^{138,139}La nuclear electric-quadrupole-moment ratio by laser-rf double resonance

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The laser-rf double-resonance technique has been used to obtain 1-ppm measurements of the largest hyperfine intervals in the ground $(5d 6s^{2} D_{3/2})$ and first excited $(5d 6s^{2} D_{5/2})$ atomic levels of 0.09% abundant ¹³⁸La with a beam of unenriched lanthanum. The hfs ratios A^{138}/A^{139} and B^{138}/B^{139} are thereby obtained. The former shows a 0.36% hyperfine anomaly with respect to the NMR ratio of the nuclear g factors. The uncertainty in the new value $B^{138}/B^{139} = +2.27\pm0.04$ arises from uncertainties in interpreting the hyperfine-anomaly effects observed. The ^{138,139}La isotope shift is evaluated for both of the lines studied.

I. INTRODUCTION

Except for the very lightest elements ($Z \le 7$), there are only five naturally occurring odd-odd isotopes, and all of them have extremely small natural abundance. ¹³⁸La, with a spin of 5, is present only to the extent of 0.09% in normal lanthanum. Sogo and Jeffries¹ were able, in 1955, to determine the spin and magnetic moment of ¹³⁸La by nuclear magnetic resonance (NMR). They found the *g*-factor ratio between ¹³⁸La and the 99.91%-abundant ¹³⁹La to be

$$g_I^{(138}La)/g_I^{(139}La) = 0.93407(3)$$
. (1)

They also deduced from the breadth of the NMR signals that the nuclear electric quadrupole moment of ¹³⁸La was somewhat larger in magnitude than for ¹³⁹La, and obtained

$$|Q^{(138}La)/Q^{(139}La)| \approx 3$$
. (2)

No further work was reported on the atomic properties of ¹³⁸La until 1972, when Fischer *et al.*² obtained a sample enriched in ¹³⁸La by a factor of 2600. By examining the hyperfine structure (hfs) of two optical lines, they were able to measure the ratios of the dipole and quadrupole hfs constants for the two isotopes. They found

$$A(^{138}La)/A(^{139}La) = 0.9328(8)$$
 (3)

and

$$B(^{138}La)/B(^{139}La) = +2.3 \pm 0.4$$
 (4)

for the two $5d^26p \rightarrow 5d^26s$ transitions studied. The 1.6 σ difference between the NMR g-factor ratio and their result for the ratio of the hfs A factors was interpreted as an indication of a hyperfine anomaly. Recently, still more precise NMR measurements by Kruger, Lutz, and Oehler³ have the results

$$g_I^{(138}La)/g_I^{(139}La) = 0.9340674(18)$$
 (5)

and

$$Q(^{138}La)/Q(^{139}La) = 2.15 \pm 0.17$$
. (6)

II. TECHNIQUE AND APPARATUS

Because of its extremely high sensitivity and precision, the laser-rf double-resonance technique, described in detail previously,^{4,5} was chosen for the experiment. A well-collimated lanthanum atomic beam was irradiated orthogonally by a tunable, single-frequency dye laser whose linewidth was about 2 MHz. The laser was tuned to a single hfs component of an optical line so that the population of the lower hfs sublevel was strongly depleted by this "pump" laser beam. As a result, very little fluorescence could be detected downstream by a "probe" laser beam of identical wavelength unless the depleted level could be repopulated in the region between the two laser beams. This was accomplished by inducing rf transitions from adjacent hfs levels in the lower atomic state of the optical transition. The rf transition occurred far from the laser beams and, for low power levels, its width arose both from the transit time for the atom through the rf field and from a slight Zeeman broadening due to the residual magnetic field of several mG. As can be seen from the figures, the full width at half maximum (FWHM) was typically ~20 kHz.

III. PROCEDURE

The close doublet $\lambda 5930.6$ (0.07 Å splitting) was chosen for study because of its relatively large fvalue and because its hfs had been carefully studied previously.⁶ The two lines $5d6s^{2}D_{3/2}$ (ground state) $-5d6s(a^{3}D)6p$ $^{2}F_{5/2}$ and $5d6s^{2}$ $^{2}D_{5/2}$ (1053 cm⁻¹) $-5d6s(a^{3}D)6p$ $^{2}F_{7/2}$ are nearly coincident because the splitting of the upper ^{2}F term is almost identical to that of the ground ^{2}D term.

Figure 1 shows the fluorescence observed from the atomic beam as the laser was scanned through the two lines. All 30 hfs components are resolved and the F values for the individual components are shown above the transitions themselves. When the detector sensitivity was raised to its maximum lev-

1922



FIG. 1. Fluorescence intensity observed as the exciting laser was swept through the lines λ 5930.68 and λ 5930.62. The spectrum seen arises entirely from the 99.91% abundant ¹³⁹La, whose hyperfine structure is well resolved. The identifying F values are given above the hfs components. The abscissa is calibrated by a 300-MHz F.S.R. Fabry-Perot.

el and the atomic beam was increased substantially from the situation of Fig. 1, the spectrum shown in Fig. 2 was obtained. In the figure, two hfs components due to ¹³⁸La can be observed; the others lie buried under the tails of the ¹³⁹La lines which are more than 1100 times stronger. Consideration of the positions of these lines, the expected relative intensities, and other factors suggests the identifications (later confirmed by double-resonance measurements) as $F_{max}(^{2}D_{J}) \rightarrow F_{max}(^{2}F_{J+1})$ with $J = \frac{3}{2}$ and $\frac{5}{2}$, the bluest and strongest ¹³⁸La hfs components. It should be noted that Fig. 2 was obtained using normal, unenriched lanthanum; an enriched sample would have made the experiment very much easier.

Because only one ¹³⁸La hfs component could be cleanly resolved and unambiguously identified in each of the two lines, the fluorescence technique alone could not be used to determine any of the ¹³⁸La hfs constants. Nevertheless, it did appear feasible to use the laser-rf double-resonance technique to measure precisely the largest hfs interval in both the ${}^{2}D_{3/2}$ and ${}^{2}D_{5/2}$ states of ${}^{138}La$. These two intervals may be expressed as

$$\Delta \nu ({}^{2}D_{3/2}; F = \frac{13}{2} \leftrightarrow \frac{11}{2}) = 6.5A^{138} ({}^{2}D_{3/2}) + 0.65B^{138} ({}^{2}D_{3/2}) ,$$
(7)
$$\Delta \nu ({}^{2}D_{5/2}; F = \frac{15}{2} \leftrightarrow \frac{13}{2}) = 7.5A^{138} ({}^{2}D_{5/2}) + 0.45B^{138} ({}^{2}D_{5/2}) .$$
(8)

In order to obtain estimates for these two frequencies, we assumed that the ratio for the hfs constants between the two isotopes is, to first approximation, independent of the atomic state considered. Thus to obtain rough values for the dipole constants we use

$$\alpha \equiv A^{138}(\psi) / A^{139}(\psi) , \qquad (9)$$

where we have^{1,3}

$$\alpha^{\rm NMR} = 0.934\,07\tag{10}$$

and

$$\alpha^{\text{opt}} = 0.9328(8),$$
 (11)



FIG. 2. A scan through the same region as in Fig. 1, but with the detector set for maximum sensitivity and with a very strong lanthanum atomic beam. Two hfs components due to the 0.089% abundant ¹³⁸La can be clearly seen. By holding the laser on each of the transitions in turn, it was possible to measure particular hfs intervals in the lower atomic level of the optical transitions with the laser-rf double-resonance technique.

(13)



FIG. 3. Radio-frequency scan through the $F = \frac{15}{2}$ $\frac{13}{2}$ hfs interval in the $5d6s^{2}{}^{2}D_{5/2}$ state (1053 cm⁻¹) of ¹³⁸La, using the laser-rf double-resonance technique. The measurement was repeated several times.

as found in Ref. 2. We also define

 $\beta \equiv B^{138}(\psi)/B^{139}(\psi) , \qquad (12)$

where

 $\beta^{\rm NMR} = 2.15 \pm 0.17$

and

 $\beta^{\rm opt} = 2.3 \pm 0.4$

from Refs. 2 and 3. From these ratios and the precisely known⁷ hfs constants for the same atomic states of 139 La, we obtain

$$\Delta \nu ({}^{2}D_{2/2}; F = \frac{13}{2} \leftrightarrow \frac{11}{2}) = 922 \pm 13 \text{ MHz}$$
 (14)

$$\Delta \nu ({}^{2}D_{5/2}; F = \frac{15}{2} \leftrightarrow \frac{13}{2}) = 1330 \pm 13 \text{ MHz},$$
 (15)

in which we have used the average of α^{NMR} and α^{opt} and the uncertainty is somewhat arbitrary.

When the laser wavelength was set exactly on the ¹³⁸La hfs component seen for the ${}^{2}D_{5/2} - {}^{2}F_{7/2}$ line and the rf swept through the region predicted by Eq. (15) in a double-resonance experiment, the curve of Fig. 3 resulted. Several runs were made at various rf power levels and although the FWHM depended on the power, the resonance frequency did not. Figure 4 shows the resonance found when the laser was set on the ¹³⁸La ${}^{2}D_{3/2} - {}^{2}F_{5/2}$ component and the rf swept through the region predicted in Eq. (14).



FIG. 4. Radio-frequency scan through the $F = \frac{13}{2}$ $\leftrightarrow \frac{11}{2}$ hfs interval in the $5d6s^{22}D_{3/2}$ atomic ground state of ¹³⁸La using the laser-rf double-resonance technique.

IV. INTERPRETATION

With these experimental results, Eqs. (7) and (8) become, after use of Eqs. (9) and (12) and the precisely known A and B values for the corresponding states of ¹³⁹La,

$$\Delta \nu ({}^{2}D_{3/2}; F = \frac{13}{2} \leftrightarrow \frac{11}{2}) = 917.773 \alpha + 29.108\beta$$
$$= 920.188 \pm 0.001 \text{ MHz}, \quad (16)$$

$$\Delta \nu({}^{2}D_{5/2}; F = \frac{15}{2} \leftrightarrow \frac{13}{2}) = 1366.280 \alpha + 24.396 \beta$$

 $= 1326.948 \pm 0.001 \text{ MHz}$. (17)

Simultaneous solution of these equations gives the results

$$\alpha = 0.930\ 74 \pm 0.000\ 03 ,$$

$$\beta = 2.267 \pm 0.001 ,$$
(18)

in which the uncertainties arise mainly from the published⁷ uncertainties in the *B* values for ¹³⁹La. Taking careful account of second-order hfs effects in both atomic states of both isotopes does not change these values within the quoted uncertainties. The large difference (0.36%) between the NMR value¹ of α [Eq. (5)] and the present value [Eq. (18)] is strong evidence of a hyperfine anomaly. The present number does not give an actual measurement of the anomaly, however, since we have assumed, in going from Eqs. (7) and (8) to Eq. (16), that α and β are the same for the ${}^{2}D_{3/2}$ and ${}^{2}D_{5/2}$ states.

Although one would not at first glance expect the states $5d6s^2 \, {}^2D_{3/2,5/2}$ to have hyperfine anomalies

TABLE I. Theoretical and experimental values for the ratios of the hfs constants for the $5d6s^{22}D_{3/2,5/2}$ states in any given isotope of lanthanum. The theoretical values are for a single *d*-electron term with no configuration interaction or relativistic effects. The experimental ratios are for ¹³⁹La. The failure of the simple model, especially for the dipole hfs interaction, is apparent. The breakdown is evidence of the strong configuration-interaction mixing not taken into account in the calculations.

hfs ratio	Theoretical	Experimental
$rac{A(^2D_{3/2})}{A(^2D_{5/2})}$	2.333	0.775
$\frac{B(^2D_{3/2})}{B(^2D_{5/2})}$	0.700	0.826

because of the apparent absence of $s_{1/2}$ or $p_{1/2}$ electrons to probe the nuclear volume, these states are in fact much more complex than they seem. Table I is chosen to demonstrate this complexity. It can be seen immediately that the ratio of the measured A values differs drastically from the prediction of the single-electron model. Detailed multiconfiguration studies^{8,9} have established that even these lowest ${}^{2}D_{3/2,5/2}$ levels contain substantial *s*-electron admixture, and can therefore be expected to show hyperfine anomalies. In addition, the anomalies for the two states are not expected to be the same. The smaller sensitivity of the quadrupole-constant ratio to large configuration-interaction admixtures is in accordance with theoretical studies by Wybourne.¹⁰

Although the ratio of the quadrupole hfs factors of the two isotopes given in Eq. (18) is nominally of high precision, it too is affected by the assumed independence of the hyperfine anomaly on atomic state. To illustrate this, it may be noted that if one forces the NMR value of α in Eqs. (16) and (17), one obtains the inconsistent results

$$\beta(^{2}D_{3/2}) = 2.1618(1),$$

$$\beta(^{2}D_{5/2}) = 2.0803(1).$$
(19)

Neither of these values should be considered correct, however, since a real hfs anomaly has been shown to exist and the NMR value for α should not therefore be used. Although it is difficult to be precise in setting an uncertainty because of the unknown size of the hfs anomaly, the result

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$$\beta \equiv B(^{138}La)/B(^{139}La) = 2.27 \pm 0.04$$
 (20)

appears conservative. This value is in good agreement with both the optical and NMR values,^{2,3} and substantially more precise.

The isotope shift between ¹³⁸La and ¹³⁹La can be evaluated for the lines studied from laser scans of the type shown in Fig. 2. For this purpose, a 25cm confocal Fabry-Perot interferometer with a free spectral range of 300.0 MHz was used to analyze the laser light during the scans. The incremental frequency scale so determined was then fine tuned by using the precise hfs intervals known from atomic-beam magnetic-resonance studies7 of the ${}^{2}D_{3/2,5/2}$ levels of ${}^{139}La$. In this way, the separations of the two ¹³⁸La hfs components from the nearby ¹³⁹La components was established. The calculated positions of the centers of gravity of the lines for the two isotopes then allowed extraction of one value of the isotope shift for each of the two lines. The results are

$${}^{2}D_{3/2} \leftrightarrow {}^{2}F_{5/2}$$
: $\nu_{CG} ({}^{138}La) - \nu_{CG} ({}^{139}La) = 331 \pm 20 \text{ MHz}$,
 ${}^{2}D_{5/2} \leftrightarrow {}^{2}F_{7/2}$: $\nu_{CG} ({}^{138}La) - \nu_{CG} ({}^{139}La) = 356 \pm 20 \text{ MHz}$.
(21)

V. CONCLUSIONS

We have shown that the laser-rf double-resonance technique has sufficient sensitivity to make measurements on one isotope in the presence of another 3 orders of magnitude stronger. The experimental precision achieved (at least 1-ppm) shows clearly that a 0.36% difference exists between the NMR ratio of the nuclear ρ factors and the hfs A values for the isotopes 138,139 La; it is almost surely due to hyperfine-anomaly effects. The ratio $Q(^{138}La)/Q(^{139}La)$ deduced from the precise experimental hfs intervals unfortunately depends on uncertainties associated with the hfs anomaly, but it is nevertheless possible to quote a value with a much smaller uncertainty than allowed by previous work.

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