

# The hyperfine interactions in CsF

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The molecular beam electric resonance technique has been used to examine the hyperfine spectrum of CsF to determine the nuclear quadrupole interaction of the cesium nucleus. A total of 95 transitions in vibrational states  $v=0-5$  and rotational states  $J=1-8$  have been included in a fit to determine the cesium nuclear quadrupole and spin-rotation interactions, the fluorine spin-rotation interaction, and the tensor and scalar parts of the spin-spin interaction. Vibration and rotation dependencies of these constants have been determined, allowing correction for zero point vibration effects. This experimental Cs nuclear quadrupole coupling constant when combined with the electric field gradient calculated using a relativistic coupled cluster method yields a nuclear quadrupole moment of the Cs nucleus equal to  $eQ = -3.43098$  mbarn. The vibrational dependence of the coupling constant is smaller than the theoretical estimate. The coupling constants we have determined are the following:  $eQ_{Cs}q_{Cs} = 1245.598(10) - 14.322(25)(v+1/2) + 0.080(14) \times (v+1/2)^2 + 0.0040(22)(v+1/2)^3 - 0.00209(59)J(J+1) + 0.00048(40)(v+1/2)J(J+1)$ ,  $c_{Cs} = 0.66177(14) - 0.01509(28)(v+1/2) + 0.000550(94)(v+1/2)^2$ ,  $c_F = 15.08163(84) - 0.1744(14) \times (v+1/2) + 0.00234(41)(v+1/2)^2 - 0.000093(13)J(J+1)$ ,  $c_3 = 0.92713(53) - 0.00917(93)(v+1/2) + 0.00097(29)(v+1/2)^2$ ,  $c_4 = 0.62745(30) - 0.00903(22)(v+1/2)$ . All values are in kHz units, with one standard deviation uncertainty estimates in the last two digits shown in ( ). © 1999 American Institute of Physics. [S0021-9606(99)00642-X]

## I. INTRODUCTION

In order to determine the nuclear quadrupole moment of a nucleus it is necessary to combine an experimental measurement of the nuclear quadrupole coupling constant (NQCC) in an atom, molecule, or solid with a theoretical calculation of the electric field gradient (EFG). For the alkali metal nuclei the ground state atoms are not suitable because, as S states, they have no field gradient at the nucleus. Excited states can and have been used, but are limited in precision because they are short lived. The molecular beam technique gives the most accurate measurements of the NQCC, but calculating the EFG is more difficult.

In the case of the Cs nucleus a recent calculation by Pernpointer, Schwerdtfeger, and Hess<sup>1</sup> produces an EFG for the Cs site in the CsF molecule that may be more accurate than the previous measurements of the NQCC.<sup>2</sup> We have now completed a new set of molecular beam measurements of the hyperfine spectrum of CsF using a higher resolution spectrometer. We have also examined a much larger number of vibrational and rotational states so that the dependence of the NQCC on rotation and vibration can be determined. The status of various previous measurements and calculations is discussed in these two references and will not be repeated here. Our experimental techniques and methods of analysis have also been described previously.<sup>3,4</sup>

## II. THEORY

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

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

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

$$\begin{aligned} \frac{H_{\text{hyperfine}}}{h} = & \mathbf{V}_{\text{Cs}}^{(2)} \cdot \mathbf{Q}_{\text{Cs}}^{(2)} + c_{\text{Cs}} \mathbf{I}_{\text{Cs}} \cdot \mathbf{J} + c_F \mathbf{I}_F \cdot \mathbf{J} + c_3 \mathbf{I}_{\text{Cs}} \cdot \mathbf{D} \cdot \mathbf{I}_F \\ & + c_4 \mathbf{I}_{\text{Cs}} \cdot \mathbf{I}_F + \boldsymbol{\omega}_{\text{Cs}}^{(3)} \cdot \boldsymbol{\Omega}_{\text{Cs}}^{(3)} + \mathbf{h}_{\text{Cs}}^{(4)} \cdot \mathbf{H}_{\text{Cs}}^{(4)} \end{aligned} \quad (2)$$

and

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

The pure hyperfine spectrum of CsF is dominated by the cesium quadrupole interaction, so that the appropriate representation to use is the one defined by the coupling

$$\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_{\text{Cs}}, \quad \mathbf{F} = \mathbf{F}_1 + \mathbf{I}_F. \quad (4)$$

We have used the techniques of Edmonds<sup>5</sup> 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. Each interaction is expressed in terms of a ‘‘constant’’ that is a product of two factors: one representing the nucleus and the other its environment in the molecule. For the nuclear quadrupole interaction, the coupling constant is expressed as  $eQq$ , where the ‘‘nuclear quadrupole moment’’ is defined as

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

$\nu$	$J$	$F_1 - F \rightarrow$	$F_1 - F$	Measured	Uncertainty	Residual
0	1	7/2-3 $\rightarrow$	5/2-2	305.1506	0.0030	-0.0018
1	1	7/2-3 $\rightarrow$	5/2-2	301.6368	0.0200	-0.0145
2	1	7/2-3 $\rightarrow$	5/2-2	298.2103	0.0050	0.0047
3	1	7/2-3 $\rightarrow$	5/2-2	294.8124	0.0100	-0.0088
0	1	7/2-3 $\rightarrow$	5/2-3	314.4338	0.0030	-0.0001
1	1	7/2-3 $\rightarrow$	5/2-3	310.8303	0.0100	0.0000
2	1	7/2-3 $\rightarrow$	5/2-3	307.2809	0.0020	-0.0021
0	1	7/2-3 $\rightarrow$	9/2-4	246.1724	0.0010	0.0005
1	1	7/2-3 $\rightarrow$	9/2-4	243.3999	0.0010	0.0007
2	1	7/2-3 $\rightarrow$	9/2-4	240.6679	0.0010	0.0006
4	1	7/2-3 $\rightarrow$	9/2-4	235.3740	0.0300	0.0296
0	1	7/2-3 $\rightarrow$	9/2-5	225.1894	0.0070	0.0085
1	1	7/2-3 $\rightarrow$	9/2-5	222.6513	0.0070	0.0034
2	1	7/2-3 $\rightarrow$	9/2-5	220.1423	0.0050	-0.0048
3	1	7/2-3 $\rightarrow$	9/2-5	217.7071	0.0200	0.0240
0	1	7/2-4 $\rightarrow$	5/2-2	308.4660	0.0020	0.0018
1	1	7/2-4 $\rightarrow$	5/2-2	304.9509	0.0300	0.0424
2	1	7/2-4 $\rightarrow$	5/2-2	301.4177	0.0100	0.0143
3	1	7/2-4 $\rightarrow$	5/2-2	297.9401	0.0100	-0.0148
4	1	7/2-4 $\rightarrow$	5/2-2	294.5698	0.0200	0.0007
0	1	7/2-4 $\rightarrow$	5/2-3	317.7426	0.0020	-0.0032
1	1	7/2-4 $\rightarrow$	5/2-3	314.0859	0.0030	-0.0016
2	1	7/2-4 $\rightarrow$	5/2-3	310.4795	0.0030	-0.0013
3	1	7/2-4 $\rightarrow$	5/2-3	306.9319	0.0050	0.0002
0	1	7/2-4 $\rightarrow$	9/2-4	249.4806	0.0020	-0.0032
1	1	7/2-4 $\rightarrow$	9/2-4	246.6525	0.0050	-0.0038
2	1	7/2-4 $\rightarrow$	9/2-4	243.8785	0.0100	0.0135
0	1	7/2-4 $\rightarrow$	9/2-5	228.4941	0.0020	0.0013
1	1	7/2-4 $\rightarrow$	9/2-5	225.9156	0.0100	0.0105
2	1	7/2-4 $\rightarrow$	9/2-5	223.3350	0.0200	-0.0099
4	1	7/2-4 $\rightarrow$	9/2-5	218.3561	0.0300	0.0307
5	1	7/2-4 $\rightarrow$	9/2-5	215.8738	0.0050	-0.0017
0	2	7/2-3 $\rightarrow$	11/2-5	199.7760	0.0030	0.0042
1	2	7/2-3 $\rightarrow$	11/2-5	197.5784	0.0100	0.0127
2	2	7/2-3 $\rightarrow$	11/2-5	195.3747	0.0100	-0.0137
0	2	7/2-3 $\rightarrow$	3/2-1	278.0795	0.0100	0.0002
0	2	7/2-3 $\rightarrow$	3/2-2	299.3322	0.0100	-0.0006
0	2	7/2-4 $\rightarrow$	11/2-5	194.3684	0.0100	-0.0045
1	2	7/2-4 $\rightarrow$	11/2-5	192.2018	0.0050	0.0005
0	2	7/2-4 $\rightarrow$	11/2-6	156.5130	0.0010	0.0007
0	2	7/2-4 $\rightarrow$	3/2-2	293.9302	0.0030	-0.0036
1	2	7/2-4 $\rightarrow$	3/2-2	290.5186	0.0200	-0.0004
0	2	9/2-4 $\rightarrow$	11/2-5	227.1243	0.0010	-0.0017
1	2	9/2-4 $\rightarrow$	11/2-5	224.5812	0.0050	-0.0071
2	2	9/2-4 $\rightarrow$	11/2-5	222.0855	0.0010	-0.0014
3	2	9/2-4 $\rightarrow$	11/2-5	219.6179	0.0200	-0.0078
0	2	9/2-4 $\rightarrow$	11/2-6	189.2613	0.0030	-0.0041
4	2	9/2-4 $\rightarrow$	11/2-6	181.0184	0.0300	0.0473
0	2	9/2-4 $\rightarrow$	3/2-2	326.6874	0.0010	0.0005
1	2	9/2-4 $\rightarrow$	3/2-2	322.9158	0.0100	0.0099
2	2	9/2-4 $\rightarrow$	3/2-2	319.1907	0.0020	0.0029
0	2	9/2-4 $\rightarrow$	5/2-2	155.6847	0.0010	0.0001
0	2	9/2-5 $\rightarrow$	11/2-5	237.1652	0.0010	0.0005
0	2	9/2-5 $\rightarrow$	11/2-6	199.3062	0.0020	0.0020
2	2	9/2-5 $\rightarrow$	11/2-6	194.8373	0.0010	0.0005
0	2	9/2-5 $\rightarrow$	5/2-3	171.2381	0.0200	-0.0261
0	3	11/2-5 $\rightarrow$	13/2-6	188.9033	0.0050	0.0055
3	3	11/2-5 $\rightarrow$	13/2-6	182.6450	0.0010	0.0002
0	3	11/2-6 $\rightarrow$	1/2-0	321.5258	0.0070	-0.0021
1	3	11/2-6 $\rightarrow$	1/2-0	317.7406	0.0030	0.0009
2	3	11/2-6 $\rightarrow$	1/2-0	314.0214	0.0050	-0.0007
3	3	11/2-6 $\rightarrow$	1/2-0	310.3132	0.0800	-0.0677
0	3	11/2-6 $\rightarrow$	13/2-6	236.9522	0.0030	0.0040
0	3	11/2-6 $\rightarrow$	13/2-7	182.9255	0.0010	0.0007
1	3	11/2-6 $\rightarrow$	13/2-7	180.8697	0.0050	-0.0050
0	3	5/2-3 $\rightarrow$	1/2-1	191.6965	0.0200	0.0234
0	3	7/2-3 $\rightarrow$	3/2-1	197.5722	0.0100	-0.0088

TABLE I. (Continued.)

$\nu$	$J$	$F_1 - F \rightarrow$	$F_1 - F$	Measured	Uncertainty	Residual
1	3	7/2-3 $\rightarrow$	3/2-1	195.3076	0.0150	0.0184
0	3	7/2-4 $\rightarrow$	13/2-6	180.6549	0.0200	-0.0224
0	3	7/2-4 $\rightarrow$	3/2-2	215.5087	0.0020	0.0027
0	3	9/2-4 $\rightarrow$	13/2-6	237.8374	0.0050	-0.0034
1	3	9/2-4 $\rightarrow$	13/2-6	235.2158	0.0050	-0.0033
2	3	9/2-4 $\rightarrow$	13/2-6	232.6168	0.0200	-0.0146
0	3	9/2-4 $\rightarrow$	3/2-2	272.6723	0.0100	0.0028
0	3	9/2-5 $\rightarrow$	13/2-6	265.0308	0.0050	-0.0039
2	3	9/2-5 $\rightarrow$	13/2-6	259.1854	0.0100	0.0043
0	3	9/2-5 $\rightarrow$	13/2-7	211.0107	0.0010	-0.0006
1	3	9/2-5 $\rightarrow$	13/2-7	208.6705	0.0050	-0.0042
3	3	9/2-5 $\rightarrow$	13/2-7	204.0483	0.0200	-0.0152
1	3	9/2-5 $\rightarrow$	3/2-2	296.3686	0.0020	-0.0032
0	4	11/2-6 $\rightarrow$	15/2-7	288.8060	0.0010	-0.0005
1	4	11/2-6 $\rightarrow$	15/2-7	285.6056	0.0010	0.0006
0	4	11/2-6 $\rightarrow$	3/2-2	322.7784	0.0100	-0.0005
0	5	11/2-6 $\rightarrow$	17/2-8	291.3003	0.0070	-0.0102
1	5	11/2-6 $\rightarrow$	17/2-8	288.1350	0.0100	-0.0009
2	5	11/2-6 $\rightarrow$	17/2-8	285.0222	0.0200	0.0211
0	5	13/2-7 $\rightarrow$	17/2-8	306.2578	0.0100	0.0018
4	5	13/2-7 $\rightarrow$	17/2-8	293.0554	0.0200	0.0324
0	6	13/2-7 $\rightarrow$	19/2-9	314.3807	0.0020	0.0030
0	6	15/2-8 $\rightarrow$	19/2-9	321.3497	0.0050	-0.0008
1	6	15/2-8 $\rightarrow$	19/2-9	317.8117	0.0100	0.0018
2	6	15/2-8 $\rightarrow$	19/2-9	314.3143	0.0040	-0.0058
0	7	15/2-8 $\rightarrow$	21/2-10	334.3166	0.0020	-0.0015
1	7	17/2-9 $\rightarrow$	21/2-10	331.7652	0.0040	0.0039
0	8	17/2-9 $\rightarrow$	23/2-11	352.2190	0.0200	-0.0272

$$Q = \langle I, M = I | \int \rho_N r^2 (3 \cos(\theta_N) - 1) d\tau_N | I, M = I \rangle \quad X(\nu, J) = \sum_{i,j} X_{ij} (\nu + 1/2)^i [J(J+1)]^j. \quad (7)$$

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

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

and the ‘‘field gradient’’ as

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

$$= \frac{\partial^2 V}{\partial z^2}. \quad (6)$$

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

The magnetic octupole and electric hexadecapole interactions are possible for the Cs nucleus (whose spin is 7/2), but were not expected to be significant, nor did adding either or both significantly improve the fit of our data. They have therefore been constrained to zero in fitting our spectra.

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  $(\nu + 1/2)$  and  $J(J+1)$ , as derived by Schlier,<sup>6</sup> and has been described in a recent paper.<sup>3</sup> It provides the justification for representing this dependence as a series of the form

### III. DATA AND ANALYSIS

The identification and fitting of the observed spectral lines has been made possible by a procedure described previously,<sup>4</sup> where a velocity-averaged Rabi lineshape 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.

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 results are shown in Table II. The uncertainties listed in the table are again one standard deviation estimates. The reduced chi value of the fit, 1.057, indicates an excellent fit in terms of the estimated line frequency uncertainties.

Our hyperfine constants, when used to calculate the values for  $\nu=0,1,2; J=1$ , all lie well within the ranges quoted by English,<sup>2</sup> with the exception of  $eQq$  for  $\nu=0$ , for which our value (1238.456 kHz) lies just outside theirs [1237.0(1.3) kHz]. In that case our value agrees with that quoted by Gräff

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

$i, j$	Constants
Cesium quadrupole ( $eQq_{Csij}$ ): <sup>a</sup>	
0,0	1245.598±0.010
1,0	-14.322±0.025
2,0	0.080±0.014
3,0	0.0040±0.0022
0,1	-0.00209±0.00059
1,1	0.00048±0.00040
Cesium spin-rotation ( $c_{Csij}$ ):	
0,0	0.66177±0.00014
1,0	-0.01509±0.00028
2,0	0.000550±0.000094
Fluorine spin-rotation ( $c_{Fij}$ ):	
0,0	15.08163±0.00084
1,0	-0.1744±0.0014
2,0	0.00234±0.00041
0,1	-0.000093±0.000013
Tensor spin-spin ( $c_{3ij}$ ):	
0,0	0.92713±0.00053
1,0	-0.00917±0.00093
2,0	0.00097±0.00029
Scalar spin-spin ( $c_{4ij}$ ):	
0,0	0.62745±0.00030
0,1	-0.00903±0.00022

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

and Runólfsson<sup>7</sup> [1238.3(6) kHz]. Our uncertainties are about 2 orders of magnitude smaller than those of previous measurements. This improvement is due to several factors. Our spectrometer has a much longer transition region, so that linewidths are narrower; we have observed a much larger number of transitions (95 compared to their 17); and our lineshape analysis procedure allows a more accurate correction for the residual Stark shifts.

Our value for  $eQq_{00}$ , 1245.598±0.010 kHz, should be very close to the NQCC for the equilibrium separation of the two nuclei. The difference is due to the term  $\alpha B^2$  in Eq. (18) of Ref. 3. The coefficient  $eQq_{20}$  is given by an expression,  $\delta B^2$ , which is similar except that the terms of  $\alpha$  are about an order of magnitude smaller than those of  $\delta$ . This suggests that the difference between  $eQq_{00}$  and  $eQq_e$  should be roughly an order of magnitude smaller than  $eQq_{20}$ , and would therefore be smaller than the experimental uncer-

tainty. A more accurate estimate of this correction, based on explicit evaluation of  $\alpha$  and  $\delta$ , is not currently feasible for two reasons: (1) It would require more accurate measurements of the harmonic coefficients  $a_i$  than are currently available; and (2) our measurements of the higher vibration and rotation coefficients  $eQq_{ij}$  are not sufficiently accurate. The value of  $eQq_e$  should, in any case, lie within the experimental uncertainty range for  $eQq_{00}$ .

Pernpointer *et al.*,<sup>1</sup> using a relativistic coupled cluster calculation, have found a value of -1.5451 a.u. for the equilibrium EFG. When this is combined with our NQCC, it yields a value for the quadrupole moment of the cesium nucleus of  $eQ = -3.4309713$  mbarn. The accuracy of this value is once again limited by the theoretical calculation of the EFG, certainly no better than 5 significant figures. It is also interesting to compare the experimental and calculated vibrational dependence of the NQCC. The calculated ratios  $q_{10}/q_{00}$  and  $q_{20}/q_{00}$  are -0.01295 and 0.0001387, respectively while the experimental values are -0.011498 and 0.000064. The measurements thus show a significantly weaker vibrational dependence than the calculations. Schwerdtfeger<sup>8</sup> has offered in explanation that the vibrational dependency was taken from a second-order many-body perturbation theory which may easily overestimate such effects, but that the equilibrium coupled cluster value should still be accurate. The present value of the Cs nuclear quadrupole moment should therefore be more accurate than any previously available.

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