Evidence for a nuclear hexadecapole interaction in the hyperfine spectrum of LiI

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The molecular beam electric resonance technique has been used to examine the hyperfine spectrum of ^{7}LiI to determine the nuclear hexadecapole interaction of the iodine nucleus. The nuclear magnetic octupole interaction was also considered but found to be marginally significant. A total of 172 transitions in vibrational states 0-3 and rotational states 1-6 have been included in a fit to determine the iodine nuclear quadrupole, spin-rotation, and hexadecapole interactions, the lithium quadrupole and spin-rotation interactions, and the tensor and scalar parts of the spin-spin interaction. Vibration and rotation dependencies of these constants have been determined. The results include: $eHh = -0.0151(30)$, $eQ_Iq_I = -194351.212(17) - 8279.521(46)(v+1/2) + 100.616(34)(v+1/2)^2 - 0.3949(73)(v+1/2)^3 - 6.41977(50)J(J+1) + 0.10593(33)(v+1/2)J(J+1)$, $eQ_{Li}q_{Li} = 172.613(52) - 3.26(14)(v+1/2) + 0.00145(87)J(J+1)$, $c_I = 6.80260(32) + 0.00303(49)(v+1/2) - 0.000118(13)J(J+1)$, $c_{Li} = 0.75872(72) - 0.0088(11)(v+1/2)$, $c_3 = 0.62834(68) - 0.0050(11)(v+1/2)$, $c_4 = 0.06223(36) + 0.00041(26)(v+1/2)$, and $e\Omega_I\omega_I' = 0.000112(73)$, all in kHz with one standard deviation uncertainties for the last 2 digits in ( ). © *1999 American Institute of Physics.* [S0021-9606(99)01804-8]

I. INTRODUCTION

Since the discovery of the deuterium nuclear electric quadrupole interaction in 1939,[1] molecular beam spectrometry has served as one of the highest resolution techniques for observing small effects of the nuclear moments on the energies of atoms and molecules. The possibility that the charge and current distributions of an atomic nucleus could be represented by electric and magnetic multipole terms, as well as the limitations imposed on these terms by quantum mechanics, were by then well understood. The parity and time-reversal symmetries prevent odd order electric moments and even order magnetic moments from occurring in a nucleus with a definite spin state, although searches continue for such moments as violations of these symmetries. When applied to the rotational symmetry, the Wigner-Eckart theorem[2] shows further that there is an upper limit on the order of multipole moment which can be observed, depending on the nuclear spin. Thus a nucleus of spin zero can have a charge, but not a magnetic dipole moment or electric quadrupole moment, a spin-1/2 nucleus can have a charge and a magnetic dipole moment, but no quadrupole moment, etc.

Experimentally, magnetic dipole moments and electric quadrupole moments have been observed for virtually all stable nuclei with sufficient spin, and many unstable ones as well. Interactions involving higher moments, including the magnetic octupole and electric hexadecapole moments, have been searched for by various techniques, in atoms, molecules and solids.[3–10] In all such cases, what is observed experimentally is the energy of interaction of the nuclear moment with its environment. Each interaction is expressed in terms of a product of two factors, one describing the nuclear moment, and the other the shape of the electric or magnetic field produced by the electrons and other atoms surrounding the nucleus.

The experiment we describe here uses the same molecular beam electric resonance technique as that of Refs. 5,7, and, in fact uses the same apparatus and molecule as Ref. 7. The iodine nucleus has the largest electric quadrupole moment of any of the stable alkali or halide atoms. That fact, together with its spin of 5/2 makes it a likely candidate for higher moments. We have utilized a refined line fitting procedure as described in Ref. 11, and have examined a considerably larger number of transitions in more vibration and rotation states. This has improved the statistics sufficiently to yield a hexadecapole interaction which we believe to be significantly different from zero.

II. THEORY

In dealing with diatomic molecules the conventional Hamiltonian is of the form

$$H = H_{elect} + H_{vib} + H_{rot} + H_{hyperfine} + H_{Stark}, \qquad (1)$$

where, in the case of LiI, the possible hyperfine terms are

$$\frac{H_{\text{hyperfine}}}{h} = \mathbf{V}_I^{(2)} \cdot \mathbf{Q}_I^{(2)} + c_I \mathbf{I}_I \cdot \mathbf{J}$$

$$+ \mathbf{V}_{Li}^{(2)} \cdot \mathbf{Q}_{Li}^{(2)} + c_{Li} \mathbf{I}_{Li} \cdot \mathbf{J}$$

$$+ c_3 \mathbf{I}_{Li} \cdot \mathbf{D} \cdot \mathbf{I}_F + c_4 \mathbf{I}_{Li} \cdot \mathbf{I}_F$$

$$+ \boldsymbol{\omega}_I^{(3)} \cdot \boldsymbol{\Omega}_I^{(3)} + \mathbf{h}_I^{(4)} \cdot \mathbf{H}_I^{(4)} + \boldsymbol{\omega}_{Li}^{(3)} \cdot \boldsymbol{\Omega}_{Li}^{(3)} \tag{2}$$

and

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

The pure hyperfine spectrum of ^{7}LiI is dominated by the iodine quadrupole interaction, so that the appropriate representation to use is the one defined by the coupling

$$\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_I, \quad \mathbf{F} = \mathbf{F}_1 + \mathbf{I}_{Li}. \tag{4}$$

We have used the techniques of Edmonds[12] to find the matrix elements of the hyperfine terms in this representation. For the quadrupole, spin-rotation, and spin-spin interactions the conventions used in defining the molecular constants are well established. The ''nuclear quadrupole moment'' is always defined as

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

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

$$= \frac{2}{e} \langle I, I | Q_0^{(2)} | I, I \rangle, \tag{5}$$

and the ''field gradient'' as

$$q = 2\langle | V_0^{(2)} | \rangle$$

$$= \frac{\partial^2 V}{\partial z^2}, \tag{6}$$

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

There is more inconsistency in the cases of the octupole and hexadecapole interactions. The nuclear octupole and hexadecapole moments are generally defined as

$$\Omega = \frac{1}{e} \langle I, I | \int (\nabla_N \cdot m_N) r^3 P_3(\cos(\theta_N)) d\tau_N | I, I \rangle$$

$$= \frac{1}{e} \langle I, I | \Omega_0^{(3)} | I, I \rangle \tag{7}$$

and

$$H = \frac{8}{e} \langle I, I | \int \rho_N r^4 P_4(\cos(\theta_N)) d\tau_N | I, I \rangle$$

$$= \frac{8}{e} \langle I, I | H_0^{(4)} | I, I \rangle. \tag{8}$$

The factor of 2 in Eq. (5) and the factor of 8 in Eq. (8) are conventionally included in order to clear the denominator of the Legendre polynomials, but, curiously, this has not been done for the magnetic octupole, Eq. (7), following a tradition

going back at least to Jaccarino.[3]

There are various conflicting definitions of the constant h which represents the environment-dependent factor of the hexadecapole interaction. At least three distinct forms have been given in the literature:

$$h_1 = \frac{\partial^4 V}{\partial z^4}, \tag{9}$$

$$h_2 = V_0^{(4)} = \frac{1}{4!} h_1, \tag{10}$$

and

$$h_3 = 8 V_0^{(4)} = \frac{1}{3} h_1. \tag{11}$$

The first of these is commonly claimed as the definition, but in several papers,[5] for example, the equations given evidently are actually using the second form. The difference is the factorial which appears in the Taylor series expansion of a function. Other authors cite the third form, which arises by removing the denominator of the Legendre polynomial. In our quoted result we have used the second definition, so that the matrix elements of the interaction are in agreement with the equation on p. 1531 of Ref. 5:

$$\langle (I, J') F' M' | \mathbf{h}_I^{(4)} \cdot \mathbf{H}_I^{(4)} | (I, J) F M \rangle$$

$$= \tfrac{1}{8} (eHh)(-1)^{I+F} [(2J+1)(2J'+1)]^{1/2}$$

$$\times \begin{Bmatrix} F & J' & I \\ 4 & I & J \end{Bmatrix} \frac{\begin{pmatrix} J & 4 & J' \\ 0 & 0 & 0 \end{pmatrix}}{\begin{pmatrix} I & 4 & I \\ -I & 0 & I \end{pmatrix}} \delta_{M'M} \delta_{F'F}. \tag{12}$$

In the case of the magnetic octupole, Jaccarino and others have generally just used the expectation value of the operator $\omega_0^{(3)}$ as the desired ''constant,'' even though it will be proportional to the rotational angular momentum in some form. Since we are attempting to fit several rotational states at once, we need to be more explicit about this dependence. Svidzinskii[13] has reasoned that the tensor operator should take the form [his Eq. (3.17)]:

$$\boldsymbol{\omega}^{(3)} = [\mathbf{J}^{(1)} \times \mathbf{G}^{(2)}]^{(3)} + [\mathbf{J}^{(1)} \times \mathbf{G}^{(4)}]^{(3)}, \tag{13}$$

where $\mathbf{G}$ are tensor operators that are constants in the molecular reference frame, representing the perturbation of the electronic states by the molecular rotation, as they give rise to the magnetic field experienced by the nucleus. This allows us to express the reduced matrix elements of this operator as

$\langle J||\boldsymbol{\omega}^{(3)}||J\rangle$

$$= \frac{\omega}{\begin{pmatrix} J & 3 & J \\ -J & 0 & J \end{pmatrix}}$$

$$= [7]^{1/2}(-1)^{2J+3}\left[\begin{Bmatrix} 1 & 2 & 3 \\ J & J & J \end{Bmatrix} \right.$$

$$\times \langle J||\mathbf{J}^{(1)}||J\rangle\langle J||\mathbf{G}^{(2)}||J\rangle + \begin{Bmatrix} 1 & 4 & 3 \\ J & J & J \end{Bmatrix}\langle J||\mathbf{J}^{(1)}||J\rangle$$

$$\left. \times \langle J||\mathbf{G}^{(4)}||J\rangle \right]$$

$$= -\frac{1}{4}\left[\frac{(2J+4)(2J+2)(2J+1)(2J)(2J-2)}{(2J+3)(2J-1)}\right]^{1/2}$$

$$\times \left[\left(\frac{3}{5}\right)^{1/2}G_0'^{(2)} + \frac{1}{2}G_0'^{(4)}\right]. \tag{14}$$

It is the expression in the final bracket of this relation, combining the effects of the two terms in $G_0'^{(2)}$ and $G_0'^{(4)}$, together with the factor $-\frac{1}{4}$, that we are using with $e\Omega$ to fit for as an octupole constant, and will call ω'. The conventional constant ω (called ''c'' in Ref. 3) is therefore related to it by

$$\omega = \left[\frac{(2J)(2J-2)}{2J+3}\right]\omega'. \tag{15}$$

The factor in each interaction that describes the nuclear environment will generally depend slightly on the vibration and rotation states of the molecule. This dependence is treated as a series in $(v+1/2)$ and $J(J+1)$, as derived by Schlier.[14] His treatment is based on the assumption that the strength of each interaction depends on the internuclear distance in a way that can be represented as a power series in the parameter

$$\xi = (R - R_e)/R_e. \tag{16}$$

He showed that any quantity [as, for example, the field gradient $q(\xi)$] which can be expanded in the series

$$q(\xi) = q_e + q_1\xi + q_2\xi^2 + \cdots, \tag{17}$$

will have an expectation value in a given vibrational state v and rotational state J which is of the form

$$q(v,J) = (q_e + \alpha B^2) + (\beta B + \gamma B^3)(v+1/2)$$

$$+ \delta B^2(v+1/2)^2 + \epsilon B^3(v+1/2)^3$$

$$+ \zeta B^2 J(J+1) + \eta B^3(v+1/2)J(J+1), \tag{18}$$

where $\alpha \dots \eta$ are known functions of the q_i and the Dunham potential coefficients a_i, and $B = B_e/\omega_e$ is the ratio of the rotational constant to the vibrational constant. This expression is complete to order $O(B^3)$ and incorporates terms in q_i up to q_6 and potential coefficients up to a_5. In what follows this expansion will be written in the form

$$q(v,J) = \sum_{i,j} q_{ij}(v+1/2)^i[J(J+1)]^j. \tag{19}$$

White[15] showed that the spin-rotation interaction for the ith nucleus in a molecule should be given approximately by an expression of the form

$$c_i = g_i B_e \frac{4\pi\mu_{0N}}{\hbar}\left[4\mu_{0B}\left\langle\frac{1}{r^3}\right\rangle\sum_n\frac{|\langle 0|L|n\rangle|^2}{E_n - E_0} - \frac{q_N}{cR}\right]. \tag{20}$$

In this expression g_i is the nuclear gyromagnetic ratio, B_e the equilibrium rotational constant, μ_{0N} and μ_{0B} the nuclear magneton and Bohr magneton, respectively, r is the distance from the ith nucleus to the valence electrons, and the sum is over the states n of the valence electrons which are excited by the rotation perturbation. The first term in the brackets gives the effect of the magnetic field produced by these valence electrons on the nucleus in question. The last term represents the effect of the magnetic field produced by the charge q_N of the other nucleus and its bound electrons, centered at the internuclear distance R.

If we regard the entire quantity in brackets as a function of the internuclear distance, then this should also be expandable in the same manner as $q(\xi)$ to give a form similar to Eq. (19). A similar argument should also apply to the other interactions. This is the justification for our seeking to find experimental values for the coefficients of $(v+1/2)^i[J(J+1)]^j$ to represent the vibrational and rotational dependence of all the interactions.

III. DATA AND ANALYSIS

The identification and fitting of the observed spectral lines has been made possible by a procedure described previously,[11] where a velocity-averaged Rabi line shape is used to deconvolute overlapping transitions. This has allowed us to take into account the small residual stark shifts of our near-zero field experiment, and fit for the zero-field line frequencies to a precision of a few Hertz.

All the observed lines are listed in Table I. The uncertainties quoted are one standard deviation estimates.

TABLE I. Comparison of experimental data with fit (all frequencies in kHz).

v	J	$F_1-F\rightarrow F_1-F$	Measured	Uncertainty	Residual	v	J	$F_1-F\rightarrow F_1-F$	Measured	Uncertainty	Residual
0	1	3/2-0→ 5/2-2	59524.7784	0.0100	−0.0088	1	3	1/2-2→ 3/2-2	18589.0980	0.0020	0.0016
2	1	3/2-0→ 5/2-2	64314.1354	0.0200	−0.0146	2	3	1/2-2→ 3/2-2	19298.0870	0.0020	−0.0004
0	1	3/2-0→ 7/2-2	17841.4944	0.0100	0.0029	2	3	1/2-2→ 5/2-2	44297.1950	0.0050	−0.0016
0	1	3/2-1→ 5/2-1	59499.6823	0.0100	−0.0059	0	3	1/2-2→ 5/2-3	41000.5640	0.0020	−0.0007
1	1	3/2-1→ 5/2-1	61924.4928	0.0020	0.0015	1	3	1/2-2→ 5/2-3	42669.5390	0.0020	−0.0019
0	1	3/2-1→ 5/2-3	59550.4977	0.0090	−0.0030	2	3	1/2-2→ 5/2-3	44297.6430	0.0100	−0.0063
1	1	3/2-1→ 5/2-3	61974.3502	0.0100	0.0021	1	3	1/2-2→ 5/2-4	42667.9200	0.0050	0.0037
2	1	3/2-1→ 5/2-3	64338.9075	0.0100	−0.0048	0	3	11/2-4→ 7/2-3	36449.1700	0.0200	0.0039
2	1	3/2-1→ 7/2-2	19285.5623	0.0070	0.0102	1	3	11/2-4→ 7/2-3	37929.7150	0.0100	−0.0031
0	1	3/2-1→ 7/2-3	17822.7858	0.0080	0.0097	0	3	11/2-5→ 7/2-4	36466.1910	0.0100	0.0158
3	1	3/2-1→ 7/2-3	19953.3780	0.0050	0.0012	0	3	11/2-6→ 9/2-4	36451.3670	0.0100	−0.0021
0	1	3/2-2→ 5/2-1	59506.8175	0.0030	0.0012	1	3	11/2-6→ 9/2-4	37932.1350	0.0200	0.0189
1	1	3/2-2→ 5/2-1	61931.4939	0.0100	0.0053	0	3	11/2-6→ 9/2-5	36441.4802	0.0050	−0.0077
0	1	3/2-2→ 5/2-2	59538.8901	0.0050	0.0024	1	3	11/2-6→ 9/2-5	37922.4700	0.0200	0.0218
1	1	3/2-2→ 5/2-2	61962.9547	0.0100	0.0024	2	3	11/2-6→ 9/2-5	39367.1600	0.0020	−0.0008
2	1	3/2-2→ 5/2-2	64327.7326	0.0020	0.0002	0	3	11/2-6→ 9/2-6	36465.2940	0.0050	−0.0020
0	1	3/2-2→ 5/2-3	59557.6299	0.0100	0.0012	1	3	11/2-6→ 9/2-6	37945.8450	0.0100	0.0027
1	1	3/2-2→ 5/2-3	61981.3497	0.0100	0.0043	0	3	11/2-7→ 9/2-6	36433.4270	0.0030	0.0007
2	1	3/2-2→ 5/2-3	64345.7790	0.0100	−0.0020	1	3	11/2-7→ 9/2-6	37914.6230	0.0050	0.0042
0	1	3/2-2→ 5/2-4	59527.9011	0.0100	−0.0024	2	3	11/2-7→ 9/2-6	39359.5690	0.0050	0.0033
1	1	3/2-2→ 5/2-4	61952.1992	0.0100	−0.0013	0	3	3/2-1→ 7/2-2	41657.9670	0.0070	−0.0091
2	1	3/2-2→ 5/2-4	64317.2038	0.0100	0.0004	1	3	3/2-1→ 7/2-2	43353.8475	0.0100	0.0164
1	1	3/2-2→ 7/2-2	18582.8920	0.0100	0.0027	2	3	3/2-1→ 7/2-2	45008.1400	0.0500	−0.0230
0	1	3/2-2→ 7/2-3	17829.9150	0.0100	0.0108	3	3	3/2-1→ 7/2-2	46621.4852	0.0100	0.0119
2	1	3/2-2→ 7/2-3	19267.6911	0.0100	0.0111	0	3	3/2-2→ 5/2-2	23137.7850	0.0030	0.0015
3	1	3/2-2→ 7/2-3	19960.1216	0.0030	−0.0001	1	3	3/2-2→ 5/2-2	24079.9860	0.0030	0.0024
1	1	3/2-3→ 5/2-1	61925.2098	0.0150	−0.0171	2	3	3/2-2→ 5/2-2	24999.1030	0.0050	−0.0062
0	1	3/2-3→ 5/2-2	59532.5000	0.0050	0.0061	1	3	3/2-2→ 5/2-3	24080.4410	0.0040	−0.0035
1	1	3/2-3→ 5/2-2	61956.6887	0.0030	−0.0018	2	3	3/2-2→ 5/2-3	24999.5550	0.0100	−0.0069
0	1	3/2-3→ 5/2-3	59551.2211	0.0070	−0.0139	0	3	3/2-2→ 7/2-4	41642.3640	0.0030	0.0001
1	1	3/2-3→ 5/2-3	61975.0884	0.0100	0.0048	1	3	3/2-2→ 7/2-4	43338.6040	0.0030	0.0008
2	1	3/2-3→ 5/2-3	64339.6414	0.0100	−0.0072	2	3	3/2-2→ 7/2-4	44993.3200	0.0100	−0.0024
0	1	3/2-3→ 5/2-4	59521.5088	0.0050	−0.0010	1	3	3/2-3→ 7/2-2	43353.9629	0.0050	−0.0011
1	1	3/2-3→ 5/2-4	61945.9396	0.0050	0.0009	2	3	3/2-3→ 7/2-2	45008.2200	0.0500	−0.0631
2	1	3/2-3→ 5/2-4	64311.0715	0.0080	0.0004	0	3	3/2-3→ 7/2-4	41649.2700	0.0070	−0.0042
0	1	3/2-3→ 7/2-3	17823.5108	0.0020	0.0004	1	3	3/2-3→ 7/2-4	43345.3700	0.0030	−0.0047
1	1	3/2-3→ 7/2-3	18551.4161	0.0020	−0.0003	2	3	3/2-3→ 7/2-4	44999.9650	0.0080	0.0069
3	1	3/2-3→ 7/2-3	19954.1110	0.0050	−0.0022	0	3	3/2-3→ 7/2-5	41657.6760	0.0050	−0.0032
3	1	3/2-3→ 7/2-5	19964.0743	0.0050	−0.0040	1	3	3/2-3→ 7/2-5	43353.5803	0.0100	0.0037
0	2	1/2-2→ 3/2-0	25480.6998	0.0100	−0.0061	2	3	3/2-3→ 7/2-5	45007.9700	0.0100	0.0075
1	2	1/2-2→ 3/2-0	26520.0738	0.0050	−0.0023	3	3	3/2-3→ 7/2-5	46621.3290	0.0200	−0.0125
2	2	1/2-2→ 3/2-0	27534.0233	0.0300	−0.0012	0	4	13/2-5→11/2-4	35242.0050	0.0100	−0.0037
0	2	1/2-2→ 3/2-1	25505.4210	0.0100	−0.0054	1	4	13/2-5→11/2-4	36674.1530	0.0070	0.0055
1	2	1/2-2→ 3/2-3	26545.7250	0.0100	−0.0011	2	4	13/2-5→11/2-4	38071.2520	0.0050	0.0062
2	2	1/2-2→ 3/2-3	27559.2003	0.0110	0.0073	0	4	13/2-6→11/2-5	35253.6000	0.0020	−0.0005
0	2	5/2-1→ 7/2-2	9939.9055	0.0100	0.0044	1	4	13/2-6→11/2-5	36685.5240	0.0050	−0.0015
0	2	5/2-4→ 7/2-5	9926.5484	0.0100	0.0032	2	4	13/2-6→11/2-5	38082.4160	0.0050	0.0042
0	2	9/2-4→ 7/2-2	38326.9034	0.0050	0.0033	0	4	13/2-7→11/2-6	35256.2300	0.0020	0.0017
0	2	9/2-4→ 7/2-3	38320.5532	0.0100	0.0018	1	4	13/2-7→11/2-6	36688.1170	0.0040	−0.0028
0	2	9/2-4→ 7/2-4	38317.5125	0.0100	0.0000	2	4	13/2-7→11/2-6	38084.9710	0.0020	0.0006
0	2	9/2-5→ 7/2-3	38333.5456	0.0100	−0.0231	0	4	13/2-8→11/2-7	35247.8340	0.0040	−0.0039
0	2	9/2-5→ 7/2-4	38330.5351	0.0050	0.0054	1	4	13/2-8→11/2-7	36679.9030	0.0020	−0.0004
0	2	9/2-5→ 7/2-5	38335.4616	0.0100	0.0116	2	4	13/2-8→11/2-7	38076.9210	0.0020	−0.0019
0	2	9/2-6→ 7/2-4	38301.3687	0.0020	−0.0001	0	4	3/2-0→ 7/2-2	42878.7100	0.0100	−0.0015
0	2	9/2-6→ 7/2-5	38306.2943	0.0100	0.0052	0	4	3/2-1→ 7/2-2	42903.7230	0.0050	0.0051
0	3	1/2-1→ 3/2-2	17861.8650	0.0040	0.0050	0	4	3/2-1→ 7/2-3	42887.7310	0.0100	−0.0076
1	3	1/2-1→ 3/2-2	18588.6640	0.0080	0.0006	0	4	3/2-2→ 7/2-3	42913.2630	0.0030	0.0005
2	3	1/2-1→ 3/2-2	19297.6950	0.0080	0.0221	0	4	3/2-3→ 7/2-5	42896.4090	0.0050	0.0016
0	3	1/2-1→ 5/2-1	40998.5580	0.0020	−0.0016	0	4	5/2-1→ 7/2-2	21638.5200	0.0100	0.0168
1	3	1/2-1→ 5/2-1	42667.5750	0.0050	−0.0065	2	4	5/2-1→ 7/2-2	23378.9500	0.0100	−0.0043
0	3	1/2-1→ 5/2-2	40999.6390	0.0040	−0.0046	0	4	5/2-1→ 7/2-3	21622.5240	0.0030	0.0001
1	3	1/2-1→ 5/2-2	42668.6470	0.0020	0.0000	1	4	5/2-1→ 7/2-3	22503.8560	0.0080	0.0167
2	3	1/2-1→ 5/2-2	44296.7830	0.0100	0.0009	0	4	5/2-2→ 7/2-2	21653.1870	0.0020	−0.0001
1	3	1/2-1→ 5/2-3	42669.1136	0.0050	0.0057	1	4	5/2-2→ 7/2-2	22533.9150	0.0040	−0.0012
2	3	1/2-1→ 5/2-3	44297.2260	0.0080	−0.0088	2	4	5/2-2→ 7/2-2	23393.0780	0.0030	−0.0009
0	3	1/2-2→ 3/2-2	17862.3130	0.0030	0.0010	0	4	5/2-2→ 7/2-3	21637.2070	0.0020	−0.0008

TABLE I. (*Continued.*)

v	J	$F_1 - F \rightarrow F_1 - F$	Measured	Uncertainty	Residual	v	J	$F_1 - F \rightarrow F_1 - F$	Measured	Uncertainty	Residual
1	4	5/2-2→ 7/2-3	22518.2480	0.0040	0.0067	1	4	5/2-4→ 7/2-5	22520.3940	0.0030	−0.0021
2	4	5/2-2→ 7/2-3	23377.7160	0.0070	0.0121	2	4	5/2-4→ 7/2-5	23379.8080	0.0030	−0.0009
0	4	5/2-2→ 7/2-4	21629.9210	0.0050	0.0007	0	5	5/2-1→ 9/2-3	43737.7372	0.0300	0.0201
1	4	5/2-2→ 7/2-4	22511.0800	0.0080	−0.0064	0	5	5/2-2→ 9/2-4	43745.7479	0.0070	0.0029
0	4	5/2-2→ 9/2-4	35533.5270	0.0040	0.0007	0	5	5/2-3→ 9/2-5	43756.2098	0.0040	0.0083
2	4	5/2-2→ 9/2-4	38393.4450	0.0020	0.0001	0	5	5/2-4→ 9/2-5	43726.2317	0.0020	−0.0006
0	4	5/2-3→ 7/2-2	21662.0530	0.0030	−0.0009	0	5	7/2-3→ 9/2-3	20622.9200	0.0050	0.0020
1	4	5/2-3→ 7/2-2	22542.6180	0.0030	0.0026	1	5	7/2-3→ 9/2-3	21461.0600	0.0150	−0.0061
0	4	5/2-3→ 7/2-3	21646.0740	0.0020	−0.0006	0	5	7/2-4→ 9/2-4	20608.7950	0.0080	0.0024
1	4	5/2-3→ 7/2-3	22526.9420	0.0020	0.0014	0	5	7/2-4→ 9/2-5	20598.9780	0.0020	−0.0038
2	4	5/2-3→ 7/2-3	23386.2370	0.0020	−0.0004	1	5	7/2-4→ 9/2-5	21437.5780	0.0030	0.0023
0	4	5/2-3→ 7/2-4	21638.7900	0.0020	0.0029	0	5	7/2-4→ 9/2-6	20620.0380	0.0060	−0.0057
1	4	5/2-3→ 7/2-4	22519.7800	0.0040	−0.0056	1	5	7/2-4→ 9/2-6	21458.2180	0.0050	−0.0038
2	4	5/2-3→ 7/2-4	23379.2200	0.0040	0.0057	0	5	7/2-5→ 9/2-4	20586.8640	0.0090	0.0101
0	4	5/2-3→ 7/2-5	21652.0030	0.0030	0.0037	0	5	7/2-5→ 9/2-6	20598.1060	0.0040	0.0010
1	4	5/2-3→ 9/2-5	36981.6330	0.0100	0.0000	1	5	7/2-5→ 9/2-6	21436.7060	0.0030	−0.0047
2	4	5/2-3→ 9/2-5	38393.8650	0.0040	0.0005	0	6	7/2-5→11/2-7	44191.2356	0.0100	−0.0011
0	4	5/2-4→ 7/2-3	21633.4950	0.0040	0.0055	0	6	9/2-4→11/2-4	19866.9800	0.0030	−0.0019
0	4	5/2-4→ 7/2-4	21626.1990	0.0050	−0.0030	0	6	9/2-5→11/2-5	19847.2240	0.0040	0.0022
1	4	5/2-4→ 7/2-4	22507.4380	0.0060	−0.0037	0	6	9/2-5→11/2-7	19861.7670	0.0100	0.0031
0	4	5/2-4→ 7/2-5	21639.4120	0.0030	−0.0022						

There are several effects which have been of concern to us for the way in which they might affect the hexadecapole interpretation. First, we had previously taken into account only second-order perturbations of the nuclear quadrupole on the rotational state. Rather than extend the analysis to third order using perturbation theory, we have combined all the rotational states into a single large matrix extending two states beyond the highest for which lines had been observed, then obtaining the energy eigenvalues and eigenvectors. Doing this made only minor changes in the fitted values, but served to eliminate any possibility of higher order effects of this nature.

The fitting of the molecular constants to these line frequencies has been done using the singular value decomposition method, which has the effect of de-correlating the errors which feed into those of the fitted parameters. It also shows that there are no linear combinations of the parameters which are undetermined by the data.

The data have been fitted using all four combinations of octupole and hexadecapole parameters: both constrained to equal zero, each fitted with the other constrained, and both fitted together. The reduced chi value of the fit when both were constrained was 1.3075. When the octupole interaction alone was fitted, it dropped to 0.9915. With the hexadecapole interaction alone fitted, it was 0.9250. With both included, it was 0.9207. Constraining the octupole changes the hexadecapole constant from −0.0151(30) to −0.0192(17) kHz, while constraining the hexadecapole changes the octupole constant from 0.000112(73) to 0.000409(41). The hexadecapole value also was more robust with respect to the inclusion or removal of other small parameters in the fit. Conversely, none of the remaining fitted parameters varied between the four fits by more than its estimated standard deviation uncertainty. These observations give us confidence that our value of the hexadecapole constant is indeed real, while the value

of the octupole constant is not yet convincing. An octupole interaction for the lithium nucleus was not expected to be significant, and was not included.

The results are shown in Table II. The uncertainties listed in the table are again one standard deviation estimates.

Our hyperfine constants, when used to calculate the values for $v = 0$, $J = 1,2$, agree with those of Ref. 7 within their quoted uncertainties combined with ours. Our values of the octupole and hexadecapole constants are also well within their quoted limits.

The complete vibrational and rotational dependence of the iodine quadrupole interaction that we report here allows for a determination of the coefficients q_i in Eq. (17). For this we need values of the rotational constant, B_e, the vibrational constant ω_e, and the Dunham potential constants a_i. The values reported by Thompson *et al.*[16] are adequate for this purpose, though additional data analyzed in a somewhat different form has been published by Guo *et al.*[17] The nuclear moment Q is not very well known, so we consider the product eQq. We have only the 6 coefficients eQq_{ij}, whereas there are 7 coefficients eQq_i in Eq. (17), but we can put reasonable limits on the value of eQq_6 and then solve Eq. (18) for the others. The results are listed in Table III. The parameter whose precision limits the precision of each coefficient is noted in the table. A similar analysis for the lithium nuclear quadrupole interaction is possible in principle, but probably not meaningful in view of the small value in relation to the uncertainty for the term eQq_{01}.

Since the nuclear moment is negative, the negative signs of eQq_e and eQq_1 mean that the field gradient is positive at the iodine nuclear equilibrium position, and becomes more so as the two nuclei separate further. We are not aware of any published *ab initio* calculations with which these results may be compared.

Even though we believe we have a statistically meaning-

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

i, j	Constants	
Iodine Quadrupole ($eQq_{\mathrm{I}ij}$):		
0,0	−194351.212	±0.017
1,0	−8279.521	±0.046
2,0	100.616	±0.034
3,0	−0.3949	±0.0073
0,1	−6.41977	±0.00050
1,1	0.10593	±0.00033
Lithium Quadrupole ($eQq_{\mathrm{Li}ij}$):		
0,0	172.613	±0.052
1,0	−3.26	±0.14
2,0	−0.028	±0.099
3,0	0.012	±0.020
0,1	0.00145	±0.00087
1,1	−0.00003	±0.00090
Iodine Spin-Rotation ($c_{\mathrm{I}ij}$):		
0,0	6.80260	±0.00032
1,0	0.00303	±0.00049
2,0	−0.00005	±0.00016
0,1	−0.000118	±0.000013
Lithium Spin-Rotation ($c_{\mathrm{Li}ij}$):		
0,0	0.75872	±0.00072
1,0	−0.0088	±0.0011
2,0	−0.00043	±0.00036
0,1	−0.000017	±0.000020
Tensor Spin-Spin (c_{3ij}):		
0,0	0.62834	±0.00068
1,0	−0.0050	±0.0011
2,0	−0.00048	±0.00036
0,1	0.000009	±0.000027
Scalar Spin-Spin (c_{4ij}):		
0,0	0.06223	±0.00036
0,1	0.00041	±0.00026
Iodine Octupole ($e\Omega\omega'_{\mathrm{I}ij}$)[a]:		
0,0	0.000112	±0.000073
Iodine Hexadecapole ($eHh_{\mathrm{I}ij}$):		
0,0	−0.0151	±0.0030

[a]X_{ij} denotes the coefficient in the expansion $X(v,J)=\Sigma_{i,j}X_{ij}(v+1/2)^i[J(J+1)]^j$. See text for our definition of the octupole constant.

TABLE III. Dependence of $eQ_{\mathbf{I}}q_{\mathbf{I}}$ on internuclear distance.

Coefficient[a]	Value (MHz)		Uncertainty	Precision limited by
eQq_e	−194.350229	±	0.000084	eQq_{11}
eQq_1	−2017.23	±	0.16	eQq_{01}
eQq_2	3597.39	±	0.64	eQq_{01}
eQq_3	−1399	±	19	eQq_{11}
eQq_4	−6710	±	130	eQq_{11}
eQq_5	15100	±	3000	eQq_6
eQq_6	−20000	±	30000	est

[a]Coefficients in expansion $eQq(\xi)=eQq_e+\Sigma_{i=1\cdot6}eQq_i\times\xi^i$.

where the denominator is the difference between the ground and first excited electronic energy levels. With an estimate of 10^{16} Hz for this difference, and a value of 2×10^8 Hz for eQq, this would be a few Hertz, comparable to our quoted experimental value. There seems to be no simple way of experimentally distinguishing between such an effect and a true nuclear hexadecapole interaction.

Observations of the hyperfine spectrum of ^{6}LiI would be helpful to confirm the observed hexadecapole interaction. We have observed a few lines in the spectrum of our natural sample which we have assigned to the mass 6 isotope, but there are not enough to provide a meaningful analysis at this point. This has to remain as a project for the future.

ACKNOWLEDGMENT

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ful observation of a hexadecapole interaction, it may still not be a true nuclear effect. Pyykkö[18] has pointed out to us the possibility that it may be an electron-coupled quadruple interaction, which we might call a ''pseudohexadecapole'' interaction by analogy with the electron-coupled spin-self-spin effect which is known as a pseudoquadrupole interaction. He notes that the order of magnitude of such an interaction would go as

$$\frac{(eQq)^2}{E_1-E_0}, \tag{21}$$