

## Quadrupole Moment of Li<sup>6</sup>

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Analysis of a relatively well-resolved molecular beam electric resonance spectrum of Li<sup>6</sup>F  $v=0, J=1; M_J=0 \rightarrow |M_J|=1$  yields  $eqQ=7.3 \pm 0.4$  kc/sec. Comparison of the coupling constants in Li<sup>6</sup>F and Li<sup>7</sup>F gives the ratio quadrupole moments of the two stable lithium isotopes to be  $Q(\text{Li}^6)/Q(\text{Li}^7) = +0.0176 \pm 0.001$ . This value is in good agreement with the earlier determination of sign by Kusch and magnitude by Cranna. Combining the measured quadrupole coupling constant in LiH with the electric field gradient calculated by Nesbet and Kahalas yields the nuclear quadrupole moments  $Q(\text{Li}^6) = -8.0 \times 10^{-28}$  cm<sup>2</sup> and  $Q(\text{Li}^7) = -4.5 \times 10^{-26}$  cm<sup>2</sup>. The errors in both quadrupole moments are estimated to be  $\pm 10\%$ .

### INTRODUCTION

LITHIUM-6 is the next-to-lightest stable nucleus having a quadrupole moment. Since the quadrupole moment is strongly sensitive to the nuclear wave function, there has been considerable effort in obtaining wave functions which predict this moment. In view of relatively large number of nucleons involved, complete dynamical models for lithium-6 are too complex to yield accurate predictions for observables.<sup>1</sup> It has therefore been used to test simplifying models of nuclear structure.

To a large extent the ground state of Li<sup>6</sup> resembles deuterium having spin 1, and a magnetic moment of  $+0.822$  nm as compared with  $+0.857$  nm. The ground state of lithium-6 is assigned as principally <sup>3</sup>S<sub>1</sub> of the configuration  $s^4p^2$ . As such its quadrupole moment should be small and should arise from the admixture of <sup>3</sup>D<sub>1</sub> and <sup>1</sup>P<sub>1</sub> components, by noncentral forces. Generally most calculations have yielded a small *positive* quadrupole moment.

It has long been known that the quadrupole moment of Li<sup>6</sup> is very small. Molecular beam magnetic resonance spectra of lithium chloride by Kusch<sup>2</sup> gave both the sign and magnitude of the quadrupole coupling constants for Li<sup>6</sup> and Li<sup>7</sup>. The coupling constant was determined to be positive in both Li<sup>6</sup> and Li<sup>7</sup> showing that both nuclei have the same sign for their electric quadrupole moments. Because of the small value of  $(eqQ)_{\text{Li}^6}$  in LiCl the sign determination was difficult. The magnitude of the ratio of quadrupole moments was determined most accurately by Cranna<sup>3</sup> by Zeeman spectra of single crystals of the mineral spodumene. The ratio found was

$$|Q_{\text{Li}^6}/Q_{\text{Li}^7}| = 0.019 \pm 0.001.$$

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<sup>1</sup> P. H. Wackman and N. Austern, Nucl. Phys. **30**, 529 (1962). This paper serves as an excellent bibliography and review of the structure and energy levels of Li<sup>6</sup>.

<sup>2</sup> P. Kusch, Phys. Rev. **92**, 268 (1953).

<sup>3</sup> N. G. Cranna, Can. J. Phys. **31**, 1185 (1953). Earlier work on spodumene by N. A. Schuster and G. E. Pake, Phys. Rev. **81**, 157 (1951) gave

$$|Q_{\text{Li}^6}/Q_{\text{Li}^7}| = 0.023 \pm 0.002.$$

The quadrupole moment of Li<sup>7</sup> has been determined in a similar manner to that of the deuteron, namely, by measurement of the quadrupole coupling constant in a simple molecule and calculation of the electric field gradient at the lithium nucleus from reliable molecular wave functions. The quadrupole coupling constant in Li<sup>7</sup>H is  $355 \pm 2$  kc/sec at the equilibrium internuclear separation.<sup>4</sup> Calculations of the electric field gradient were made by Nesbet and Kahalas<sup>5</sup> using an approximate Hartree-Fock function for the molecular wave function. This function shows good agreement with several other molecular parameters and should be reliable for the electric field gradient since considerable effort was expended to include a large enough basis set around the lithium center. From this combination of experiment and computation the quadrupole moment of Li<sup>7</sup> is  $Q_{\text{Li}^7} = -4.5 \times 10^{-26}$  cm<sup>2</sup>. Using the value of the ratio of moments of Cranna and the sign determined by Kusch the quadrupole moment of Li<sup>6</sup> is the  $Q_{\text{Li}^6} = -8.6 \times 10^{-28}$  cm<sup>2</sup>. The present work is a redetermination of the ratio  $Q_{\text{Li}^6}/Q_{\text{Li}^7}$  using a different technique. The present results, as shall be shown, are entirely in agreement with the earlier work.

### EXPERIMENT AND RESULTS

The molecular beam electric resonance spectrometer used in this investigation is described elsewhere.<sup>6</sup> Briefly, it has electric quadrupole *A* and *B* fields for state selection. The *C* field, transition region, is 27 cm long. The molecular beam is detected with a hot tungsten surface ionizer and mass spectrometer. This readily enables separation of Li<sup>6</sup> from Li<sup>7</sup> and gives good signal-to-noise levels for Li<sup>6</sup>F with natural LiF. The resonance is observed as a decrease in detected beam intensity.

<sup>4</sup> L. Wharton, L. P. Gold, and W. Klemperer, J. Chem. Phys. **37**, 2149 (1962).

<sup>5</sup> S. L. Kahalas and R. K. Nesbet, Phys. Rev. Letters **6**, 549 (1961) and J. Chem. Phys. **39**, 529 (1963). The small difference in  $Q_{\text{Li}^7}$  in the present paper and that of Kahalas and Nesbet is that we use  $(eqQ)_{\text{Li}^7}$  in Li<sup>7</sup>H = 355 kc/sec at the equilibrium internuclear separation. These authors actually used a wave function which included configuration interaction. It is not expected that electron correlation should appreciably alter the expectation value of one electron operators such as the electric field gradient at the lithium nucleus.

<sup>6</sup> L. Wharton and W. Klemperer, J. Chem. Phys. **39**, 1881 (1963).

TABLE I. Experimental hyperfine constants of the ground vibrational state of Li<sup>7</sup>F and predicted values for Li<sup>6</sup>F (all constants are given in kc/sec).

	$eqQ$	$C_{Li}$	$C_F$	$T_{LiF}$	$J_{LiF}$
Li <sup>7</sup> F	416.02 ± 0.6	1.80 ± 0.03	32.37 ± 0.3	11.390 ± 0.015	0.21 ± 0.04
Li <sup>6</sup> F		0.765 ± 0.01	36.31 ± 0.4	4.310 ± 0.010	0.080 ± 0.015

The electric resonance spectra of Li<sup>6</sup>F and Li<sup>7</sup>F have been studied extensively.<sup>7-11</sup> The rotational reorientation spectrum in an electric field is well fitted by the Hamiltonian:

$$\begin{aligned} \mathcal{H} = & -\mu \cdot E - (eqQ)_{Li} \frac{3(\mathbf{I}_{Li} \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_{Li} \cdot \mathbf{J}) - \mathbf{I}_{Li}^2 \mathbf{J}^2}{2I_{Li}(2I_{Li} - 1)(2J - 1)(2J + 3)} \\ & + C_{Li}(\mathbf{I}_{Li} \cdot \mathbf{J}) + C_F(\mathbf{I}_F \cdot \mathbf{J}) \\ & + T_{LiF} \frac{3(\mathbf{I}_{Li} \cdot \mathbf{J})(\mathbf{I}_F \cdot \mathbf{J}) + 3(\mathbf{I}_F \cdot \mathbf{J})(\mathbf{I}_{Li} \cdot \mathbf{J}) - 2(\mathbf{I}_{Li} \cdot \mathbf{I}_F)\mathbf{J}^2}{(2J + 3)(2J - 1)} \\ & + J_{LiF} \mathbf{I}_{Li} \cdot \mathbf{I}_F. \quad (1) \end{aligned}$$

Table I lists the constants of Li<sup>7</sup>F obtained from a recent investigation.<sup>12</sup> With the exception of the quadrupole coupling constant these constants are readily transferred to those appropriate for Li<sup>6</sup>F, since the ratio of masses and of nuclear magnetic moments of Li<sup>6</sup> and Li<sup>7</sup> are well known.<sup>13</sup> The constants of Li<sup>6</sup>F computed from those of Li<sup>7</sup>F are listed in Table I.

The transition  $v=0, J=1; M_J=0 \rightarrow |M_J|=1$  of Li<sup>6</sup>F was studied at an electric field strength of 600 V/cm. The observed spectrum is shown in Fig. 1(a). The spectrum as shown was observed with the earth's magnetic field reduced to  $25 \pm 5$  mG. Without this reduction, the earth's field is almost perpendicular to our applied electric field and produces observable changes in the spectrum.

The spectrum was fitted using the Hamiltonian of

<sup>7</sup> R. Braunstein and J. W. Trischka, Phys. Rev. **88**, 1085 (1952).

<sup>8</sup> R. Braunstein and J. W. Trischka, Phys. Rev. **98**, 1992 (1955).

<sup>9</sup> S. O. Kastner, A. M. Russell, and J. W. Trischka, J. Chem. Phys. **23**, 1730 (1955); A. M. Russell, Phys. Rev. **111**, 1558 (1957).

<sup>10</sup> A. J. Hebert, Ph.D. thesis, University of California, Berkeley, California, 1962 (unpublished).

<sup>11</sup> L. P. Gold, Ph.D. thesis, Harvard University, 1961 (unpublished).

<sup>12</sup> L. Wharton, L. P. Gold, and W. Klemperer, J. Chem. Phys. (to be published).

<sup>13</sup> These constants were obtained by fitting 20 lines of the transition  $v=0, J=1; M_J=0 \rightarrow |M_J|=1$  and  $v=0, J=2; |M_J|=1 \rightarrow |M_J|=2$ . The above five hyperfine constants plus the two Stark coefficients were fitted by a least-squares procedure. The errors quoted are  $1\frac{1}{2}$  standard deviations. The standard deviation between observed and calculated spectra (199 cps) agrees well with the standard deviation of line measurement (180 cps). Analysis of the  $v=1, J=1; M_J=0 \rightarrow |M_J|=1$  and  $v=2, J=1; M_J=0 \rightarrow |M_J|=1$  yielded constants of somewhat lower accuracy than those appropriate to the ground vibrational state. In general it was observed that the variation of hyperfine constants with vibrational state was small (less than 5% per vibration). The variation of constants due to differences in zero-point vibrational amplitude of the ground vibrational states of Li<sup>6</sup>F and Li<sup>7</sup>F is only 4% of the variation of the constant per vibrational state, no appreciable errors are, therefore, incurred due to zero-point vibration.

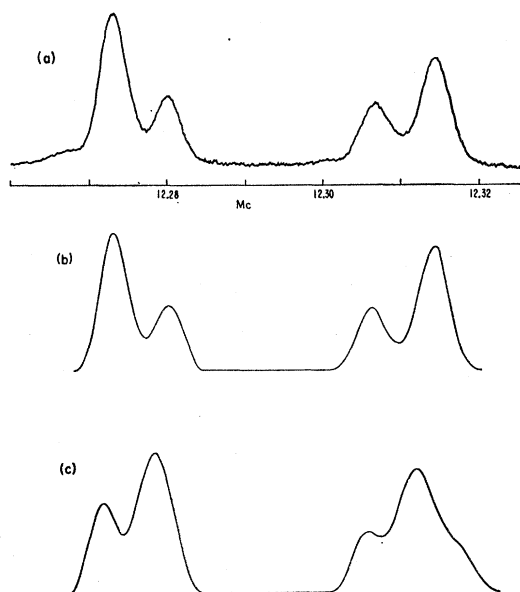


FIG. 1. Stark spectrum of Li<sup>6</sup>F<sup>19</sup>  $v=0, J=1, M_J=0 \rightarrow M_J=1$  in a strong electric field. The spectrum was observed at a field strength of 600 V/cm. (a) Observed spectrum; (b) spectrum calculated with  $eqQ=+7.9$  kc/sec; (c) spectrum calculated with  $eqQ=-7.9$  kc/sec.

Eq. (1) and the constants listed in Table I, all of which are obtained from the analysis of Li<sup>7</sup> spectra. Figures 1(b) and 1(c) show calculated spectra using  $eqQ$  of  $+7.9$  and  $-7.9$  kc/sec, respectively. (This is the value expected on the basis of Cranna's ratio of nuclear quadrupole moments.)

The observed spectrum is composed of thirteen hyperfine lines. There are a number of lines in each resolved feature. The spectra are calculated by using the linewidth of 4.2 kc observed in Li<sup>7</sup>F (in Li<sup>7</sup>F there are a number of unblended lines) and a Gaussian shape. The lines of Li<sup>7</sup>F do show a Gaussian shape down to about 15% of their peak height. Since we are primarily interested in the separation of the maxima of the resolved features, the exact shape of the lines near their base is relatively unimportant. The intensities of individual hyperfine lines were assumed to be proportional to the line strengths calculated by diagonalization of Eq. (1).

From examination of Fig. 1 there can be no doubt that the quadrupole coupling constant in Li<sup>6</sup>F is positive. The value of the coupling constant was obtained from the splitting of the low-frequency doublet. A best fit to the measured splitting of 6.91 kc/sec was obtained with  $eqQ=7.25$  kc/sec. We estimate that the splitting can be measured to  $\pm 70$  cps.

The Hamiltonian contains several terms whose effect upon the spectrum is larger than the quadrupole coupling constant. The largest term (neglecting the Stark term which only determines the frequency location of the whole pattern) is the fluorine spin-rotation constant. Its effect upon the spectrum is to vary the large separation (40 kc/sec) between the high- and low-

frequency doublets. The uncertainty of 300 cps estimated for this constant changes the doublet separation by 3 cps and therefore has no effect upon the quality of the quadrupole coupling constant deduced. The next largest term is the tensor spin-spin interaction which consists of two parts, by far the largest is the classical dipole-dipole interaction of the two nuclear magnetic moments. This part can be calculated to 1 cps.<sup>14</sup> The second term, the electron coupled tensor spin-spin interaction cannot be well estimated at present. For the lowest vibrational state of Li<sup>7</sup>F the total tensor spin-spin interaction differs from the calculated classical dipole-dipole interaction by approximately 6 cps. This is considerably less than the experimental uncertainty in the constant. The uncertainty of 10 cps in the tensor spin-spin interaction in Li<sup>6</sup>F results in an uncertainty of 12 cps in the calculated doublet separation. The lithium spin rotation constant is small and well known from the spectra of Li<sup>7</sup>F. Its uncertainty of 10 cps in Li<sup>6</sup>F introduces an error of 18 cps in the calculated doublet separation. The electron coupled scalar spin-spin interaction is very small in Li<sup>6</sup>F and its uncertainty of 15 cps introduces 7-cps error into the calculated doublet separation.

The quadrupole coupling constant is determined from its effect upon the calculated low-frequency doublet separation. Unfortunately the variation of the splitting of this doublet is relatively slow with variation of the quadrupole coupling constant. The error of 70 cps in *measuring* the low-frequency doublet separation is by far larger than any of the above listed errors in calculating the doublet separation. The error in the quadrupole coupling constant is therefore determined from the measuring error and is 0.4 kc/sec.

The ratio of quadrupole coupling constant in Li<sup>6</sup>F and Li<sup>7</sup>F, corrected to a common vibrational energy, which is the ratio of nuclear quadrupole moments is  $+0.0176 \pm 0.001$ . This result is in excellent agreement with the earlier ratio of Cranna,  $0.019 \pm 0.001$  in magnitude and agrees with the magnetic resonance determination of sign by Kusch.

#### DISCUSSION

The best present value of the nuclear quadrupole moment of Li<sup>7</sup> is  $Q_{\text{Li}^7} = -4.5 \times 10^{-26}$  cm<sup>2</sup>. The uncertainty in this value derives entirely from the uncertainty in the calculated value of the electric field gradient at the lithium nucleus in LiH. At present this uncertainty is difficult to estimate reliably but is probably less than 10%. The quadrupole moment of Li<sup>6</sup>, using the presently determined ratio, is therefore  $Q_{\text{Li}^6} = -8.0 \times 10^{-28}$  cm<sup>2</sup>. The uncertainty of this value is similar to that in Li<sup>7</sup>, namely 10%, since the ratio of quadrupole moments is known to 5%.

There have been a number of discussions of the

quadrupole moment of Li<sup>6</sup>. Quite generally the ground-state wave function is taken as

$$\psi = C_1 {}^3S_1 + C_2 {}^1P_1 + C_3 {}^3D_1.$$

The quadrupole moment is then<sup>14a</sup>

$$Q = -(1/5)e\langle r^2 \rangle [(4/5)C_1C_3 + (7/10)C_3^2 - C_2^2].$$

Pinkston and Brennan<sup>15</sup> have shown that although the energy levels of Li<sup>6</sup> may be fitted with an interaction between the valence nucleons consisting of a central potential plus spin-orbit terms, the quadrupole moment is then positive for all values of the spin-orbit coupling strength. They do show that a weak tensor interaction between the two nucleons results in a negative quadrupole moment. The magnitude of the quadrupole moment is quite sensitive to the orbital functions assumed and to the range of the tensor force. The above authors show that a range of parameters will give the observed quadrupole moment.

The calculation of Wackman and Austern<sup>1</sup> is considerably less empirical than that of Pinkston and Brennan. The coefficients in the wave function of Wackman and Austern are obtained from a variational treatment of a relatively complete Hamiltonian (for the two outer nucleons). These authors obtain  $Q = +3.3 \times 10^{-28}$  cm<sup>2</sup>. It is not clear whether relatively minor changes in the functional form of the radial part of their variational function will produce agreement with the observed quadrupole moment, or if it is necessary to regard the alpha particle as nonrigid. From the work of Pinkston and Brennan it appears that small changes in the form of the radial function produce appreciable changes in the quadrupole moment calculated.

*Note added in proof.* Wackman and Austern have examined in considerable detail this question.<sup>16,17</sup> They conclude that the quadrupole moment is quite insensitive to the changes in the radial part of the variational function. Furthermore, they point out that as the effect of the tensor force becomes more important, good agreement with the experimental binding energy is obtained. The quadrupole moment is then calculated to be of opposite sign from that observed here. Thus, it appears necessary to assume a nonrigid alpha particle to explain the quadrupole moment of lithium-6.

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<sup>14a</sup> This expression assumes infinite mass for the core. A complete expression is given by Wackman and Austern, Ref. 1.

<sup>15</sup> W. T. Pinkston and J. G. Brennan, Phys. Rev. **109**, 499 (1958).

<sup>16</sup> N. Austern and P. H. Wackman, Bull. Am. Phys. Soc. **8**, 56 (1963).

<sup>17</sup> N. Austern and P. H. Wackman (private communication).

<sup>14</sup> See L. Wharton, W. Klemperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. **38**, 1203 (1963), for the microwave spectrum and potential energy curve of LiF.