

# An anomaly in the isotopomer shift of the hyperfine spectrum of LiI

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A high-precision examination of the hyperfine spectrum of <sup>6</sup>LiI in comparison with <sup>7</sup>LiI shows a shift in the iodine nuclear electric quadrupole moment that cannot be accounted for by a model in which the electric field gradient at the iodine site is assumed to depend only upon the internuclear distance between Li and I. The other hyperfine interactions are consistent between the two isotopomers, including the previously reported electric hexadecapole interaction of the iodine nucleus. © 2005 American Institute of Physics. [DOI: 10.1063/1.2052588]

## I. INTRODUCTION

The technique of molecular-beam spectroscopy is a very precise method of measuring molecular hyperfine interactions. In a previous paper<sup>1</sup> we reported our measurements for <sup>7</sup>LiI, from which we found evidence for a nuclear electric hexadecapole. The present experiment was intended to determine whether this interaction would also appear, with a consistent magnitude, for <sup>6</sup>LiI. Commercial <sup>6</sup>LiOH was reacted with HI, and the water baked off to obtain the anhydrous salt. We have measured a total of 163 transitions, with a precision that ranges between 1.4 and 140 Hz, including vibrational states  $v=0-3$  and rotational states  $J=1-5$ . From these we have fitted for the coefficients that describe the dependence of these interactions on the vibration and rotation states, including the two isotopomers together by using the expected dependence on atomic masses and magnetic moments.

In doing this we find that a term with the angular momentum dependence of the hexadecapole interaction is identifiable in both isotopomers. More significantly, however, we find that the iodine nuclear electric quadrupole coupling constant (NQCC) shifts by about 14 kHz when the lithium isotope is changed. We do not have an explanation for this shift but assume that it must be due to either a violation of the

Born-Oppenheimer approximation or a dependence of the pseudoquadrupole effect on the position of the center of mass of the molecule.

The apparatus used for this experiment will not be discussed since it has been described previously.<sup>1-5</sup>

## II. THEORY

For diatomic molecules, such as the alkali-halide salts, the conventional Hamiltonian is of the general form

$$H = H_{\text{elect}} + H_{\text{vib}} + H_{\text{rot}} + H_{\text{hyperfine}} + H_{\text{Stark}}. \quad (1)$$

The possible hyperfine terms with LiI include the nuclear electric quadrupole interactions for I and Li, the spin rotation for both nuclei, the tensor spin-spin, the scalar spin-spin, the magnetic octupole interaction for I, and the electric hexadecapole interaction for I, as represented by the following tensor product forms:

$$\begin{aligned} \frac{H_{\text{hyperfine}}}{h} = & \mathbf{V}_I^{(2)} \cdot \mathbf{Q}_I^{(2)} + \mathbf{V}_{Li}^{(2)} \cdot \mathbf{Q}_{Li}^{(2)} + c_1 \mathbf{I}_I \cdot \mathbf{J} + c_{Li} \mathbf{I}_{Li} \cdot \mathbf{J} \\ & + c_3 \mathbf{I}_I \cdot \mathbf{D} \cdot \mathbf{I}_{Li} + c_4 \mathbf{I}_I \cdot \mathbf{I}_{Li} + \omega_I^{(3)} \cdot \mathbf{Q}_I^{(3)} \\ & + \mathbf{h}_I^{(4)} \cdot \mathbf{H}_I^{(4)}. \end{aligned} \quad (2)$$

The Stark hamiltonian is given by

$$H_{\text{Stark}} = -\boldsymbol{\mu} \cdot \mathbf{E}. \quad (3)$$

A magnetic octupole interaction would also be allowed for <sup>7</sup>Li, but was not expected to be significant and not included in the fit. The magnetic octupole interaction for iodine was tested but found to not contribute significantly. The iodine electric hexadecapole interaction, on the other hand, does remain significant for the <sup>6</sup>LiI isotopomer as it was for the <sup>7</sup>LiI.

The iodine quadrupole interaction dominates the hyperfine spectrum, so that we used the coupling

$$\mathbf{F}_I = \mathbf{J} + \mathbf{I}_I, \quad \mathbf{F} = \mathbf{F}_I + \mathbf{I}_{Li}. \quad (4)$$

Edmonds<sup>6</sup> describes techniques to represent the hyperfine terms with matrix elements. The NQCC is defined as a product of two factors that represent the nucleus ( $eQ$ ) and

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the environment ( $q$ ). This product is expressed as  $eQq$ , where the “nuclear quadrupole moment” ( $Q$ ) is defined as

$$Q = \langle I, M = I | \int \rho_N r^2 (3 \cos(\theta_N) - 1) d\tau_N | I, M = I \rangle$$

$$= \frac{2}{e} \langle I, I | \int \rho_N r^2 P_2(\cos(\theta_N)) d\tau_N | I, I \rangle = \frac{2}{e} \langle I, I | Q_0^{(2)} | I, I \rangle, \quad (5)$$

and the “field gradient” ( $q$ ) or electric field gradient (EFG) as

$$q = 2 \langle |V_0^{(2)}| \rangle = \frac{\partial^2 V}{\partial z^2}. \quad (6)$$

$V_0^{(2)}$  and  $z$  relate to the molecule-fixed symmetry axis.

If the field gradient  $q$  is assumed to depend only on the distance between the two atomic nuclei, then it can be expanded in a Taylor series about the equilibrium separation distance  $r_e$ , using the expansion parameter  $\xi = (r - r_e)/r_e$ , as

$$q(\xi) = q_e + q_1 \xi + q_2 \xi^2 + \dots \quad (7)$$

Schlier<sup>7</sup> has evaluated the expectation values of the powers of  $\xi$  in any vibration and rotation state using the Dunham<sup>8</sup> treatment. The result is that the expectation value of the field gradient depends on  $v$  and  $J$  in a series of the form

$$q(v, J) = \sum_{i,j} q_{ij} (v + 1/2)^i [J(J + 1)]^j. \quad (8)$$

The coefficients  $q_{ij}$  in this expansion are known functions of the Dunham potential coefficients  $a_1, a_2, \dots$ ; the Taylor expansion coefficients  $q_1, q_2, \dots$  of the EFG about the equilibrium nuclear separation; and the ratio  $B_e/\omega_e$ . Only the latter ratio should depend on the isotope through the reduced mass.

A similar expansion would be expected for each of the other interactions as well. For the nuclear electric hexadecapole interaction, where our fit includes a nonzero contribution to the  $eHh_{00}$  term, we follow the definitions of  $H$  and  $h$  that were used in our earlier paper.<sup>1</sup> Thyssen, *et al.*<sup>9</sup> report a calculation of the hexadecapole interaction indicating that what we observe is not a true hexadecapole interaction, but rather a “pseudohexadecapole” involving the perturbation of the electron wave functions by the electric quadrupole moment of the nucleus acting back on the same electric quadrupole moment. This would have the same angular momentum dependence as the true hexadecapole and is therefore experimentally indistinguishable from it.

### III. DATA AND ANALYSIS

The pure hyperfine spectrum of LiI is spread out over the frequency range from zero up to about 70 MHz. By adjusting the voltage applied to the quadrupole lenses we can optimize the spectrometer for any rotational state up to  $J=10$ . The lines for different vibrational states simply occur at different frequencies and can be identified by the sequences of nearly equally spaced lines with intensities dropping off in accordance with the Boltzmann factor for the vibrational energy differences.

Fitting the data is a two-stage process. First we use the calculated line shape with the calculated Stark splittings to fit

the individual transition runs and determine the Stark unshifted frequencies. We then use these frequencies to fit for the molecular constants. The process is iterative because the calculation of the line shapes and Stark shifts requires the molecular constants.

The 2-m-long transition plates in our spectrometer give transitions with a linewidth of 100–200 Hz that fit nicely to a Rabi line shape averaged over a velocity distribution that we have calculated from the dimensions of the rods forming the quadrupole lenses. The pure hyperfine transitions violate the familiar  $\Delta J = \pm 1$  selection rule of infrared and microwave spectroscopies, but by using a combination of dc and rf fields of sufficient size we can achieve nearly complete saturation of the transitions. These second-order transitions follow a  $\Delta F = 0, \pm 1, \pm 2$  selection rule. In our configuration the dc and rf fields are parallel so that there is a  $\Delta M_F = 0$  selection rule. It is the strong-field Stark effect that determines whether a hyperfine state is focused or defocused by the lenses. The close match of our experimental lines to the theory makes it possible for us to determine line frequencies to a small fraction of the linewidth and also deconvolute overlapping lines.

The dc and rf fields needed to produce the transitions also give rise to a Stark splitting of the levels that is a function of the sum of the squares of the dc and rf (rms) fields. For some transitions these shifts can be small compared to the linewidth but are rarely negligible compared to our fitted precision. For this reason we need to correct for the Stark shifts in order to achieve the full precision of the experimental data. This in turn requires that we know the fields with reasonable accuracy. The dc field is fairly straightforward to determine, but the rf field is more problematic because of standing-wave effects in the cables and the plates themselves. An rf probe located on the plates gives a useful measurement, but still does not tell us what the effective average of the field is over the length of the plates. In fact two different averages of this rf field are needed. To determine the effective average of the square of the rf over the plates we have turned to the molecules themselves, by using fields that are just large enough to fully resolve the Stark components of each line, and then fitting for the rf amplitude squared, averaged over the length of the plates, that corresponds to this splitting. The line shape, on the other hand, depends on the averaged product of the rf and dc fields. We obtain this product from our fit as well. An example of such a fit is shown in Fig. 1.

Because of the spin ( $I=1$ ) of the  ${}^6\text{Li}$  nucleus and the small size of its nuclear electric quadrupole moment (the smallest known for any nucleus), the hyperfine energies come in sets of three closely spaced levels that share the same  $F_1$  quantum number but differ in the value of  $F$ . Our observed transitions therefore come in sets of nine, with an additional Stark splitting, as can be seen in the example shown. These are mostly resolved but there is some overlap at our experimental linewidth. The nine transition frequencies in each set are not independent; for example, if the upper three levels are called  $a, b$ , and  $c$ , and the lower three levels 1, 2, and 3, then the difference between the transitions  $a \rightarrow 1$  and  $a \rightarrow 2$  would be the same as the difference between  $b \rightarrow 1$  and  $b \rightarrow 2$ . Thus only five of the nine frequencies in

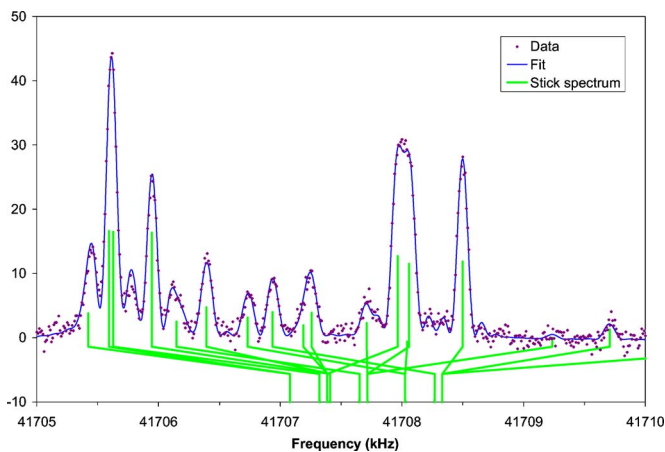


FIG. 1. Fitted data showing the set of nine Stark-split lines for  $\nu=0$ ,  $J=3$ , and  $F_1=3/2 \rightarrow 7/2$ .

each set are independent. We have built these constraints into our fitting of the lines, so that only the five arbitrarily chosen independent frequencies are listed in the table.

The results of the fits for the observed lines are listed in a table filed with EPAPS.<sup>10</sup> The Stark-corrected measured line frequencies are shown there, along with our estimates of their one-sigma statistical uncertainties, their quantum-number identifications, and the predicted frequencies and residuals. The measured frequencies are fitted, both isotopes together, to determine the molecular constants that are listed in Table I. The values of the constants for  $^6\text{LiI}$  are not fitted independently from those for  $^7\text{LiI}$  (except for the nuclear electric quadrupole interaction) but are calculated using the expected dependence on  $B_e/\omega_e$  and the known nuclear magnetic moments. The NQCC terms for lithium are scaled from  $^7\text{LiI}$  to  $^6\text{LiI}$  using the ratio  $^6Q/^7Q$  determined from the LiF measurements reported previously.<sup>4</sup> When we fitted the new  $^6\text{LiI}$  data separately from the earlier  $^7\text{LiI}$  we obtained similar results, although this required reducing the number of expansion parameters. Because of this we present here only the results of the combined fit.

The fitting of the molecular constants to these line frequencies utilizes the singular value decomposition (SVD) method. This method separates the fitted parameters and the associated errors by finding linear combinations of the fitted parameters to eliminate correlations. In order to take into account the matrix elements of the nuclear electric quadrupole interactions that are off-diagonal in the rotational states, we combine the rotational Hamiltonian with the hyperfine and Stark terms. The energy levels are then found as the eigenvalues of this combined matrix. The isotopomers and vibrational states are diagonalized separately but combined into a single SVD fit. The reduced  $\chi$  value for the fit is about 2.14. This means that there are probably some other small effects, either terms in the expansion or systematic errors in the frequency measurements, that we have not accounted for. The uncertainties in the molecular parameters have been scaled to take this into account.

TABLE I. Molecular constants determined from fit (all in kHz).

$i, j$	$^7\text{LiI}$ constants	$^6\text{LiI}$ constants
Iodine quadrupole ( $eQq_{\text{Li}ij}$ ) <sup>a</sup>		
0,0	$-194\,352.41 \pm 0.20$	$194\,338.34 \pm 0.20$
1,0	$-8275.78 \pm 0.60$	$-8904.34 \pm 0.64$
2,0	$97.69 \pm 0.46$	$113.09 \pm 0.53$
3,0	$0.26 \pm 0.10$	$0.32 \pm 0.13$
0,1	$-6.419\,69 \pm 0.000\,88$	$-7.4320 \pm 0.0010$
1,1	$0.104\,93 \pm 0.000\,72$	$0.130\,71 \pm 0.000\,90$
Lithium quadrupole ( $eQq_{\text{Li}ij}$ )		
0,0	$172.19 \pm 0.22$	$3.4912 \pm 0.0045$
1,0	$-1.92 \pm 0.66$	$-0.042 \pm 0.014$
2,0	$-1.09 \pm 0.51$	$-0.026 \pm 0.012$
3,0	$0.25 \pm 0.11$	$0.0064 \pm 0.0028$
0,1	$-0.0001 \pm 0.0019$	$-0.000\,002 \pm 0.000\,044$
1,1	$0.0014 \pm 0.0020$	$0.000\,036 \pm 0.000\,050$
Iodine spin rotation ( $c_{\text{Li}ij}$ )		
0,0	$6.8433 \pm 0.0061$	$7.9224 \pm 0.0070$
1,0	$-0.115 \pm 0.018$	$-0.143 \pm 0.022$
2,0	$0.089 \pm 0.014$	$0.119 \pm 0.019$
3,0	$-0.0198 \pm 0.0031$	$-0.0285 \pm 0.0045$
0,1	$-0.000\,239 \pm 0.000\,025$	$-0.000\,320 \pm 0.000\,034$
1,1	$0.000\,181 \pm 0.000\,024$	$0.000\,261 \pm 0.000\,035$
Lithium spin rotation ( $c_{\text{Li}ij}$ )		
0,0	$0.7583 \pm 0.0014$	$0.332\,41 \pm 0.000\,59$
1,0	$-0.0094 \pm 0.0026$	$-0.0044 \pm 0.0012$
2,0	$-0.000\,39 \pm 0.000\,93$	$-0.000\,20 \pm 0.000\,47$
Tensor spin-spin ( $c_{3ij}$ )		
0,0	$0.6287 \pm 0.0015$	$0.238\,05 \pm 0.000\,58$
1,0	$-0.0075 \pm 0.0028$	$-0.0030 \pm 0.0011$
2,0	$0.000\,80 \pm 0.000\,96$	$0.000\,35 \pm 0.000\,42$
Scalar spin-spin ( $c_{4ij}$ )		
0,0	$0.0656 \pm 0.0012$	$0.024\,85 \pm 0.000\,45$
1,0	$-0.0034 \pm 0.0021$	$-0.001\,38 \pm 0.000\,85$
2,0	$0.000\,47 \pm 0.000\,75$	$0.000\,21 \pm 0.000\,33$
Iodine hexadecapole ( $ehH_{ij}$ )		
0,0	$-0.0201 \pm 0.0025$	$-0.0201 \pm 0.0025$

<sup>a</sup> $X_{ij}$  denotes the coefficient in the expansion  $X(\nu, J) = \sum_{i,j} X_{ij}(\nu+1/2)^i [J(J+1)]^j$ .

As shown by Schlier,<sup>7</sup> the coefficient  $eQq_{00}$  in the series that describes the vibration and rotation dependences, of the iodine NQCC is equal to the equilibrium value  $eQq_e$  plus an additional term proportional to the square of the parameter  $B_e/\omega_e$ . This term can be estimated from the fitted values of the other terms in the expansion to have a value of about  $-0.2$  kHz. Our experimental data require a value of  $eQq_{00}$  for the  $^6\text{LiI}$  that differs from that for  $^7\text{LiI}$  by an additional  $+14.22 \pm 0.20$  kHz that we are unable to explain.

Our fitted value of the hexadecapole interaction constant is consistent with that reported for  $^7\text{LiI}$  previously<sup>1</sup> but is now a bit more precisely determined with the addition of our  $^6\text{LiI}$  measurements. As noted in the Theory section above, it is probably a pseudohexadecapole effect rather than a true nuclear electric hexadecapole interaction. Note also that the definition used here is smaller by a factor of 6 than that used by Thyssen *et al.*<sup>9</sup>

The ratio of the nuclear electric quadrupole moments of the two lithium isotopes was determined from the fit to be  $0.020\,28 \pm 0.000\,14$ , consistent within its uncertainty with the more accurate value obtained from LiF that was reported in Ref. 4 of  $0.020\,161 \pm 0.000\,013$ .

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<sup>1</sup>J. Cederberg, D. Olson, A. Nelson, D. Laine, P. Zimmer, M. Welge, M. Feig, T. Höft, and N. London, *J. Chem. Phys.* **110**, 2431 (1999).

<sup>2</sup>D. Olson, J. Cederberg, P. Soulen, H. Ton, K. Urberg, and B. Mock, *J. Mol. Spectrosc.* **166**, 158 (1994).

<sup>3</sup>J. Cederberg, J. Ward, G. McAlister, G. Hilk, E. Beall, and D. Olson, *J. Chem. Phys.* **111**, 8396 (1999).

<sup>4</sup>J. Cederberg, D. Olson, J. Larson, G. Rakness, K. Jarausch, J. Schmidt, B. Borovsky, P. Larson, and B. Nelson, *Phys. Rev. A* **57**, 2539 (1998).

<sup>5</sup>J. Cederberg, D. Olson, P. Soulen, K. Urberg, H. Ton, T. Steinbach, B. Mock, K. Jarausch, P. Haertel, and M. Bresnahan, *J. Mol. Spectrosc.* **154**, 43 (1992).

<sup>6</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Wiley, New York, 1957).

<sup>7</sup>C. Schlier, *Fortschr. Phys.* **9**, 455 (1961).

<sup>8</sup>J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).

<sup>9</sup>J. Thyssen, P. Schwerdtfeger, M. Bender, W. Nazarewicz, and P. Semmes, *Phys. Rev. A* **63**, 022505 (2001).

<sup>10</sup>See EPAPS Document No. E-JCPSA6-123-018536 for the table of measured line frequencies. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).