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## Hyperfine Structures of Optically Inaccessible Excited Atomic States\*

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Cascade transitions have been used to produce polarized atoms in optically inaccessible excited states. The polarized fluorescent light which is emitted when the atoms decay can be used to measure hyperfine structures, lifetimes, and other atomic parameters of these inaccessible states. Preliminary measurements of the hyperfine interval for the second excited *S* states of  $K^{39}$ ,  $Rb^{85}$ ,  $Rb^{87}$ , and  $Cs^{133}$  are (in MHz) 46(2), 271(15), 565(40), and 684(50), respectively. To our knowledge, these are the first measurements of excited *S*-state hyperfine intervals in alkali atoms.

The alkalis form a particularly interesting group of atoms since their low-lying energy spectra are due principally to the motion of a single valence electron under the influence of the nucleus and closed shells of inner electrons. However, excitations of the core do have a significant influence on many atomic parameters such as hyperfine coupling constants, fine structure, and oscillator strengths. Thus, the properties of alkali atoms form natural test cases for modern many-body computational techniques. In particular, considerable theoretical work has been done on the hyperfine structure of alkali atoms in the past few years.<sup>1</sup> Precision measurements of hyperfine structures in these atoms are available only for the ground states and the excited *P* states. It would be very interesting to obtain hyperfine-structure measurements for other excited states such as *S* states, *D* states, *F* states, etc. For instance, the low-lying *D*- and *F*-state fine-structure intervals are often inverted. This inversion is believed to be due to core excitations.<sup>2</sup> Precision hyperfine-structure measure-

ments in these inverted doublets would help to pinpoint the cause of the anomaly. In this Letter we report on a simple new experimental technique which will make it possible to measure the hyperfine structures of many previously inaccessible excited states.

With few exceptions the excited-state hyperfine structure of alkali atoms is smaller than the Doppler width of optical lines. Thus, techniques such as optical double-resonance<sup>3</sup> or level-crossing spectroscopy<sup>4</sup> are necessary for precision measurements, since these methods are limited only by the natural linewidths of the excited states. However, excited *S* states, *D* states, *F* states, etc., have not yet been studied by level-crossing or double-resonance techniques because one cannot excite the states by allowed electric dipole transitions from the ground state. The optically inaccessible states can, however, be excited by electrons, and an electron beam can produce alignment in non-*S* states. Archambault *et al.*<sup>5</sup> have investigated some of the *D* states in sodium and cesium, but they were only

able to set rather rough limits on the hyperfine structures. Electron excitation of the excited  $S$  states cannot produce polarization unless a polarized electron beam or polarized target atoms are used. We have produced polarized excited  $S$  states with a weak electrical discharge in an optically pumped alkali vapor. However, no hyperfine-structure measurements were attempted because of the difficulty of applying large rf fields to the weakly ionized plasma. Kibble and Pancharatnam<sup>6</sup> and Smith and Eck<sup>7</sup> have used stepwise fluorescence to excite optically inaccessible states. This method seems very promising but it requires very intense and carefully designed lamps to develop the necessary population of the intermediate state.

The method we have developed relies on cascading to populate the inaccessible states. A typical experiment is sketched in Fig. 1. The third resonance line of rubidium (3587 and 3592 Å) is used to excite the  $7P$  state of rubidium vapor. Atoms in the  $7P$  state can decay spontaneously into all of the lower  $S$  and  $D$  states, and there is a 25% branching ratio to the  $7^2S_{1/2}$  state. If the ultraviolet exciting light is circularly polarized, part of the photon's angular momentum

is transferred into the  $7^2S_{1/2}$  state by the cascade. After a mean lifetime of about 100 nsec,<sup>8</sup> the  $7^2S_{1/2}$  state decays spontaneously to one of the lower  $P$  states. The fluorescent light accompanying the  $7^2S_{1/2}$  transition passes through a circular analyzer and is detected with a photomultiplier tube. One can show that the intensity  $I$  of this fluorescent light, detected in a small solid angle  $\Delta\Omega$ , is

$$I \propto (\frac{1}{2} + \langle \vec{J} \rangle \cdot \vec{s}) \Delta\Omega \quad (1)$$

for a transition to a  $P_{1/2}$  state and

$$I \propto (1 - \langle \vec{J} \rangle \cdot \vec{s}) \Delta\Omega \quad (2)$$

for a transition to a  $P_{3/2}$  state. Here  $\vec{s}$  is the mean spin of the detected photons and  $\langle \vec{J} \rangle$  is the mean electronic spin of the  $7^2S_{1/2}$  state. Equations (1) and (2) imply that the fluorescent light is circularly polarized by an amount proportional to  $\langle \vec{J} \rangle$ . The spin-dependent parts of the  $^2P_{3/2}$  and  $^2P_{1/2}$  fluorescence are very nearly equal and opposite [see (1) and (2)], and it is necessary to separate these lines with a filter or monochromator if a large net circular polarization is to be observed. Such cancellation occurs only for the  $S$  states and is not a problem for  $P$  states,  $D$  states,  $F$  states, etc. Thus, by observing the degree of polarization of the fluorescent light which is emitted in the second step of the cascade, one can monitor the polarization of the optically inaccessible  $S$  (or  $D$ ) state. Transitions induced by radio-frequency fields between the magnetic sublevels of the state can be detected by observing the accompanying changes in the polarization of the fluorescent light.

We would like to report preliminary measurements of  $S$ -state hyperfine intervals which were obtained by a simple method, first used, apparently, by Ellett and Heydenburg.<sup>9</sup> If the exciting light has a flat spectral profile and if the magnetic field is large enough to decouple the nuclear spin  $I$  from the electronic spin  $J$  in the upper  $P$  state, the atomic polarization is carried solely by the electrons and the nuclear spin remains unpolarized until the atom reaches the  $7^2S_{1/2}$  state by spontaneous decay. However, in the  $7^2S_{1/2}$  state the hyperfine interaction between  $I$  and  $J$  is much larger than the hyperfine interaction in the  $7P$  states, and a magnetic field which is just sufficient to decouple the  $7P$  states will be too small to decouple the  $7S$  state. Thus, a "low field" for the  $7S$  state can be a "high field"

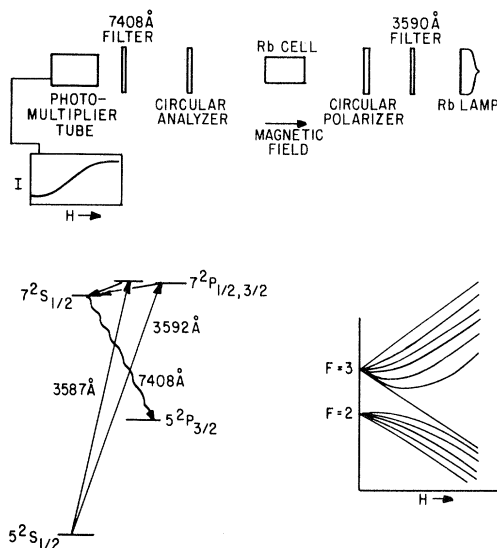


FIG. 1. Schematic diagram of our experimental arrangement (top). Circularly polarized 3587- and 3592-Å resonance lines from a Rb-vapor lamp are used to populate the  $7P$  levels of Rb vapor. Electronic polarization of the  $7S_{1/2}$  state, produced by the cascade transitions from the  $7P$  levels, is detected by monitoring the circular polarization of the 7408-Å fluorescent radiation (lower left). Also shown (lower right) is the Zeeman splitting of the  $7S_{1/2}$  hyperfine levels in the presence of a magnetic field.

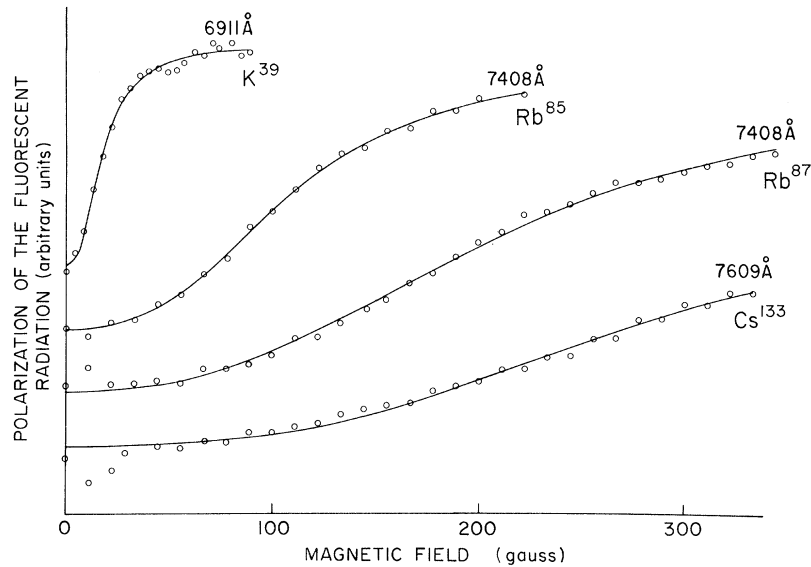


FIG. 2. Polarization of the fluorescent radiation as a function of the magnetic field for various alkali atoms. The circles are experimental points and the solid lines are the theoretical fits to these data. The zero has been suppressed by differing amounts for different curves, and each curve has a somewhat different vertical scale. In rubidium, the observed magnitudes of the polarizations range from around 6% at low fields to around 15% at high fields. In cesium the polarizations were somewhat higher whereas in potassium the polarizations were about 4 times smaller as a result of poor filtering of the fine-structure components of the fluorescence. The large deviation of the experimental points from the theoretical curve at low fields is believed to be caused by incomplete decoupling of the  $P$  states.

for the  $7P$  states, and of course a high field for the  $7S$  state will also be a high field for the  $7P$  states. Henceforth, when we speak of low fields or high fields we shall always be referring to the  $7S$  state and we shall always assume that the field is high enough to completely decouple the  $7P$  states. A very simple way to determine the hyperfine interval of the  $S$  state is to measure the mean electronic polarization  $\langle \vec{J} \rangle$  of the  $S$  state as a function of an external magnetic field  $H$ . At high fields the electronic angular momentum is decoupled from  $I$ , and  $\langle \vec{J} \rangle$  remains the same from the instant the  $S$  state is generated by spontaneous decay from the higher  $P$  state until the  $S$  state decays again to the lower  $P$  state. However, at low fields  $J$  and  $I$  tumble about each other, and part of the electronic angular momentum is converted to nuclear angular momentum. Thus,  $\langle \vec{J} \rangle$  is smaller at low fields

than at high fields. Some typical measurements of  $\langle \vec{J} \rangle$  (i.e., the circular polarization of the fluorescent light) as a function of magnetic field are shown in Fig. 2. Roughly speaking, the widths  $\Delta H$  (in gauss) of the curves are related to the hyperfine intervals  $\Delta \nu$  of the  $S$  states by

$$\hbar \Delta \nu \approx g_J \mu_B \Delta H, \quad (3)$$

where  $g_J$  ( $= 2.00$ ) is the gyromagnetic ratio of the  $S$  state and  $\mu_B$  is the Bohr magneton. Note that the widths increase systematically from potassium to cesium.

The detailed theory of the experiment is straightforward and we shall give only the final results here. We assume that the spectral profile of the exciting light is flat in the neighborhood of the absorption lines. Then, one finds that the electronic polarization in the direction of the magnetic field  $H$  is

$$\langle J_z \rangle = \frac{C}{2(2I+1)} \left\{ 1 + \sum_m \frac{1}{v^2 + z^2} \left[ z^2 + \frac{v^2}{1 + [4\pi \Delta \nu \tau / (2I+1)]^2 (z^2 + v^2)} \right] \right\}, \quad (4)$$

where

$$v^2 = (I + \frac{1}{2})^2 - m^2, \quad (5)$$

$$z = m + (I + \frac{1}{2}) g_J \mu_B H / \hbar \Delta \nu. \quad (6)$$

The term involving the natural lifetime  $\tau$  of the state is negligibly small for these experiments. The quantities  $v$  and  $z$  both depend on the azimuthal quantum number  $m$ , which ranges in in-

TABLE I. Experimental values of the hyperfine-structure interval and those calculated by the semiempirical formula (Ref. 10).

Atom	State	Hyperfine interval	
		Experiment (MHz)	Semiempirical formula (MHz)
K <sup>39</sup>	4 <sup>2</sup> S <sub>1/2</sub>	461.80	497
	6 <sup>2</sup> S <sub>1/2</sub>	45.8 ± 2 <sup>a</sup>	47
Rb <sup>85</sup>	5 <sup>2</sup> S <sub>1/2</sub>	3035.7	3259
	7 <sup>2</sup> S <sub>1/2</sub>	271 ± 15 <sup>a</sup>	312
Rb <sup>87</sup>	5 <sup>2</sup> S <sub>1/2</sub>	6834.7	7365
	7 <sup>2</sup> S <sub>1/2</sub>	565 ± 40 <sup>a</sup>	703
Cs <sup>133</sup>	6 <sup>2</sup> S <sub>1/2</sub>	9192.8	9375
	8 <sup>2</sup> S <sub>1/2</sub>	684 ± 50 <sup>a</sup>	922

<sup>a</sup>Results of this work.

integral steps from  $-(I - \frac{1}{2})$  to  $+(I - \frac{1}{2})$  in the summation of (4). The constant  $C$  depends on the relative amounts of  $D_1$  and  $D_2$  exciting light.

The solid lines in Fig. 2 are the best-fitting theoretical curves based on Eq. (4). The hyperfine interval  $\Delta\nu$  was used as a free parameter in the fits. Agreement between the predictions of the semiempirical formula<sup>10</sup> and the experimental values of the hyperfine intervals gets progressively worse with increasing atomic number (see Table I). We believe that our error estimates are adequate to account for small systematic deviations between theory and experiment. At very low fields these deviations are due to the decoupling of the upper  $P$  state while at high fields the deviation is believed to be due to the magnetic scanning of the absorption lines. The high-field scanning is particularly troublesome in Rb<sup>87</sup> and Cs<sup>133</sup>, which have large hyperfine intervals, and we have quoted larger uncertainties for these elements. As is evident from Fig. 2 our magnetic field was not large enough to completely decouple  $I$  and  $J$  in cesium, and, although we were always able to obtain unambiguous fits to all our data, we are not certain that the results were not biased by the limited field range. Much more precise values for the

hyperfine intervals will be available when the radio-frequency-spectroscopy experiments have been completed, and we should be able to measure the hyperfine anomaly for Rb<sup>85</sup> and Rb<sup>87</sup>.

Preliminary experiments have verified that even larger polarizations are produced in the  $D$  states. Unfortunately, the simple decoupling technique is not particularly useful for the  $D$  states and hyperfine-structure measurements will have to be done with rf spectroscopy. We are also able to observe the third excited  $S$  states, and we will measure the hyperfine intervals in these states very shortly. The first excited  $S$  states are more difficult to measure since the fluorescent wavelengths lie well in the infrared and cannot be detected with conventional photomultiplier tubes. Also, very large magnetic fields are required to decouple  $I$  and  $J$ , and the short natural lifetimes of the first excited  $S$  state necessitate the use of very large radio-frequency fields.

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