

## Hyperfine Structure of Indium Fluoride\*

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The radiofrequency spectrum of the indium fluoride molecule,  $^{115}\text{In}^{19}\text{F}$ , has been measured with a high resolution molecular beam electric resonance spectrometer. We determined the hyperfine structure in the  $J=1$  and the  $J=2$  rotational states of several vibrational levels under conditions of very weak external electric and magnetic fields. The  $\sim 700$  MHz electric quadrupole interaction constant of the indium nucleus changes by 0.010(1) MHz between adjacent rotational states. We looked for, but did not find, an electric hexadecapole interaction of the indium nucleus; the upper limit for the (hexadecapole) interaction constant is 2 kHz.

### I. INTRODUCTION

We used a high-resolution molecular beam electric resonance (MBER) spectrometer to measure the radiofrequency spectrum of the  $J=1$  ( $v=0, 1, 2$ ) and the  $J=2$  ( $v=0, 1$ ) states of indium monofluoride,  $^{115}\text{In}^{19}\text{F}$ . This experiment is the first to obtain a completely resolved hyperfine structure of an indium halide. Our goal was to get information on the variation of the hyperfine coupling constants with quantum state to augment the data already available on the alkali halides and the thallium halides; in addition, we had a particular interest in trying to identify and measure a nuclear hexadecapole interaction. In this paper we emphasize the molecular structure information; the interpretation of our limit for the hexadecapole interaction of the indium nucleus is given elsewhere.<sup>1,2</sup>

### II. EXPERIMENT

Most of the essential features of the MBER spectrometer used for this work have been described previously.<sup>1,3</sup> For these measurements we modified the insulators on the quadrupole state-selecting fields so that voltages up to 40 kV could be applied, and we improved the oxygenation system for the surface ionization detector. Moreover, since InF is not available commercially, we produced the beam by allowing metallic indium to react with  $\text{MgF}_2$  in a tantalum tube oven at a temperature of about 1300°K.

To observe the InF spectrum, it was necessary to use about five times the rf amplitude that is necessary for work with the alkali halides<sup>3</sup> and the thallium halides<sup>4</sup> in our apparatus. This is ascribable to the smaller effective dipole moment of InF. There was no evidence for power broadening of the spectral lines, however, since the observed 500 Hz-linewidth is about that known to result from the 50 cm length of the C-field.

We were able to measure eight lines in the  $J=1, v=0$  spectrum (the most intense being those at 162 841.7, 162 836.7, and 30 066.5 kHz), two lines in  $J=1, v=1$ , and one line in  $J=1, v=2$ . For the  $J=2$  rotational state, we were able to measure nine lines in  $v=0$  (the most intense being those at 154 774.75,

154 742.1, 112 162.2, 113 141.1, and 90 444.8 kHz) and a single line in  $v=1$ .

### III. RESULTS

#### A. Hyperfine Structure Constants

The hyperfine structure of indium fluoride observed in this experiment can be described with a Hamiltonian<sup>5,6</sup> which contains the electric quadrupole interaction of the indium nucleus ( $eqQ$ ), the spin-rotation interactions of both nuclei ( $c_1$  for indium,  $c_2$  for fluorine), and the tensor and scalar parts of the nuclear spin-spin interactions ( $c_3$  and  $c_4$ ). Stark and Zeeman operators are not included. Calculations of the molecular energy levels include corrections up to third order for contributions of the indium quadrupole interaction which are off diagonal in  $J$ . Contributions from the magnetic interaction of the fluoride nucleus (i.e., those involving  $c_2, c_3$ , and  $c_4$ ) which are off diagonal in  $F_1$  are also taken into account.

The  $J=1, v=0$ , and  $J=2, v=0$  interaction constants are calculated on the basis of the best, least square fit of the energy differences between hyperfine levels, as predicted by the Hamiltonian, to the observed transition frequencies. Table I shows these interaction constants. The constants given in Table I are calculated assuming that the hexadecapole moment of the In nucleus is zero and that the Stark and Zeeman energies are zero.

The quadrupole interaction constants for the higher vibrational states,  $v=1$  (or 2), are calculated by ascribing the change in frequency between the observed ( $v=0, J, F_1, F$ )  $\rightarrow$  ( $v=0, J, F_1', F'$ ) and the [ $v=1$  (or 2),  $J, F_1, F$ ]  $\rightarrow$  [ $v=1$  (or 2),  $J, F_1', F'$ ] transitions to a change in  $eqQ$ .

The principal source of error in this experiment lies in the use of a zero-field Hamiltonian to interpret the spectra. This is equivalent to neglecting the Stark and Zeeman effects produced by the very weak electric and magnetic fields in the C region of the spectrometer.

Measurements testing the field dependence of several lines, along with calculations of the Stark and

TABLE I. Hyperfine interaction constants of  $^{115}\text{In}^{19}\text{F}$  in kHz.

This experiment (MBER)		$eqQ$	$c_1$ (In)	$c_2$ (F)	$c_3$	$c_4$
State						
$J=1, v=0$		-723 799.6(2)	17.50(1)	18.77(10)	2.62(3)	-2.15(3)
$J=1, v=1$		-717 115(50)	17.50 <sup>a</sup>	18.77 <sup>a</sup>	2.62 <sup>a</sup>	-2.15 <sup>a</sup>
$J=1, v=2$		-710 490(50)	17.50 <sup>a</sup>	18.77 <sup>a</sup>	2.62 <sup>a</sup>	-2.15 <sup>a</sup>
$J=2, v=0$		-723 789.6(2)	17.50(1)	18.76(3)	2.62(1)	-2.11(1)
$J=2, v=1$		-717 062(50)	17.50 <sup>a</sup>	18.76 <sup>a</sup>	2.62 <sup>a</sup>	-2.11 <sup>a</sup>
Previous experiment <sup>b</sup> (microwave absorption)						
$J=1 \rightarrow 2, v=0$		-723 740(150)	17(4)			
$J=1 \rightarrow 2, v=1$		-717 100(150)	17(4)			
$J=1 \rightarrow 2, v=2$		-710 460(150)	17(4)			

<sup>a</sup> The constants  $c_1, c_2, c_3,$  and  $c_4$  in the higher vibrational states were assumed to be the same as in the  $v=0$  state so that  $eqQ$  could be calculated.

<sup>b</sup> J. Hoeft, F. J. Lovas, E. Tiemann, and T. Törring, Z. Naturforsch. 25a, 1029 (1970).

Zeeman effects, show that the weak fields (4.5 V/cm and 0.05 G) shift line frequencies by an amount on the order of 100 Hz. Since the centers of the spectral lines cannot be chosen much more accurately than this, it is appropriate<sup>6</sup> to neglect the external field terms in the Hamiltonian for the analysis of the spectral lines. The excellent fit of the predicted transition frequencies to the observed spectra is further justification for this procedure.

The uncertainties in the  $v=0$  interaction constants listed in Table I are estimated from the changes in the constants when the observed transition frequencies were given various weights in the least squares calculations. The values quoted are calculated with all lines weighted equally.

The major uncertainties in the  $v=1$  and 2 quadrupole interaction constants arise because they are calculated with the assumption that  $c_1, c_2, c_3,$  and  $c_4$  do not change with  $v$ . By assuming that these interaction constants change with  $v$  by the same percentage as the rotational constant, we can estimate the error in  $eqQ$  for the  $v=1$  and  $v=2$  levels to be at most 50 kHz.

#### B. Upper Limit for Hexadecapole Moment of $^{115}\text{In}$ Nucleus

When the electric hexadecapole interaction<sup>6</sup> of the indium nucleus is included in the least squares calculation of the interaction constants,  $ehH$  is calculated to be 300 Hz, and the calculated transition frequencies change by 30 Hz at most. Since the uncertainty in the observed transitions is greater than 100 Hz, and since  $\{\Sigma[\text{freq}(\text{obs}) - \text{freq}(\text{calc})]^2\}$  is not reduced when the hexadecapole interaction is included in the calculation of the interaction constants, the calculated value for  $ehH$  is not significantly different from zero.

On the other hand, if a hexadecapole interaction were to shift the calculated frequencies for InF by 100 to

200 Hz, i.e., by more than the uncertainty in the observed frequencies, it would have been observed in this experiment. Hence  $ehH$  in InF is smaller than 2000 Hz. Since  $h$  is about  $7 \times 10^{30}$  esu (see Sec. IV.B), the hexadecapole moment of the In nucleus is less than  $1 \times 10^{-48}$  cm<sup>4</sup>. This upper limit for  $H$  depends directly on the antishielding factor for In<sup>+</sup> ion. Here it is assumed to be -3680, which is the value calculated for In<sup>+</sup> by Sternheimer.<sup>7</sup>

## IV. DISCUSSION

### A. Change of the Quadrupole Interaction Constant with Rotational State

For diatomic molecules, the rotational motion has only a small effect on the size of the nuclear quadrupole interaction. In the Tl halides, for example, it is known<sup>4</sup> that  $eqQ$  does not change by more than 100 Hz between adjacent  $J$  states. Although some evidence for the change of  $eqQ$  with  $J$  was found by Zeiger and Bolef,<sup>8</sup> the first direct measurements of such changes were done by Kaiser<sup>9</sup> who found a  $(19.6 \pm 0.6)$  kHz shift in  $eqQ$  between the  $J=1$  and  $J=2$  states in HCl, and by the authors who found a  $(10.0 \pm 0.4)$  kHz shift in  $eqQ$  between the  $J=1$  and  $J=2$  levels in InF.

Zeiger and Bolef,<sup>8</sup> and also Kaiser<sup>9</sup> show that  $q$  should depend on  $v$  and  $J$  in the following way:

$$q = q_0 + (2B_e/\omega_e)^2 q_1 2(J+1) + \{3q_1(B_e/\omega_e) \times [1 + (\alpha_e \omega_e / 6B_e)^2] + 2q_2(B_e/\omega_e)\} (v + \frac{1}{2}),$$

where  $q_1$  and  $q_2$  are parameters defined by the expansion of  $q(R)$  in terms of  $(R - R_e)/R_e$

$$q(R) = q_0 + q_1(R - R_e)/R_e + q_2[(R - R_e)/R_e]^2 + \dots$$

Thus  $\Delta eq_J Q$ , defined as  $e(q_{v,J+1} - q_{v,J})Q$ , is given by

$$\Delta eq_J Q = e(2B_e/\omega_e)^2 q_1 Q 2(J+1),$$

and  $\Delta eq_v Q$ , defined as  $e(q_{v+1,J} - q_{v,J})Q$ , is given by

$$\Delta eq_v Q = e \{ 3q_1 (B_e / \omega_e) [1 + (\alpha_e \omega_e / 6B_e^2)] + 2q_2 (B_e / \omega_e) \} Q.$$

To get a rough approximation of  $\Delta eq_v Q$ , one can assume that  $q_2 = 0$  so that  $q_1$  can be calculated from the easily observed  $\Delta eq_v Q$ . For InF this predicts  $\Delta eq_v Q = 5$  kHz, which can be compared to the measured 10 kHz. The predicted  $\Delta eq_v Q$  is at least in approximate agreement with the observed shift.

Since  $\Delta eq_v Q$  and  $\Delta eq_s Q$  are known from the experiment, the last two expressions can be solved<sup>10</sup> as simultaneous equations in the unknowns  $q_1$  and  $q_2$ . The results,  $q_1 = 43.1 \times 10^{-15}$  esu and  $q_2 = -109 \times 10^{-15}$  esu, show that the expansion parameters have about the same magnitude as expected from the calculations of Zeiger and Bolef.<sup>8</sup>

How large should  $q_1$  and  $q_2$  be? Using the simplest point charge model, one finds  $q = -K/R^3$ . Then a series expansion of  $q$  around  $R_e$  gives

$$q = \left( -\frac{K}{R^3} \right)_{R_e} - 3 \left( -\frac{K}{R^3} \right)_{R_e} \frac{\Delta R}{R_e} + 6 \left( -\frac{K}{R^3} \right)_{R_e} \left( \frac{\Delta R}{R_e} \right)^2 + \dots,$$

that is,  $q_1$  is 3 times, and  $q_2$  is 6 times larger than  $q_0$ . The experimentally derived values of  $q_1$  and  $q_2$  are approximately 4 and 9 times, respectively, larger than the experimentally derived  $q_0$  ( $-12.1 \times 10^{15}$  esu). There is at least qualitative agreement.

#### B. Estimate of the Fourth Derivative of the Electric Potential at the In Nucleus

The factor  $q_2$  defined in the previous section is related to the fourth derivative of the electric potential at the In nucleus,  $h$ , when the internuclear separation is  $R_e$ . This is recognized by comparing the  $q(R)$  expansion in terms of  $q_1$  and  $q_2$ , given above, to a Taylor Series expansion of  $q(R)$ :

$$q(R) = q(R_e) + (\partial q / \partial R)_{R_e} (R - R_e) + \frac{1}{2} (\partial^2 q / \partial R^2)_{R_e} \times (R - R_e)^2 + \dots$$

Thus

$$(\partial^2 q / \partial R^2)_{R_e} = 2q_2 / R_e^2.$$

The  $q$  in the above equation is  $(1 - \gamma_\infty) (\partial^2 V' / \partial R^2)$ , where  $V'$  is the electric potential at the In nucleus when the antishielding effect is turned off. Assuming that  $(1 - \gamma)$  does not vary with  $R$  one finds

$$h' \equiv (\partial^4 V' / \partial R^4)_{R_e} = 2q^{(2)} / (1 - \gamma_\infty) R_e^2.$$

Using  $q_2$  calculated above and  $(1 - \gamma_\infty) = 76.5^{11}$  this gives

$$h' = -7.2 \times 10^{30} \text{ esu.}$$

On the other hand, if one assumes that  $V'$  is due to a point charge at a distance  $R_e$ , one finds  $h' = -3.6 \times 10^{30}$  esu. Thus, the point-charge model predicts a value for  $h'$  which is only a factor of 2 smaller than the experimentally derived value.

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<sup>7</sup> R. M. Sternheimer, private communication.

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<sup>9</sup> E. W. Kaiser, *J. Chem. Phys.* **53**, 1686 (1970).

<sup>10</sup> Here  $Q = 0.834 \times 10^{-24}$  cm<sup>2</sup> as reported by G. F. Koster [*Phys. Rev.* **86**, 148 (1952)] was used. The rotational and vibrational constants are from R. F. Barrow, D. V. Glaser, and P. B. Zeeman, *Proc. Phys. Soc. London* **68A**, 962 (1955).

<sup>11</sup>  $(1 - \gamma_\infty) = 76.5$  is calculated from the experimentally determined value of  $eqQ$  and H. W. de Wijn's theory [*J. Chem. Phys.* **44**, 810 (1966)] for the quadrupole interaction assuming that the ionic character of InF is one and using  $Q = 0.834 \times 10^{-24}$  cm<sup>2</sup>.