

Ratio of the Electric Quadrupole Moments of Ba¹³⁷ and Ba¹³⁵ Nuclei*

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The Zeeman-split quadrupolar resonances of Ba¹³⁷ and Ba¹³⁵ in barium bromide dihydrate were observed by using coincident enhancement of proton magnetic resonance as a detector. It was found that Q_{137}/Q_{135} is 1.543 ± 0.003 and that the asymmetry parameter of the electric field gradient about the Ba site is 0.726 ± 0.006 .

INTRODUCTION

THE nuclear electric quadrupole moment, Q , has been measured for about 100 different nuclei. Only their ratios have been measured for several isotopic pairs.

While studying the structure of the water molecule in hydrated compounds,¹ we investigated barium bromide dihydrate.^{2,3} Its spin-lattice relaxation time, T_1 , for the proton was so long that the proton magnetic resonance (PMR) experiment had to be run with considerable saturation. However, at certain orientations of the crystal with respect to the magnetic field, T_1 shortened to a few seconds, the saturation largely disappeared, and the PMR was greatly enhanced.²

Investigation revealed that T_1 shortened when the crystal orientation and the field strength, H , were such that the ^{137}Ba nucleus matched its quadrupolar resonance frequency to the PMR frequency. The resulting spin exchange between the two kinds of nuclei and the subsequent passing of energy from the barium to the crystal lattice markedly reduced T_1 for the proton. The relationship between the crystal orientation and the field were traced out carefully. It was found that Dean's theory⁴ of the Zeeman splitting of quadrupolar resonance was well obeyed. His theory is exact for any possible value of η , the asymmetry parameter of the electric field gradient (FG), and for nuclear spin $\frac{3}{2}$, the case here. It is good to first order in H . That experimental study yielded knowledge of η and the orientation of the FG about the Ba nucleus with respect to the crystal and of the pure quadrupolar resonance frequency, ν_Q , of Ba¹³⁷.

Ba¹³⁷ gives a very weak resonance signal in a super-regenerative quadrupole resonance spectrometer.⁵ 11.32% of the barium nuclei are Ba¹³⁷ while only 6.59% are Ba¹³⁵. One could expect even more difficulty in detecting the Ba¹³⁵ resonance in the usual manner. Our method (PMR enhancement) is laborious but it is much

more sensitive to quadrupolar resonances in cases of this kind.⁶ Furthermore, it yields good resolution in ν_Q . One could hope only to obtain the ratio of the Q 's for Ba¹³⁷ and Ba¹³⁵, since the atomic positions in BaBr₂·2H₂O are unknown and the FG could not be computed.

EXPERIMENT

We used a slightly modified Pound-Watkins spectrometer and our usual parameters.² Frequencies ranged from 13 to 20 Mc/sec and the corresponding magnetic fields ranged from 3100 to 4600 G. Rf frequencies were set and measured using a General Radio frequency calibrator, 1213-C. This had been standardized against WWV. The rf amplitude was the smallest for which the rf oscillator was stable. The barium bromide crystals had volumes of about 2 cc. They were observed at room temperature.

The first crystal orientation was such that its crystallographic c axis was parallel to H . In this case the y axis of the FG was parallel to H .⁶ Our search began with a frequency of 31.6 Mc/sec and the frequency was lowered 0.1 Mc/sec for each trial. Segel had noted that the line shape of the weak pure quadrupolar resonance of Ba¹³⁷ in this crystal suggested the presence of two resonances. Therefore, we believed that ν_Q for Ba¹³⁷ and for Ba¹³⁵ might be essentially coincident. Hence, the Zeeman-split resonances for Ba¹³⁵ should lie in the same region as those for Ba¹³⁷. As the frequency was lowered we found again the four resonances of Ba¹³⁷. At 18.90 Mc/sec the first new resonance was detected by PMR enhancement. The observation was continued with progressively lowered rf until all four resonances were located. At each resonance the tests were run with frequency differentials as small as 0.02 Mc/sec in order to locate well the frequency for

TABLE I. Zeeman-split quadrupolar resonance frequencies (in Mc/sec) of Ba¹³⁵. The transitions are labeled in the usual fashion.^{4,6}

Transition \ Orient.	$z \parallel H$	$y \parallel H$	$x \parallel H$
β^+	19.37	18.90	17.95
α^+	17.58	14.45	15.69
α^-	14.30	17.65	16.51
β^-	13.32	13.70	14.58

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¹ J. W. McGrath and A. A. Silvidi, J. Chem. Phys. **34**, 322 (1961).
² J. W. McGrath and A. A. Silvidi, J. Chem. Phys., **33**, 644 (1960).
³ J. W. McGrath and A. A. Silvidi, J. Chem. Phys. **36**, 1082 (1962).
⁴ C. Dean, Phys. Rev. **96**, 1053 (1954).
⁵ We are indebted to Professor S. L. Segel for searching for the barium resonances in this crystal with a super-regenerative spectrometer. The Ba¹³⁷ resonance was very weak and the Ba¹³⁵ resonance did not appear.

⁶ J. W. McGrath and A. A. Silvidi, J. Chem. Phys. **36**, 1496 (1962).

greatest PMR enhancement. To ensure parallelism between the y axis and H (within $\pm 2^\circ$), we turned the crystal 200 mils one way and then the other. Parallelism was indicated by equality of the PMR enhancement frequencies at the latter two orientations. (See Fig. 1 in reference 6.) Similar observations were made when the z and x FG principal axes were successively parallel to H .

DATA AND RESULTS

The data are shown in Table I. When PMR enhancement occurred the resonance intensity increased by a factor of 5 or more. Enhancement was greater for all transitions when y was parallel to H , for the $\alpha+$ and $\beta+$ transitions when z was parallel to H , and for $\beta+$ when x was parallel to H than for the other cases.

Values of the asymmetry parameter and ρ [a useful factor equal to $(1+\eta^2/3)^{1/2}$] were computed using Eqs. (A6) from the Appendix. These values, along with those obtained⁶ for Ba^{137} , are listed in Table II. The values of ν_Q , computed by using Eqs. (A7) in the Appendix, are listed in Table III.

The ratios of the electric quadrupole moments (Q_{137}/Q_{135}) for the three crystal orientations are 1.542, 1.539, and 1.548 for the z , y , and x axes, respectively, parallel to H . The average value of Q_{137}/Q_{135} is 1.543 ± 0.003 .^{6a}

DISCUSSION

The results on FG orientation and asymmetry parameter (here and in reference 6) show that the sites for Ba^{137} and Ba^{135} nuclei are identical. Since the electric environments around either nucleus are the same, the ratio of the pure quadrupole resonance frequencies must be the same as the ratio between the moments.

There seems to be a progressive upward shift in ν_Q for the z , y , and x axes successively parallel to H . This

TABLE II. Values of the asymmetry parameter and ρ for the FG at the barium sites in barium bromide dihydrate. The second set of values for z parallel to H when Ba^{137} was used were obtained with the crystal rotated 90° about an axis parallel to H .

Crystal orientation	Isotope	η	ρ
$z \parallel H$	135	0.700	1.079
$z \parallel H$	137	0.760	1.092
$z \parallel H$	137	0.729	1.085
$y \parallel H$	135	0.736	1.087
$y \parallel H$	137	0.722	1.083
$x \parallel H$	135	0.724	1.084
$x \parallel H$	137	0.714	1.081
Average		0.726 ± 0.006	1.084 ± 0.001

^{6a} Note added in proof. H. Bucka, H. Kopfermann, and G. zu Putlitz [Z. Physik **165**, 72 (1961)] recently have measured the quadrupole moments to be $+0.30$ and 0.20×10^{-24} cm² for Ba^{137} and Ba^{135} , respectively. They find their ratio to be 1.54, in excellent agreement with our value. They observed the hyperfine structure in the spectrum from a barium atomic beam, using a double resonance method.

TABLE III. Values of the pure quadrupolar resonance frequencies (in Mc/sec) of Ba^{135} and Ba^{137} in $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$. Average values of η and ρ from Table II were used in the computation. The two sets of values for Ba^{137} when z is parallel to H have been averaged. The probable errors in the average values of ν_Q for Ba^{135} and Ba^{137} are estimated to be ± 0.03 and ± 0.05 Mc/sec, respectively.

Isotope	Transition	$z \parallel H$	$y \parallel H$	$x \parallel H$
135	β^+	15.80	15.90	16.16
	α^+	15.82	15.89	16.09
	α^-	15.73	15.89	16.09
	β^-	15.77	15.88	16.04
	Average	15.78	15.89	16.09
137	β^+	24.30	24.50	25.14
	α^+	24.34	24.35	24.83
	α^-	24.34	24.47	24.90
	β^-	24.35	24.50	24.82
	Average	24.33	24.45	24.92

is most marked for the x axis for Ba^{137} . Thus, ν_Q is slightly dependent on crystal orientation. Further evidence is the essential equality of the moment ratios for the three orientations. Possibly a theoretical treatment that is good to second order in H would show that ν_Q should be weakly dependent on orientation.

The graph of measured quadrupole moments for many nuclei given by Townes, Foley, and Low⁷ leads one to expect Q_{137}/Q_{135} to be about 0.5. Our value does not agree. It would require the curve to cross the line, $Q=0$, at an odd-nucleon value less than 81 and that Q_{137} be negative and perhaps Q_{135} also. Our experiment does not indicate sign.

APPENDIX

Equations for computing η , ρ , and ν_Q can be derived as follows. Dean⁴ has shown that, for a quadrupolar nucleus of spin $\frac{3}{2}$, the energy levels in a magnetic field are given by

$$E_{\pm\frac{3}{2}} = E_0 + \xi \left[\frac{3}{2} \right], \quad E_{\pm\frac{1}{2}} = -E_0 \pm \xi \left[\frac{1}{2} \right], \quad (\text{A1})$$

where the square bracket terms are

$$[m] = [a_m^2 \cos^2 \theta + (b_m^2 + c_m^2 + 2b_m c_m \cos 2\phi) \times \sin^2 \theta]^{\frac{1}{2}}, \quad (\text{A2})$$

and m stands for the quantum numbers $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$. The coefficients are given by

$$\begin{aligned} a_{\frac{3}{2}} &= -1 - 2/\rho, & a_{\frac{1}{2}} &= -1 + 2/\rho, \\ b_{\frac{3}{2}} &= 1 - 1/\rho, & b_{\frac{1}{2}} &= 1 + 1/\rho, \\ c_{\frac{3}{2}} &= \eta/\rho, & c_{\frac{1}{2}} &= -\eta/\rho, \\ \rho &\equiv (1 + \eta^2/3)^{\frac{1}{2}}. \end{aligned} \quad (\text{A3})$$

ξ is defined to be $\gamma h H / 2$. θ is the polar angle between H and the z axis of the FG while ϕ is the azimuthal angle between the x axis of the FG and H . E_0 is $e^2 q Q \rho / 4$ where e , q , and Q have their usual meanings. E_0 also equals $\hbar \nu_Q / 2$.

⁷ C. H. Townes, H. M. Foley and W. Low, Phys. Rev. **76**, 1414 (1949).

Equations (A1), (A2), and (A3) are correct for any possible value of η and to first order in H . Dean states that the first-order theory is adequate when $\gamma\hbar H \ll e^2 q Q$. In this case, the left side of the inequality ranged from 1/22 to 1/15 of the right side.

Equations (A1) indicate that the quadrupolar resonance frequencies are given by

$$\nu = \frac{2E_0}{h} \pm \frac{\xi}{h} \left\{ \left[\frac{3}{2} \right] \pm \left[\frac{1}{2} \right] \right\}. \quad (\text{A4})$$

Now $\xi = \gamma_{\text{Ba}} \hbar H / 2$ and the proton resonance frequency, ν_p , is equal to $\gamma_p H / 2\pi$. This in turn must equal ν for enhancement. Thus, we have

$$\nu_p = \frac{2E_0/h}{1 \mp (\gamma_{\text{Ba}}/2\gamma_p) \left\{ \left[\frac{3}{2} \right] \pm \left[\frac{1}{2} \right] \right\}} \quad (\text{A5})$$

as the relation between the frequency of the enhanced PMR and the orientation of the FG within the crystal with respect to H .

When the FG axes are parallel to H , Eq. (A5) takes simpler forms that can be used for computing the value of η . A little algebraic manipulation results in these equations.

When $z \parallel H$:

$$\rho = \pm \frac{2\gamma_{\text{Ba}}}{\gamma_p} \frac{\nu_{p\beta+} + \nu_{p\beta-}}{\nu_{p\beta+} - \nu_{p\beta-}}. \quad (\text{A6})$$

(α transitions give no information.)

When $y \parallel H$:

$$\frac{\rho}{1+\eta} = \pm \frac{\gamma_{\text{Ba}}}{\gamma_p} \frac{\nu_{p\beta+} + \nu_{p\beta-}}{\nu_{p\beta+} - \nu_{p\beta-}}. \quad (\text{A6}')$$

(α transitions give no information.)

When $x \parallel H$:

$$\frac{\rho}{1-\eta} = \pm \frac{\gamma_{\text{Ba}}}{\gamma_p} \frac{\nu_{p\alpha+} + \nu_{p\alpha-}}{\nu_{p\alpha+} - \nu_{p\alpha-}}. \quad (\text{A6}'')$$

(β transitions give no information.)

Further manipulation of Eqs. (A5) results in these equations that can be used to compute ν_Q .

When $z \parallel H$:

$$\beta \pm \text{ transitions, } \nu_Q = \nu_p [1 \mp 2\gamma_{\text{Ba}}/\gamma_p \rho],$$

$$\alpha \pm \text{ transitions, } \nu_Q = \nu_p [1 \mp \gamma_{\text{Ba}}/\gamma_p].$$

When $y \parallel H$:

$$\beta \pm \text{ transitions, } \nu_Q = \nu_p [1 \mp \gamma_{\text{Ba}}(1+\eta)/\gamma_p \rho], \quad (\text{A7})$$

$$\alpha \pm \text{ transitions, } \nu_Q = \nu_p [1 \mp \gamma_{\text{Ba}}/\gamma_p].$$

When $x \parallel H$:

$$\beta \pm \text{ transitions, } \nu_Q = \nu_p [1 \mp \gamma_{\text{Ba}}/\gamma_p],$$

$$\alpha \pm \text{ transitions, } \nu_Q = \nu_p [1 \mp \gamma_{\text{Ba}}(1-\eta)/\gamma_p \rho].$$