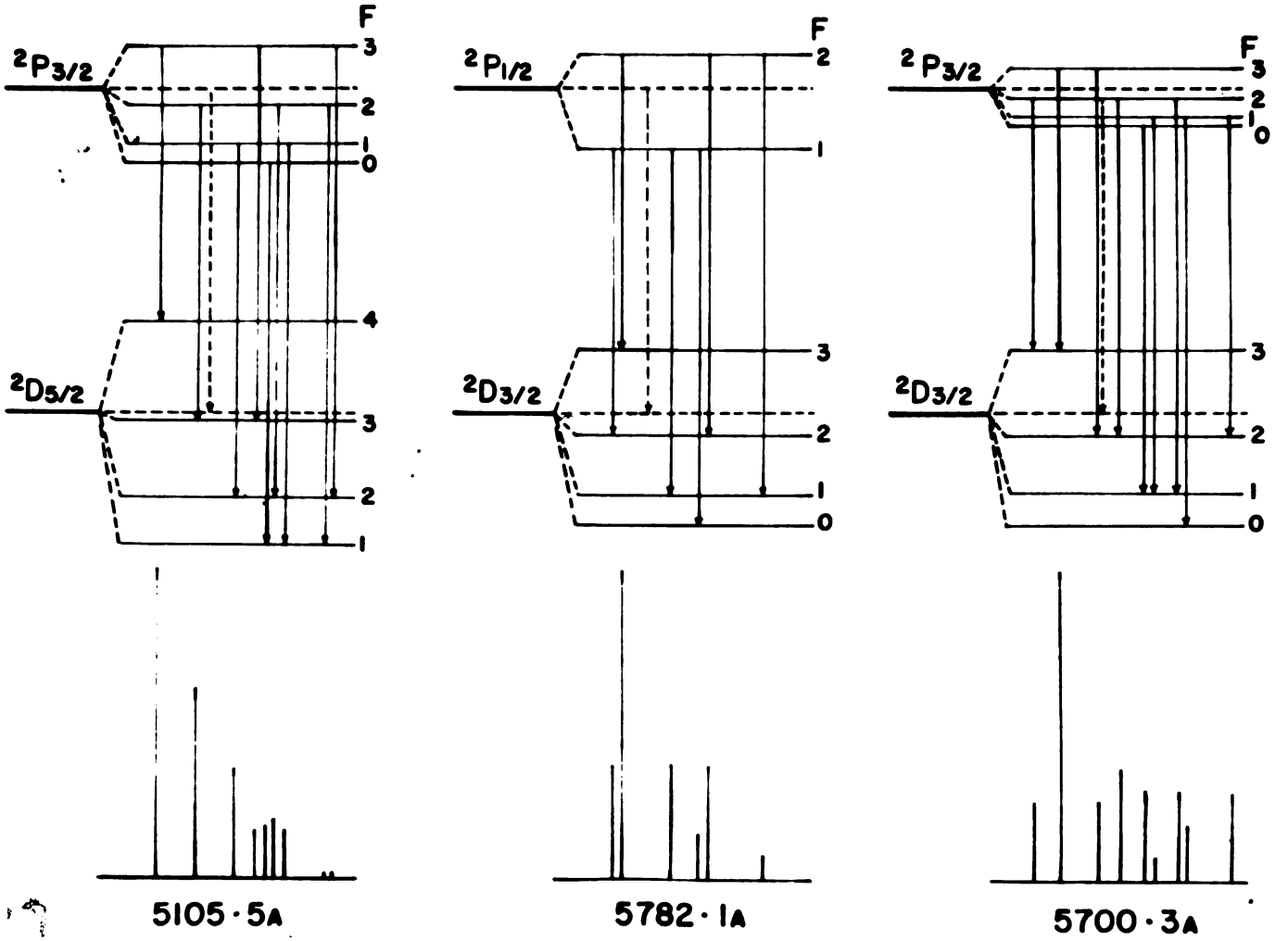

F
$^2P_{3/2}$
3
2
1
0
4
$^2D_{5/2}$
3
2
1
5105·5A
F
$^2P_{1/2}$
2
1
3
$^2D_{3/2}$
2
1
0
5782·1A
F
$^2P_{3/2}$
3
2
1
0
3
$^2D_{3/2}$
2
1
0
5700·3A

Figure 1

GENERAL EXPERIMENTAL PROCEDURE

The Source

In order to excite the copper radiation a hollow cathode discharge tube was used. This system was designed and built by McBryde (Ref.) and with some variations is similar to that used by Arroe and Mack (Ref.). A picture of the discharge tube and associated optical equipment appears in Figure 2.

Since drastic cooling is employed, liquid nitrogen is used for best operation, the main body of the tube is of monel metal. Within this body is a glass tube closed at the upper and by a quartz observation window. Within the glass tube is suspended an aluminum anode. A hollow cathode of the desired metal is placed in the removable base. The base is sealed to the monel tube with a compressed fuse wire ring. The hollow cathode is so designed that its interior is continuously bathed with argon which flows slowly through the system the pressure being maintained at about 2 mm of Hg. The argon flow is controlled by adjustable leak valves placed both ahead and beyond the discharge tube. Additional control is obtained with a large glass flask for ballast beyond the second leak valve and immediately preceding the vacuum pump.

The necessary power for operation was supplied by a 2300 volts 1.2 KW filtered full wave rectifier. A ballast resistance of 2700 ohms was placed in series with the discharge tube. No difficulty in operation was experienced when the system was free of leaks and the hollow cathode properly sealed in its base. With copper cathodes brilliant hollow cathode discharges were obtained with tube currents as low as 100 ma.

Optical Equipment

For high resolution a quartz Fabry-Perot interferometer was crossed with a higher constant deviation glass spectroscope. The interferometer plates and separators were quartz. The plates were aluminized to give a high reflecting power and resultant resolution. Separators of 15 and 30 mm were available.

Before use, the interferometer was carefully adjusted for parallelism with a low pressure mercury arc filtered to give the mercury green line (5461 A). This may be done visually with high precision by scanning the field from a distance of 1 to 2 meters.

With the source in operation the fringe patterns were first focused carefully visually with the spectroscope and then photographed with a plate camera, the camera lens being placed adjacent to the

spectrometer eyepiece. Focusing was completed by viewing the fringes and the illuminated pointer in the spectrometer on the camera ground glass plate with an eyepiece. For the final pictures Kodak film was used. With this film, and tube currents of 150 ma the intensities were such that suitable exposures of the 5105 copper line could be obtained with 5 minute exposures. The 5782, and 5700 lines required 15 minutes.

The interferometer plates were slightly inclined to the axis of the spectrometer such that the center of the interference pattern appeared at the top of the field. The photographs were analyzed by measuring the fringe separations with a comparator (least count 0.001 mm.). Using these measured separations the components were calculated, using the method discussed in Tolawsky (Ref.) for off-center Fabry-Perot fringes.

With the 15 mm separator (actually 15.037 mm), the spectral range (wave number separation of successive orders) was 0.333 cm^{-1}.

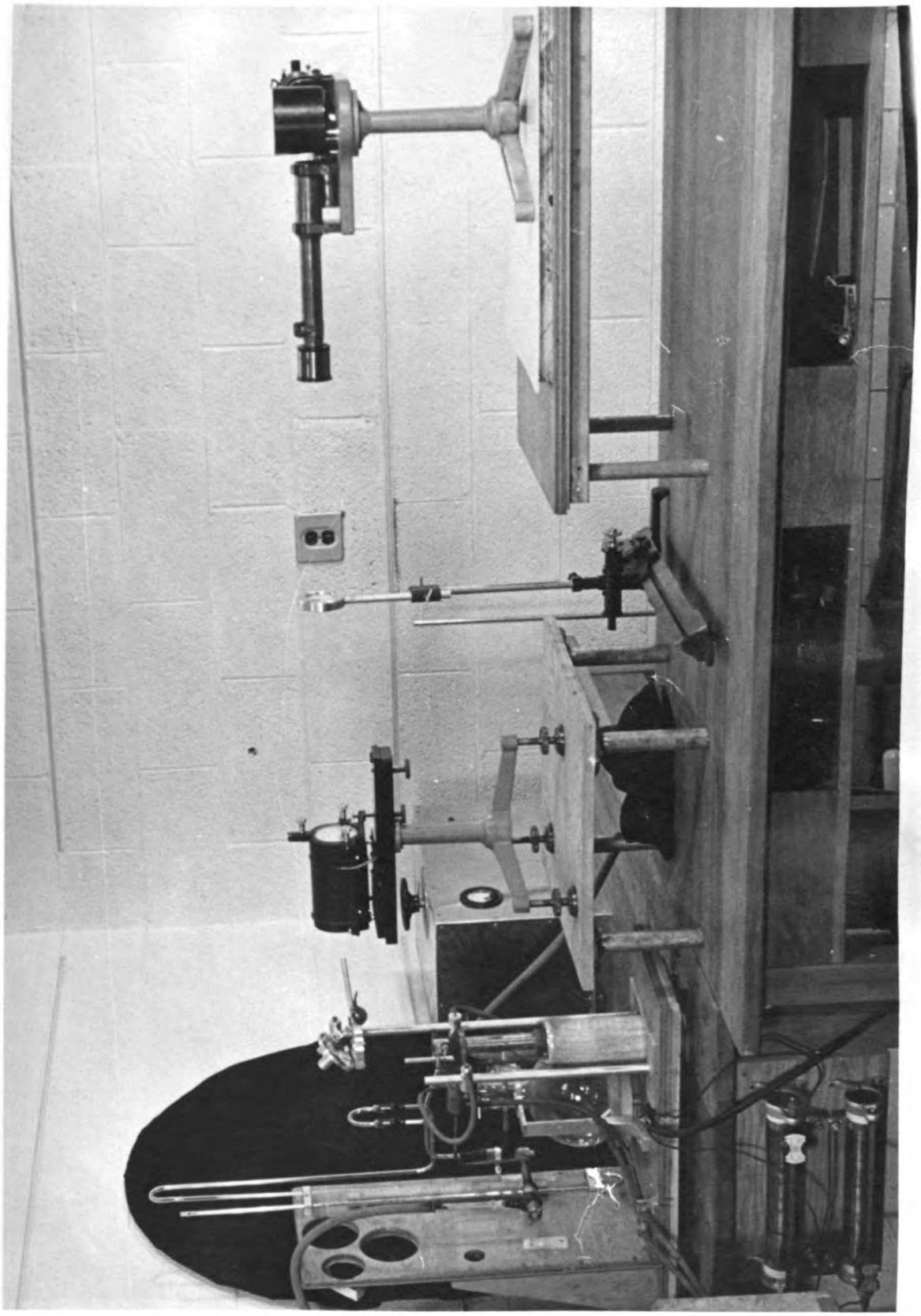


Figure 2a

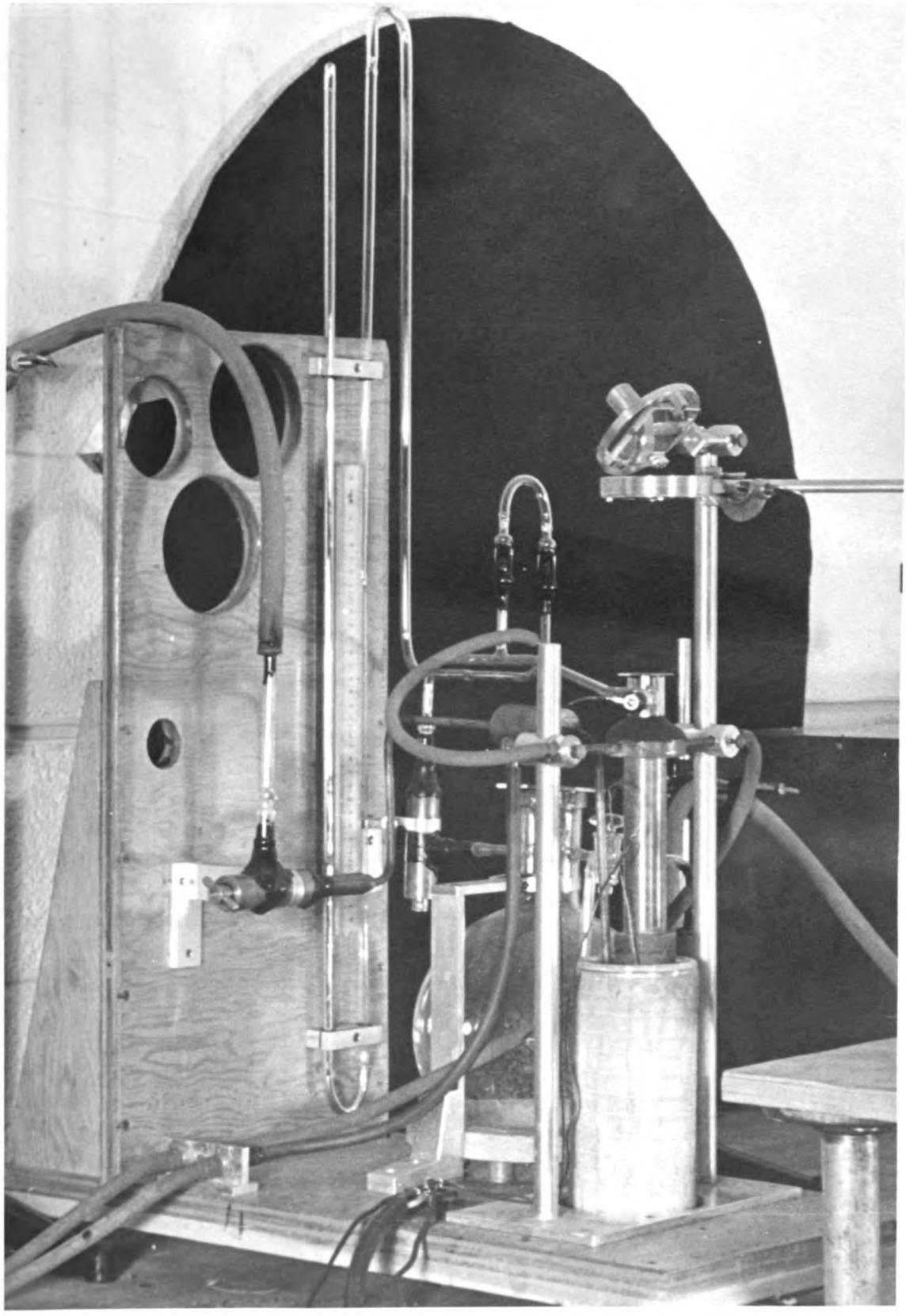


Figure 2b

PROCEDURE WITH ENRICHED Cu^{63}

In order to obtain the radiation of an element in the hollow cathode either the cathode is made of that element or is coated with it. Thus with proper design quite small amounts of materials can be investigated.

Copper is a mixture of two isotopes 63 and 65. Each isotope has a similar spin of 3/2 and shows similar hyperfine structure patterns with a slight relative shift. It seemed worthwhile therefore to obtain a sample of enriched Cu^{63} and attempt to obtain the structure of the single isotope.

A small amount (100 mg) of Cu^{63} (98.2% pure) was loaned by the Stable Isotopes Branch of the Atomic Energy Commission for experimental purposes. This was in the form of CuO and a special procedure was necessary to use it.

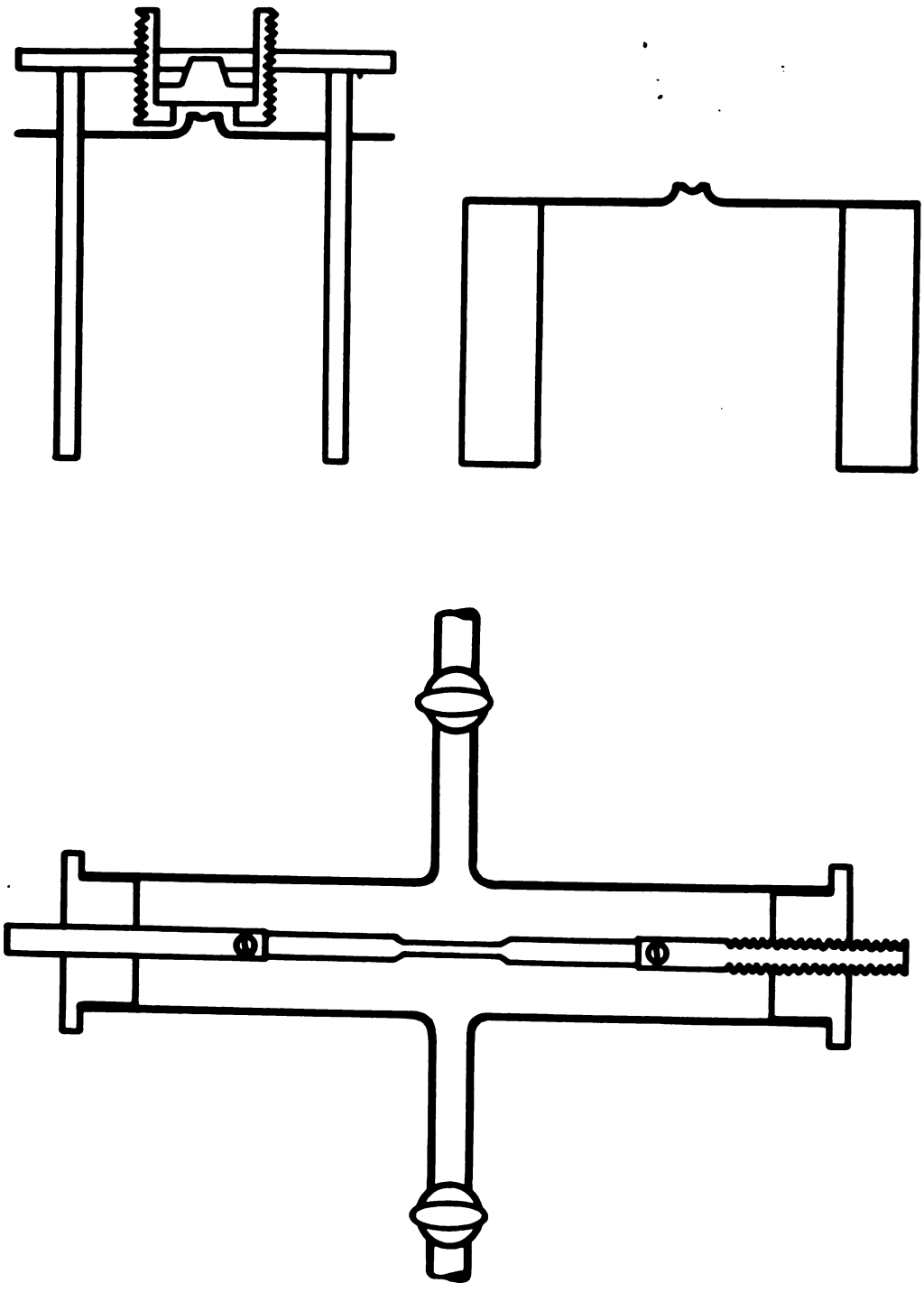
Since excitation in the hollow cathode depends upon the sputtering action of the rare gas and aluminum is difficult to sputter a hollow cathode of aluminum was constructed and then coated with copper.

To do this the CuO was first reduced to Cu by heating the oxide in an atmosphere of hydrogen. A molybdenum boat with the

CuO was sealed in a glass tube and evacuated. Hydrogen was introduced to about half an atmosphere of pressure and the boat heated electrically until reduction was complete. The arrangement is shown in Figure 3a.

After reduction the resultant copper was placed on a molybdenum ribbon in an evaporator and evaporated under high vacuum into the aluminum hollow cathode.

In order to conserve the copper a special form of molybdenum ribbon and cathode holder was constructed. These are shown in Figure 3b. This method insured that at least 90 per cent of the copper will enter directly into the hollow cathode.



Figures 3a and 3b

RESULTS

Using ordinary copper as the hollow cathode the three copper lines have been photographed with tap water, dry ice and acetone, and liquid nitrogen as coolants, respectively. Prints of the negatives appear in Figure 4. The patterns taken with liquid nitrogen as coolant have been carefully measured and reduced.

A comparison of these results with those of previous investigators is shown in Figure 5. The agreement with the work of Schuler and Schmidt seems to be as good as can be expected. However, in the case of the 5105 line the variation from the results of Ritschl is larger than can be accounted for by experimental error.

There seems to be little doubt of the reality of this variation. All the patterns were taken with the same interferometer, one after the other with short exposures. It would seem, therefore, that adjustment errors giving rise to variations would be present in all three patterns. Yet the agreement is good for the 5700 and 5782 lines.

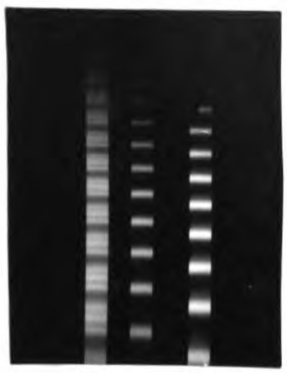
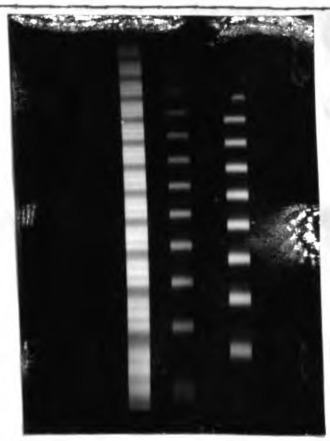
If we accept these results the isotope shift is more nearly $0.080\ cm^{-1}$ in 5105 than 0.085 as given by Ritschl. In addition the interaction constant "a" for $^2D_{5/2}$ becomes $0.024\ cm^{-1}$ rather than

0.022 cm^{-1} as given by Ritschl (due to neglect of a splitting factor in the $^2P_{3/2}$ state this is in error and should be 0.025 cm^{-1}).

This change in the constant removes a discrepancy which has been present in the ratio of the constants for the $^2D_{3/2}$ and $^2D_{5/2}$ states and essentially rules out any measurable shift due to admixture of an S state.

Hyperfine structure patterns with enriched Cu^{63} have been observed visually. With the small amounts available the lines were very weak and could not be photographed with the present system. It was therefore decided that this should be abandoned until a faster spectrograph was available.

Figure 4

Coolants	5100 A	5700 A and 5782 A
Water		
Dry Ice and Acetone		
Liquid Nitrogen		

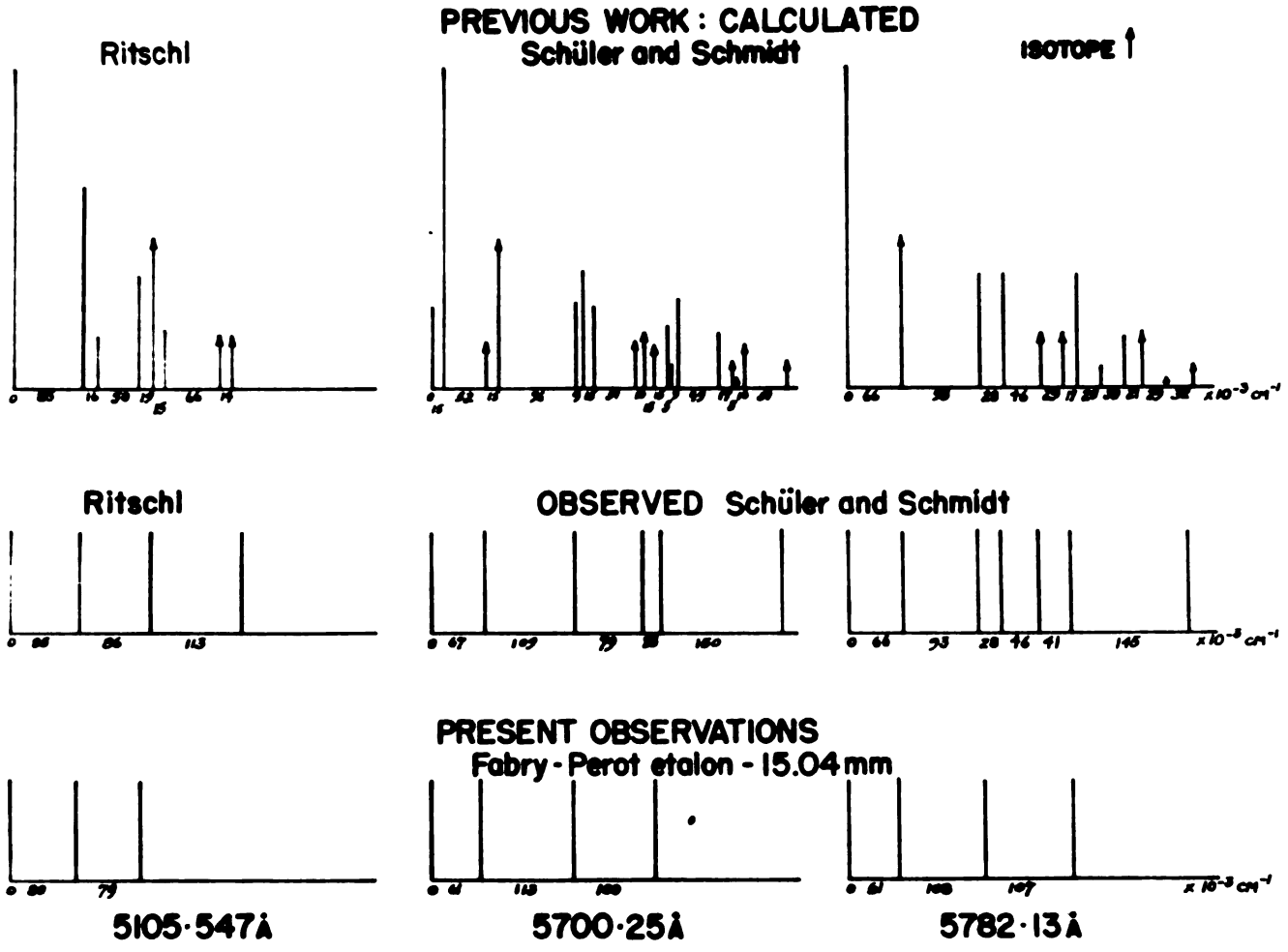

PREVIOUS WORK : CALCULATED
Ritschl
Schüler and Schmidt
ISOTOPE
Ritschl
OBSERVED Schüler and Schmidt
PRESENT OBSERVATIONS
Fabry - Perot etalon - 15.04 mm
5105·547Å
5700·25Å
5782·13Å

FIGURE 5

CONCLUSIONS

1. The theory of hyperfine structure has been discussed briefly.

2. Using the Fabry and Perot interferometer with a 15 mm separator, three components of the 5100.5 A. line are resolved. In 5782 A and 5700 A four components are sufficiently well resolved to allow measurements.

3. Comparison of this work with results of Ritschl and Schuler and Schmidt indicates a variation in the 5105 line and gives a different value for the isotope shift and the interaction constant.

4. The procedure for using the small sample in the hollow cathode is satisfactory. Using Cu^{63} the hyperfine structure for ^2P-^2D lines has been observed but not photographed.

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