

Fine-structure measurements in the 6^2F and 7^2F states of rubidium by radio-frequency spectroscopy*

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We have used radio-frequency spectroscopy in conjunction with a multistep optical excitation scheme involving a cw dye laser to measure the fine-structure intervals in the 6^2F and 7^2F states of Rb. We find that the fine-structure intervals δw (in MHz) are $\delta w(6^2F) = -486(4)$ and $\delta w(7^2F) = -347.6(10)$.

I. INTRODUCTION

It has been known for quite some time that there are peculiar anomalies in the fine structures of the D and F states of alkali metal atoms.¹ Recently, similar anomalies have been discovered in the hyperfine structure of the D states of rubidium and cesium.²⁻⁴ There has been a resurgence of interest in the measurement⁵⁻¹⁶ and calculation¹⁷⁻¹⁹ of fine-structure intervals in these states, particularly in sodium. Gallagher *et al.* have measured fine-structure intervals in the F states¹⁴ and G and H states¹⁶ of sodium and have found them to be normal. On the other hand, the F states of heavy alkali atoms (rubidium and cesium) are known to have inverted fine structures.¹ Although the inversion of these states is known from conventional spectroscopy, the magnitudes are very poorly known. In this paper, we report first precision measurements of the fine structure in the (inverted) F states of heavy alkali-metal atoms.

Before we describe our measurements, we would like to briefly discuss the peculiarities of alkali-metal fine structures. The simple Landé formula²⁰ predicts that the fine-structure intervals should be proportional to $1/n^{*3}$ where n^* is the effective principal quantum number of the state. n^* can easily be derived from the measured binding energies.

In Fig. 1, we have plotted fine-structure interval $\delta w \times n^{*3}$ as a function of the principal quantum number n for the D states of alkali atoms. According to the Landé formula $\delta w \times n^{*3}$ should be a constant, independent of n . Although this is true for hydrogen, the fine structures in the D states of Na and K do not even have the right sign.⁵⁻⁷ The heavy alkali metal atoms behave quite differently, however. Except for the first excited D state of rubidium, which is inverted,¹ all other D states have noninverted fine structure. Even though these fine structures are noninverted, their magnitudes are quite small compared to the prediction of Landé formula.

Recently Kato and Stoicheff⁸ have extended these

measurements to very highly excited states of Rb and Curry *et al.*¹³ have reported measurements in the highly excited D states of Cs. It is worth pointing out that $\delta w \times n^{*3}$ is constant, as expected from the Landé formula, for the P states of alkali atoms.

In Fig. 2 we show a similar plot for the F states of the alkali atoms. We would like to point out two important features. Firstly, the fine structures in the F states of light alkali metal atoms are normal while they are inverted in the heavy alkali atoms — in complete contrast to the D -state fine structures. Secondly, the magnitude of the fine-structure intervals in the F states of Rb and Cs are very poorly known. In Fig. 2, we have not shown the error bars on the Rb and Cs data since we are not quite sure about them. These measurements have been made by conventional optical spectroscopy^{21,22} and the quoted *average* uncertainty in the

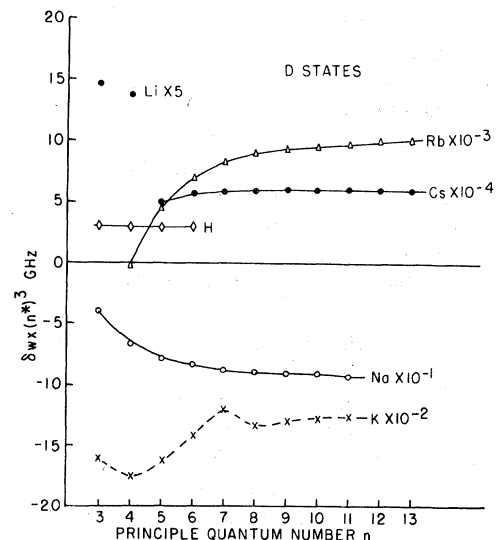


FIG. 1. $\delta w \times (n^*)^3$ is plotted against the principal quantum number n for the D states. Here δw is the fine-structure interval and n^* is the effective principal quantum number. According to the Landé formula $\delta w \times (n^*)^3$ should be a positive constant.

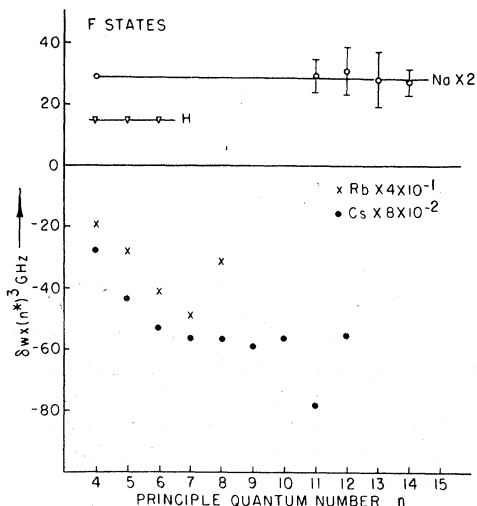


FIG. 2. $\delta w \times (n^*)^3$ is plotted against the principal quantum number n for the F states of hydrogen, sodium, rubidium, and cesium. The data for hydrogen is from Ref. 1, for sodium from Refs. 14 and 15, for rubidium from Ref. 21, and for cesium from Ref. 22. The F -state finite-structure intervals in Rb and Cs are inverted and their magnitudes are very poorly known. We have not put error bars on the data for Rb and Cs as we are not sure about them (see text).

term values are 0.001 cm^{-1} for Cs and 0.01 cm^{-1} for Rb. We believe that the uncertainty in the fine structure (difference between two term values) may be considerably better than 0.01 cm^{-1} for Rb. However, the uncertainty could easily be as much as 100% for some of the states.

When we started our investigation of these states a few years ago, no precision measurement of the F -state fine structure in any alkali metal was available. Although recently Gallagher *et al.*¹⁴ and Liao and Bjorkholm¹⁵ have measured fine structures in the F states of Na, the measurements reported here are the first precision measurements in the more interesting case of the heavy alkali-metal atoms.

It is worth pointing out that the technique that we have used has an advantage over some others that have recently been used^{14,15} in that it measures the frequency intervals of interest directly and not by taking a difference between two relatively large frequencies. Therefore this method gives a relatively precise measurement. Also, it does not use a dye laser in the first excitation step and therefore it is not restricted to sodium and can be used for all alkali metals.

II. METHOD

We populate the n^2F state of Rb by spontaneous decay of the $n'^2D_{5/2}$ state, as shown in Fig. 3. The

$n'^2D_{5/2}$ state is populated by stepwise excitation of the ground-state atoms. The atoms in the ground $5^2S_{1/2}$ state are excited to their first excited $P_{3/2}$ state by a resonance lamp. $5^2P_{3/2}$ state atoms are further excited to the $n'^2D_{5/2}$ state by a cw dye laser. We use circularly polarized laser light to excite the $5^2P_{3/2}$ state atoms and thus produce electronic polarization in the $n'^2D_{5/2}$ state. When some of the $n'^2D_{5/2}$ -state atoms decay to the n^2F state, this electronic polarization is partially carried over to the n^2F states. In this manner we produce nonisotropic population distribution among different m_j sublevels of the n^2F state. The hyperfine structure in these states is unresolved and can be ignored for the purposes of this experiment. We monitor the polarization of the n^2F states by observing the circular polarization of the fluorescent light λ_0 which is emitted in the decay of the n^2F states to the lowest 2D state. A quasistatic longitudinal magnetic field is maintained at the site of the Rb cell. We induce magnetic dipole transitions between a pair of magnetic sublevels whose magnetic quantum numbers differ by one. These transitions tend to equalize the population of that pair of sublevels, resulting in a decrease in the polarization of the n^2F state. We observe these transitions as a change in circular polarization of the fluorescent $n^2F \rightarrow 4^2D$ light. From the frequency of the rf and value of the magnetic field at which we observe the rf transition, we deduce the fine-structure interval as described below.

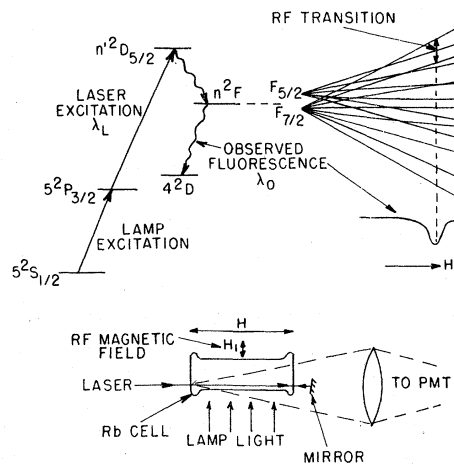


FIG. 3. Schematic illustration of our experimental technique. The Rb atoms in the n^2F states are populated by spontaneous decay of the $n'^2D_{5/2}$ states, which are populated by stepwise excitation of the ground-state atoms. rf transitions, induced among the magnetic sublevels of the n^2F states, are detected as a change in the intensity of the polarized $n^2F \rightarrow 4^2D$ fluorescence. Lower part of the figure shows a sketch of the experimental arrangement.

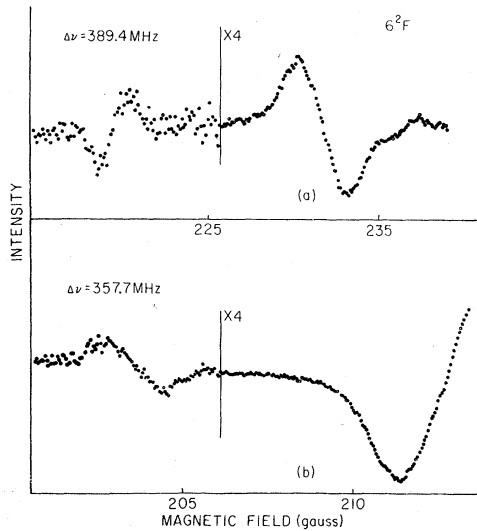


FIG. 4. rf resonances in the 6^2F and $8^2D_{5/2}$ states at transition frequencies of (a) 389.6 MHz and (b) 357.7 MHz. The large resonances on the right are for the D state. The curves have a dispersion shape because we have done a lock-in detection of the signal with magnetic field modulation.

The fine-structure Hamiltonian for atoms with orbital and spin angular momenta L and S , and placed in an external magnetic field H is given by

$$\mathcal{H} = \xi \vec{L} \cdot \vec{S} + \mu_B (g_l \vec{L} + g_s \vec{S}) \cdot \vec{H}, \quad (1)$$

where $\xi = \delta w / (L + \frac{1}{2})$, δw being the zero-field fine-structure interval. The energy eigenvalues are given by

$$E(\pm) = -\frac{\delta w}{2(2L+1)} + g_l \mu_B H m_J \pm \frac{\delta w}{2} \left((1+X^2) + \frac{4m_J X}{2L+1} \right)^{1/2}, \quad (2)$$

where

$$X = \frac{\mu_B H (g_s - g_l)}{\delta w},$$

and plus sign refers to the $J = L + \frac{1}{2}$ fine-structure component and the minus sign to the $J = L - \frac{1}{2}$ component. The energy levels given by (2) for an inverted fine structure in a 2F state are shown in Fig. 3. We use (2) to determine δw from the observed position of the rf resonance.

The schematic sketch of the experimental setup is shown in the bottom of Fig. 3. Rb is distilled under vacuum into a cylindrical 1720 glass cell. The Rb cell is heated to obtain the desired vapor pressure of Rb. D_2 resonance line from a Rb discharge lamp is incident on the Rb cell from the side. Circularly polarized laser light, tuned to $5^2P_{3/2} \rightarrow n^2D_{5/2}$ wavelength, passes through the

cell along its axis and is reflected back by a small mirror. The $n^2F \rightarrow 4^2D$ fluorescence along the axis of the cell is analyzed for circular polarization and is detected by a photomultiplier tube. The quasi-static magnetic field, produced by a pair of Helmholtz coils, is maintained along the direction of the laser. A rf magnetic field of the order of a gauss and of frequency about 400 MHz is applied perpendicular to the quasistatic magnetic field. The frequency of rf is kept fixed and the quasistatic magnetic field is swept through the resonance. We modulate the magnetic field at 1300 Hz and do a lock-in detection. Therefore we observe dispersion shaped signals. Further signal averaging is performed by the aid of a PDP8e computer.

III. RESULTS

Figure 4 shows some of our data for the 6^2F state of Rb. The large resonances on the right are the rf resonances in the $8^2D_{5/2}$ state. The hyper-fine structure in this state is unresolved and the fine-structure interval $8^2D_{5/2} - 8^2D_{3/2}$ is so large that the quadratic splitting is negligible at this magnetic field. Therefore we observe a single resonance in the $8^2D_{5/2}$ state centered at $H = h\Delta\nu / g_J \mu_B$, where $\Delta\nu$ is the transition frequency. The resonances to left of the D state resonances are in the 6^2F state and we identify these resonances to be due to $J = \frac{7}{2}$, $m_J = \frac{7}{2} \rightarrow J = \frac{7}{2}$, $m_J = \frac{5}{2}$ transition. The fine-structure interval in this state is small enough that this particular transition splits out from the other $\Delta m_J = \pm 1$ transitions due to the quadratic splitting. In order to ascertain that our identification of the quantum numbers for this resonance is correct, we have repeated this experiment at two different transition frequencies, namely $\Delta\nu = 389.4$ MHz and $\Delta\nu = 375.7$ MHz, shown by the top and the bottom curves in Fig. 4, respectively. We find that our designation of the quantum numbers is indeed correct and the only value of the fine-structure interval that is consistent with our data is that listed in Table I.

In Fig. 5 we show rf resonance curves for the 7^2F state of Rb. In this case we have observed both $\Delta J = 0$, $\Delta m_J = 1$, and $\Delta J = 1$ and $\Delta m_J = 1$ transitions. $\Delta J = 1$ transition frequencies are more sensitive to the fine-structure intervals than are the $\Delta J = 0$ transition frequencies. Therefore we have considerable improvement in the precision of the fine-structure interval measurement of the 7^2F state over that of the 6^2F state. We identify the curves (a) and (b) in Fig. 5 as $(J, m_J) = (\frac{7}{2}, +\frac{7}{2}) \rightarrow (\frac{5}{2}, +\frac{5}{2})$ and $(\frac{7}{2}, +\frac{7}{2}) \rightarrow (\frac{7}{2}, +\frac{5}{2})$ transitions, respectively. In order to confirm our identification of these quantum numbers, we have repeated the experiment at a different transition frequency, name-

TABLE I. Table of relevant experimental parameters and the results.

State	Exciting light wavelength λ_L	Detected light wavelength λ_0	Transition frequency (MHz)	Approximate magnetic field (G)	Quantum numbers of observed transitions	Fine-structure interval δw (MHz)
6^2F *	5432 Å ($5^2P_{3/2} \rightarrow 8^2D_{5/2}$)	8870 Å ($6^2F \rightarrow 4^2D$)	357.7	203.6	$J = \frac{7}{2}, m_J = \frac{7}{2} \leftrightarrow \frac{5}{2}$	-486 ± 4
			389.4	219.5	$J = \frac{7}{2}, m_J = \frac{7}{2} \leftrightarrow \frac{5}{2}$	
7^2F	5260 Å ($5^2P_{3/2} \rightarrow 9^2D_{5/2}$)	8272 \AA ($7^2F \rightarrow 4^2D$)	393.4	210.9	$J = \frac{7}{2}, m_J = \frac{7}{2} \leftrightarrow \frac{5}{2}$	-347.6 ± 1.0
			393.4	352.3	$J, m_J = (\frac{7}{2}, \frac{7}{2}) \leftrightarrow (\frac{5}{2}, \frac{5}{2})$	
			354.6	193.3	$J = \frac{7}{2}, m_J = \frac{7}{2} \leftrightarrow \frac{5}{2}$	
			353.1	327.1	$J, m_J = (\frac{7}{2}, \frac{7}{2}) \leftrightarrow (\frac{5}{2}, \frac{5}{2})$	

ly at about 354 MHz. The results are listed in Table I, and they confirm the above identification. In Table I we have listed the transition frequencies, the approximate magnetic fields, and the quantum numbers of the transitions for all the resonances observed. In this table we have also listed the excitation (laser) wavelength λ_L and the wavelength of the observed fluorescence λ_0 . We have taken several curves for each transition listed in this table, and we have used Eq. (2) to determine the fine-structure interval δw from the measured magnetic fields and transition frequencies of the observed resonances. Our results are shown in Table I and the quoted error bars represent two standard deviations of the mean plus allowance for any systematic uncertainties, for example, those due to calibration of Helmholtz coils, etc. We calibrated the Helmholtz coils by optical pumping of the ground state of Rb.

The fine-structure intervals in the 6^2F and 7^2F states have been observed to be inverted by conventional optical spectroscopy.²¹ Although rf spectroscopy gives very precise absolute values of the fine structure, the sign cannot conveniently be determined. Although, our observations of the relative magnitudes of the rf resonances for σ_+ and σ_- detection seem to show that the sign is inverted, our observation is not unambiguous due to effects like selective excitation of Zeeman sublevels by laser. However, we believe that the optical determination of the sign is correct and we have listed a negative value in Table I.

IV. DISCUSSION

As was pointed out in the Introduction, our interest in the measurement of the fine-structure intervals in alkali-metal atoms was stimulated by the intriguing anomalies in the fine and hyperfine structures of these atoms. The inversions in the fine structures of the F states are especially sur-

prising because, as far as the electrostatic properties are concerned, these states are almost completely hydrogenic. For example, 6^2F and 7^2F states of Rb are characterized by a very small quantum defect — 1.5×10^{-2} .

As a first step in the understanding of these anomalies, it may be interesting to find out, for example, (a) for a sufficiently high value of the principal quantum number n , when the valence electron is very far away from the core, does the fine structure become normal again? (b) In which way does the magnitude of the fine-structure intervals depend²³ on n^* ? Unfortunately, we have been able to measure the fine-structure intervals only in the 6^2F and the 7^2F states. The lower states, namely 4^2F and 5^2F states, fluoresce well

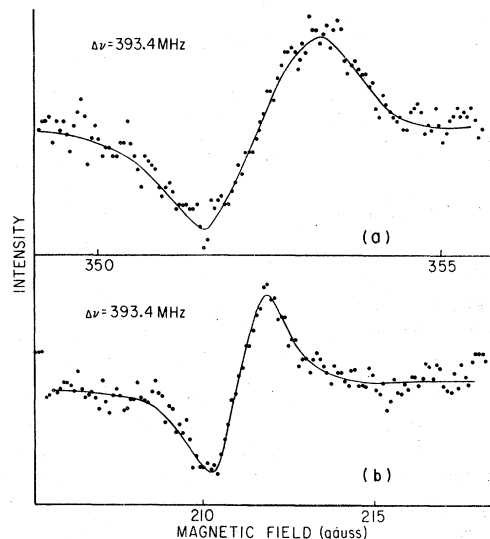


FIG. 5. rf resonances in the 7^2F state at the transition frequency of 393.4 MHz. The upper curve is due to $J, m_J = (\frac{7}{2}, +\frac{7}{2}) \rightarrow (\frac{5}{2}, +\frac{5}{2})$ transition while the lower one is due to $(\frac{7}{2}, +\frac{7}{2}) \rightarrow (\frac{7}{2}, +\frac{5}{2})$ transition.

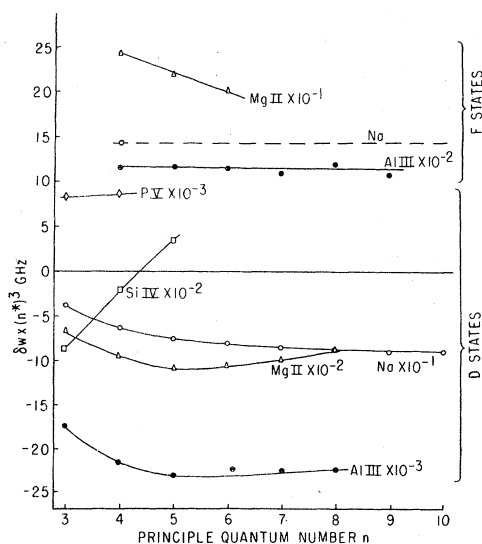


FIG. 6. $\delta w \times (n^*)^3$ is plotted against the principal quantum number n for the D and F states of Na and for some ions which are isoelectronic with Na.

in the infrared, where we cannot use the photomultiplier tubes. The states higher than 7^2F state require dye-laser radiation of wavelengths shorter than 5200 \AA , and are inaccessible to us as we do not have a uv pumped cw dye laser. We have, however, examined the fine-structure data for ions,²⁴ isoelectronic with alkali atoms, and the results are very interesting as shown in Fig. 6. Here we have plotted $(n^*)^3 \delta w$ for the D states of Na, and for the D states of Mg II, Al III, Si IV, and P V, which are isoelectronic with Na. We also show similar curves for the F states of Na, Mg II, and Al III. Unfortunately, the n^2F -state fine structure for the $n=5$ to $n=10$ states of Na has not been measured and the dashed line represents interpo-

lation between $n=4$ and $n=11$. The data for the ions is from optical measurements^{1,25-27} and we have not indicated the error bars.²⁸

Examination of Fig. 6 shows two things: (a) Fine structures in the D states of Na are negative and so they are for the isoelectronic ions of low ionization. Fine structures in the F states of Na are positive and so they are for the isoelectronic ions. Moreover, in complete contrast to Na, the fine structures in the D states of Cs are normal, and so they are for Ba II¹ which is isoelectronic with Cs. However, the F -state fine structures are inverted in Cs while they are normal in Ba II. (b) With increasing degree of ionization, the fine structures tend to become normal again. As a matter of fact the fine-structure interval goes through zero for Si IV as shown in Fig. 6.

Recently, Holmgren *et al.*¹⁹ have been able to obtain inversions in the $4d$ state of Na and in some isoelectronic states of the ions using many-body calculational techniques. Foley and Sternheimer¹⁷ have explained the inversion in the fine structure of $3d$ state of Na as due to a second-order effect between the electrostatic dipole exchange interaction and the magnetic spin-orbit interaction acting on the internal np electrons of the core. Luc-Koenig,¹⁸ on the other hand, has done a relativistic calculation and is able to get inversions both in the nD series of Na and in the nF series of Cs. No calculations, to our knowledge, have yet been performed in the n^2F states of Rb. We hope these calculations will be forthcoming soon, since we now have accurate measurements available.

V. ACKNOWLEDGMENTS

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