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Fine Structure of the n^2D Series in Rubidium near the Ionization Limit*

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Two-photon, Doppler-free spectroscopy with counter-propagating beams from a cw dye laser and a new type of thermionic detector have been used to study the $^2D_{3/2}$ and $^2D_{5/2}$ levels of Rb for Rydberg states up to $n = 85$, only 16 cm^{-1} from the ionization limit. It is shown that the fine-structure spacing varies as n_{eff}^{-3} for $n > \sim 25$, and as a linear combination of n_{eff}^{-5} and n_{eff}^{-3} for $n < \sim 25$.

Recently, the study of highly excited states of alkali atoms, particularly of the ^2D states which exhibit inversion of fine structure, has attracted considerable attention. Experiments with quantum beats,[1] level crossing,[2] and two-photon absorption[3,4] have been employed. In general, these investigations have been limited to values of the principal quantum number $n < 20$, because of the small oscillator strengths of transitions to high n values, and the long lifetimes of these states.

Here we report the results of experiments on rubidium, with excitation to Rydberg states up to $n = 85$, only 16 cm^{-1} from the ionization limit. It is well known that the lowest ^2D level of rubidium is inverted[5] and its hyperfine structure exhibits anomalies.[6] The fine-structure splitting $n^2D_{5/2} - n^2D_{3/2}$ has been measured by classical spectroscopy[5] up to $n = 13$, and recently, by Doppler-free two-photon absorption[4] to $n = 32$. The present experiments have extended the precise measurement of the ^2D fine structure up to $n = 65$, when the doublets merge. These data now establish that the fine-structure spacing varies as the effective quantum number[7] n_{eff}^{-3}, for $n > 25$, and as a function of n_{eff}^{-5} and n_{eff}^{-3} in the region of crossover of the ^2D states ($n < 25$) from inverted to normal. The present results thus constitute the first complete study of the variation of fine-structure spacing with principal quantum number, for an alkali atom.

The present observations of highly excited Rydberg states in rubidium were made possible by the use of a sensitive thermionic detector in conjunction with the technique of Doppler-free two-photon spectroscopy.[8,9] Figure 1 shows the experimental arrangement. An Ar^+ laser was used to pump a dye laser (Spectra Physics Model 580)

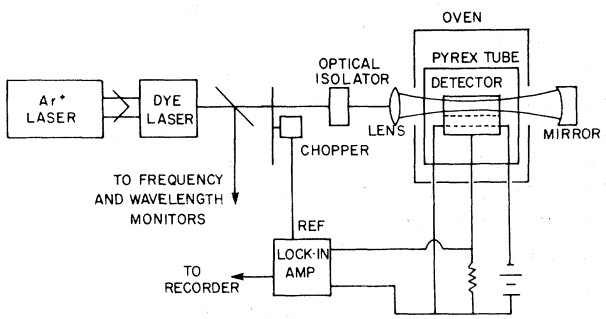

FIG. 1. Schematic diagram of the experimental arrangement.

producing a cw output of ~ 50 mW with a linewidth of 10 to 15 MHz, in the region of 5950 Å. The laser beam was chopped at 10 Hz, a small part was directed to wavelength monitors, and the main portion directed through an optical isolator consisting of a Glan-Thompson prism and Fresnel rhomb. This circularly polarized beam was focused with a 10-cm lens into the Rb-cell-detector combination, and reflected back on itself with a totally reflecting concave mirror (of 10-cm radius of curvature) to form the counter-propagating beams.

The thermionic detector is similar to that originally described by Kingdon[10] and Hertz[11] in 1923, and recently by Curry *et al.*,[12] but has been designed with the present application in mind. In its simplest form, the detector consists of a long cylindrical anode surrounding a wire cathode. In operation, it may be thought of as a simple diode: The highly excited atoms produced by the laser beam may be ionized by thermal collisions; the ions are trapped electrostatically in a region surrounding the cathode, and their presence in a space-charge–limited diode affects the flow of current. The trapping of the ions greatly enhances the sensitivity of the device, so that almost 100% efficiency is achieved, resulting in gains of 10^5 or higher. This compares favorably with the gain of a photomultiplier. Moreover, the long lifetimes of the states being studied, and the weak fluorescence improve the efficiency of this detector in contrast to earlier methods which employed the fluorescence as a means of detection. However, since the polarizabilities for highly excited atomic states are very large, even the small electric fields (< 1 V/cm) used in such detectors are sufficient to broaden (and for $n > 40$, to completely split) the observed resonances. Thus, for the present study an electrostatically shielded detector was constructed, and no Stark effects were observed even at $n = 85$. The anode was made of nickel, and consisted of two compartments, each 2 cm long and with 7×7 mm^2 cross section, separated by a fine nickel mesh. The cathode, of 5-mil tungsten wire, was centered along the axis of one compartment; and the counter-propagating laser beams were focused in the second, field-free compartment (as shown in Fig. 1). With this detector configuration, the excited atoms now diffuse into the detection region containing the cathode. The detector was sealed in a Pyrex envelope, baked and evacuated to 10^{-8} Torr, and filled with high-purity rubidium. It was placed in a two-chamber oven so that the temperature of the detector and that of the rubidium supply could be controlled independently. The detector was maintained at 220°C and the cold finger with rubidium at 180°C, corresponding to a vapor pressure in Rb of 10^{-2} Torr. In operation, a voltage of 0.6 V was applied across the cathode wire and anode, the connection to the latter being through a 30-kΩ resistor. A typical diode current of 10 μA passed through the resistor. Ions produced in the detector affected the space-charge–limited current, and the resulting voltage across the resistor was monitored by a lock-in amplifier (PAR 121).

Experimental data were obtained by scanning the dye-laser frequency sequentially over each resonance region, and then recording simultaneously the Rb two-photon spectra along with a frequency reference, using a two-pen chart recorder. The absolute frequencies of the transitions were measured by calibration with I_2 absorption lines of known frequency,[13] and the fine-structure splittings were determined by comparison with the transmission peaks (spaced by 124.9 MHz) of a confocal interferometer. (This interferometer consisted of a quartz spacer 1.2 m long, with Invar mirror mounts and adjustment screws, and was hermetically sealed in a quartz tube.) Corrections for any nonlinearities in the dye-laser scanning were made by using a quadratic fit to the interferometer peaks. Each scan covered a range of ~ 400 MHz, and lasted 2 to 5 min, the time constant of the recorder being $\frac{1}{3}$ sec.

Two-photon absorption spectra ($5^2S \rightarrow n^2D$) of Rb were recorded for $n = 25$ to $n = 85$. The spectra formed a simple Rydberg series with a series limit at 33 691.2 cm^{-1}, in agreement with the known ionization limit at 33 691.02 cm^{-1}. The energy of the highest observed transition, namely $5S$ to 85^2D, is 33 675.0 cm^{-1}, only 16 cm^{-1} from the ionization limit. Fine-structure splittings were observed up to $n = 65$, where the doublets merged, and the separations were accurately measured for $n = 25$ to $n = 55$ (with the doublets free from any overlap). The measured fine-structure splittings are listed in Table I. For these measurements, the transitions from $5^2S_{1/2}(F = 3)$ to $n^2D_{3/2,5/2}$ in ^{85}Rb were typically used, since they produced the strongest singnals. For example, at $n = 45$, a signal-to-noise ratio of 50:1 was obtained, the signal voltage being 0.5 mV. The signal was observed to diminish as n^{-3}, and was just measurable at $n = 85$. The errors in the fine-structure measurements arise primarily from the the frequency jitter of the dye laser. This insta-

TABLE I. Experimental fine-structure intervals (Δ_{fs}) and effective quantum numbers (n_{eff}) of the Rb $nd^2D_{3/2,5/2}$ states.

n	n_{eff}[a]	Δ_{fs} (MHz)	n	n_{eff}	Δ_{fs} (MHz)
25	23.65	800 ± 10[b]	46	44.59	116
26	24.63	718	47	45.57	110
27	25.63	638	48	46.59	102
28	26.60	568	49	47.66	98
29	27.63	514	50	48.57	94
30	28.62	458	51	49.67	86
31	29.62	408	52	50.67	82
32	30.63	364	53	51.74	80
33	31.61	338	54	52.60	74
34	32.62	304	55	53.6	76
35	33.60	280	56	54.5	63[c]
36	34.61	258	57	55.4	65[c]
37	35.60	242	58	56.4	61[c]
38	36.60	218	59	57.4	59[c]
39	37.60	204	60	58.4	47[c]
40	38.59	190	61	59.4	46[c]
41	39.59	172	62	60.5	47[c]
42	40.59	166	63	61.4	45[c]
43	41.58	152	64	62.3	38[c]
44	42.59	140	65	63.3	35[c]
45	43.58	130			

[a]The term values used to calculate n_{eff} were taken from Ref. 5 for $n = 25$ to 54, and from the present measurements for $n > 54$.

[b]Error for all Δ_{fs} from $n = 25$ to 55 is ± 10 MHz.

[c]Overlapping doublets.

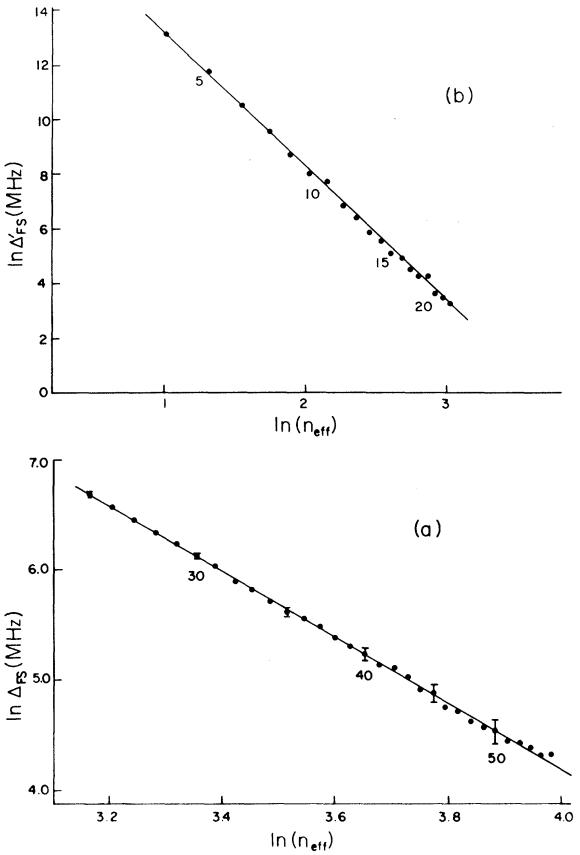

FIG. 2. (a) The fine structure Δ_{fs} as a function of the effective quantum number n_{eff}, for the levels investigated in this experiment. Error bars are given for selected data points. The slope of the straight line is -2.987 ± 0.033. (b) The "reduced" fine structure Δ_{fs}' $[= (1.08 \times 10^7) n_{eff}^{-3} - \Delta_{fs}]$ as a function of n_{eff}. The slope of the straight line is -4.976 ± 0.062.

bility also leads to a laser linewidth of 10 to 15 MHz, and results in observed linewidths for the two-photon resonances of twice the frequency jitter of the individual counter-propagating laser beams. Other sources of error, including effects of collisions are considered to be small. Transit broadening was estimated to be ~ 2 MHz, and light shifts less than 1 MHz. Self-broadening is predicted[14] to be larger than pressure shifts (in contrast to broadening by rare gases); however, since no broadening was detected, the shifts are also believed to be negligible.

A graph of the fine-structure splittings, Δ_{fs}, showing their dependence on n_{eff} is given in Fig. 2(a). All of the data are seen to lie on a straight line. A least-squares fit of $\ln\Delta_{fs}$ as a function of $\ln n_{eff}$ to a straight line gave a slope of -2.987 ± 0.033. A similar fit of $\ln\Delta_{fs}$ as a function of $\ln n$ gave -3.112 ± 0.034. Thus, it was concluded that, in the limit of high n values ($n > 25$), the fine-structure splitting of the ^2D states of Rb, may be represented (in GHz) by

$$\Delta_{fs} = 10\,800 n_{eff}^{-3}. \quad (1)$$

This expression was then used to calculate the contribution to each of the doublets $n = 4$ to 25, whose spacings were earlier shown[4] not to vary as n_{eff}^{-3}. When this contribution was subtracted from the measured splittings, and the resultant Δ_{fs}' plotted as before, the graph of Fig. 2(b) was obtained. A least-squares fit to a straight line gave a slope of -4.976 ± 0.062. The proper expansion for the fine-structure splitting of the ^2D states of Rb thus appears to be

$$\Delta_{fs} = A n_{eff}^{-3} + B n_{eff}^{-5}. \quad (2)$$

Finally, a least-squares fit to Eq. (2) of the present measurements (Table I) for $n = 25$ to 55, and

of those in Refs. 4–6 for $n = 4$ to 24 gave

$$A = 10\,800 \pm 15 \text{ GHz}, \quad B = -84\,870 \pm 100 \text{ GHz}. \quad (3)$$

An expansion in odd powers of the principal quantum number was used by MacAdam and Wing[15] to fit the fine structures of the $n = 8$, 9, 16, 17, and 18 D states in He. Fabre, Gross, and Haroche[1] have also used such an expansion, but with reversal of signs, to fit the inverted fine-structure intervals for the nD states ($n = 3$ to 16) of Na. In a recent theoretical calculation of the inverted fine structure of the 4^2D state of Rb, Lee *et al.*[16] estimated the direct contribution to be $\Delta\nu = 15.15$ cm^{-1} and the exchange core-polarization term to be $\Delta\nu = -24.3$ cm^{-1}, leading to a fine-structure splitting of -9.1 cm^{-1}. While this value explains the observed negative splitting, it does not agree in magnitude with the experimental value of -0.44 cm^{-1}. The individual contributions estimated by Lee *et al.*,[16] may be compared with the values of 16.99 and -17.43 cm^{-1} obtained here for the contributions An_{eff}^{-3} and Bn_{eff}^{-5}, respectively, for the 4^2D state (with $n_{\text{eff}} = 2.767$). Such a comparison would indicate that the negative term due to exchange core polarization estimated by Lee *et al.*[16] is perhaps ~40% too large. However, the term An_{eff}^{-3} agrees well with the calculated direct term for the 4^2D state, and moreover it explains the observed fine structure for the high Rydberg states studied here. Thus, we conclude that the fine structure for the high n^2D states of Rb may be adequately described by a single-electron model.

We have demonstrated here a method of selectively exciting very high atomic Rydberg states with high resolution. The method has been used to investigate the fine structure of the ^2D states in rubidium, near the ionization limit, where the splittings are found to vary as An_{eff}^{-3}. And all of the observed fine-structure splittings from $n = 4$ to 55 are shown to obey the relation $\Delta\nu = An_{\text{eff}}^{-3} + Bn_{\text{eff}}^{-5}$. Moreover, this method may be extended to other atomic and molecular systems with comparable or even much improved resolution, and thus contribute to the systematic study of Rydberg states. Finally, the present work suggests the feasibility of new collision studies, which have recently been proposed.[17]

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