

## Hyperfine Structure of Thallium Bromide\*

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The hyperfine structure of the  $J=2$  and  $J=3$  rotational states of TlBr has been measured with a molecular-beam electric resonance spectrometer. Hyperfine transition frequencies were measured under conditions of very weak electric and magnetic fields. The linewidth was 500 Hz. The hyperfine interaction constants have been determined for  $^{205}\text{Tl}^{79}\text{Br}$ ,  $^{205}\text{Tl}^{81}\text{Br}$ ,  $^{203}\text{Tl}^{79}\text{Br}$ , and  $^{203}\text{Tl}^{81}\text{Br}$  in the first five vibrational states for  $J=2$ . In addition, the interaction constants for  $J=3$ ,  $v=0$  were determined for  $\text{Tl}^{79}\text{Br}$  and  $\text{Tl}^{81}\text{Br}$ , but it was not possible to resolve the effect of the two thallium isotopes in the  $J=3$  state. The spectra measured are well described by a hyperfine Hamiltonian containing the bromine quadrupole interaction, the spin-rotation interactions of both the thallium and the bromine nuclei, and both the scalar and tensor parts of the spin-spin interaction between the nuclei. The dependence of the magnetic hfs constants on vibrational state and on isotopic composition shows good agreement with theory. The magnetic octupole interaction of the bromine nucleus in TlBr is negligibly small, and we find no evidence for nuclear polarization or pseudoquadrupole effects.

### I. INTRODUCTION

The thallium bromide molecule is interesting for hyperfine structure measurements because there are four stable isotopic species of the molecule ( $^{205}\text{Tl}^{79}\text{Br}$ ,  $^{203}\text{Tl}^{79}\text{Br}$ ,  $^{205}\text{Tl}^{81}\text{Br}$ ,  $^{203}\text{Tl}^{81}\text{Br}$ ) which are abundant enough to yield reasonably strong spectral lines. Since the nuclear spins of the two Tl isotopes are both  $\frac{1}{2}$  and the spins of the two Br isotopes are both  $\frac{3}{2}$ , measurements of the transition frequencies for all four isotopic species allow a comparison of the various hyperfine interaction constants between molecules having the same number of electrons and the same nuclear spins, but slightly different nuclear electric and magnetic moments and nuclear masses. Moreover, since a comparable situation exists with the four naturally abundant species of thallium chloride (both  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  have spin  $\frac{3}{2}$ ), a detailed comparison can be made with the case when the mass of the halogen is reduced by a factor of 2.

Since TlBr has a vibrational constant which is small enough ( $\omega_e=192\text{ cm}^{-1}$ ) so that higher vibrational states have appreciable populations at relatively low source temperatures ( $500^\circ\text{C}$ ), a study of the hyperfine interactions as a function of vibrational state can be made.

With the work<sup>1</sup> of Gräff and his collaborators on TlF, our studies<sup>2,3</sup> of TlCl and TlI, and the present experiment<sup>4,5</sup> on TlBr, the hyperfine structure of the entire family of thallium halides is now as well measured as is the hfs of any alkali halide.

### II. EXPERIMENT

A molecular-beam electric resonance (MBER) spectrometer, described in more detail elsewhere,<sup>5,6</sup> was used for this investigation of the hyperfine structure of TlBr. Transitions were measured at minimal dc electric and magnetic fields (1.5 V/cm and 0.05 G, respectively); the oscillatory electric field was about 1.3 V/cm(rms). A linewidth of 500 Hz was obtained with a transition

region 50 cm long. The quadrupole interaction in TlBr was known to about 1% from microwave absorption spectroscopy,<sup>7</sup> and this information reduced the range we had to search for the radio-frequency spectrum of the molecule.

Transitions within the  $J=1$  rotational state were weak but proved useful for confirming that the  $J=1$  spectrum was indeed in the expected place. These transitions were weak because of the small effective aperture of the four-pole focusing fields for  $J=1$  TlBr molecules. Bennewitz *et al.*<sup>8</sup> have shown that the effective aperture is proportional to the ratio of the rotational constant to the source temperature, and this ratio is considerably smaller for TlBr than for diatomic molecules such as RbF and CsF whose  $J=1$  hfs spectra have been observed with our spectrometer.

Hyperfine transitions within the  $J=2$  rotational state were measured for all four isotopic species of TlBr in states up to  $v=4$ . In many cases, corresponding spectral lines from molecules with the same bromine isotope but different thallium isotope were only partially resolved. The centers of each of the overlapping lines were determined by taking an assumed ideal line shape obtained from resolved lines, superimposing two such lines with relative amplitudes of 70:30 (the ratio of the natural abundance of the two thallium isotopes), and using the superposition which matched the line shape most completely to establish the frequencies of the two components. An estimate of the uncertainty in the line centers is  $\pm 100$  Hz.

Transitions within the  $J=3$  rotational state were also measured. In most cases these lines were not as strong nor as well resolved as the lines in the  $J=2$  spectrum.

### III. RESULTS

The hyperfine structure of thallium bromide as observed in this experiment can be described with a

TABLE I. Hyperfine interaction constants for the  $J=2$  state of TlBr.<sup>a</sup>

TlBr	$eqQ$	$c_1$	$c_2$	$c_3$	$c_4$
$v=0$					
205, 79	126 310.88(10)	3.690(5)	42.74(5)	-1.65(5)	-6.35(5)
205, 81	105 516.34(20)	3.915(5)	42.02(5)	-1.77(5)	-6.84(5)
203, 79	126 310.96(20)	3.691(10)	42.55(8)	-1.55(8)	-6.39(8)
203, 81	105 516.50(20)	3.909(10)	41.83(8)	-1.68(8)	-6.91(8)
$v=1$					
205, 79	126 808.31(20)	3.681(8)	42.60(5)	-1.67(5)	-6.28(5)
205, 81	105 928.26(20)	3.908(8)	41.85(5)	-1.79(5)	-6.81(5)
203, 79	126 808.75(25)	3.687(10)	42.14(8)	-1.68(8)	-5.95(8)
203, 81	105 928.73(25)	3.915(10)	41.59(8)	-1.73(8)	-6.76(8)
$v=2$					
205, 79	127 302.61(20)	3.67(2)	42.43(8)	-1.68(8)	-6.28(8)
205, 81	106 337.52(20)	3.89(2)	41.72(8)	-1.78(8)	-6.77(8)
203, 79	127 303.64(25)	3.68(2)	42.15(10)	-1.68(8)	-6.15(10)
203, 81	106 338.39(25)	3.94(2)	41.44(10)	-1.71(8)	-6.52(10)
$v=3$					
205, 79	127 793.58(30)	3.66(3)	42.31(10)	-1.66 <sup>b</sup>	-6.12 <sup>b</sup>
205, 81	106 744.19(30)	3.88(3)	41.62(10)	-1.79(10)	-6.79(10)
203, 79	127 795.20(30)	3.68(3)	42.00(10)	-1.68 <sup>b</sup>	-6.12 <sup>b</sup>
203, 81	106 746.05(30)	3.89(3)	41.52(10)	-1.86(10)	-6.90(10)
$v=4$					
205, 79	128 281.82 <sup>c</sup>	3.65 <sup>c</sup>	42.22 <sup>c</sup>	-1.66 <sup>c</sup>	-6.04 <sup>c</sup>
205, 81	107 148.06 <sup>c</sup>	3.87 <sup>c</sup>	41.52 <sup>c</sup>	-1.78 <sup>c</sup>	-6.73 <sup>c</sup>

<sup>a</sup> All constants in units of kilohertz.<sup>b</sup> Values predicted from change in  $c_3$  and  $c_4$  with  $v$ .<sup>c</sup> Values predicted from change in constants with  $v$  and confirmed by observation on a few lines.

Hamiltonian<sup>3</sup> which contains the electric quadrupole interaction of the bromine nucleus ( $eqQ$ ), the spin-rotation interactions of both nuclei ( $c_1$  for bromine,  $c_2$  for thallium), and the tensor and scalar parts of the nuclear spin-spin interactions ( $c_3$  and  $c_4$ ). The very weak electric and magnetic fields in the transition region of our spectrometer shift the lines by less than 100 Hz, so Stark and Zeeman operators are not included in our Hamiltonian. Calculations of the molecular energy levels include corrections up to third order for contributions of the bromine quadrupole interaction which are off diagonal in  $J$ ; contributions from the magnetic interactions of the thallium nucleus (i.e., those involving  $c_2$ ,  $c_3$ , and  $c_4$ ) which are off diagonal in  $F_1$  are also taken into account.

A least-squares criterion is used to choose the set of five constants that provide the best fit between the energy levels of the Hamiltonian and the observed spectra. The major source of error in this experiment lies in the uncertainty in choosing the central frequency of the individual spectral lines; the errors quoted for the

hfs constants have been estimated by seeing how these constants change when different weights are assigned to the input frequencies.

Table I lists the calculated hyperfine interaction constants for the  $J=2$  spectra observed. For some of the higher vibrational states there were too few lines measured to determine all of the constants. In these cases reasonable values for some of the constants, say  $c_3$  and  $c_4$ , could be provided by extrapolation from the corresponding constants of lower vibrational state, and the remaining constants calculated from the measured lines. (The constants so determined are marked by the letter c in Table I.) All the hfs constants for  $J=2$ ,  $v=4$  given in Table I are extrapolated from  $v \leq 3$  data; they have been confirmed by observations on a few  $J=2$ ,  $v=4$  lines in each of the isotopes of TlBr.

Table II lists the hyperfine constants obtained for  $J=3$ ,  $v=0$ ; because not enough lines were observed to determine all of the Tl<sup>203</sup>Br constants independently, values of  $c_3$  and  $c_4$  for this state were taken to be equal to those of  $J=2$ ,  $v=0$ , which can be justified since  $c_3$

TABLE II. Hyperfine interaction constants for  $J=3$ ,  $v=0$  state of TlBr.<sup>a</sup>

	$eqQ$	$c_1$	$c_2$	$c_3$	$c_4$
Tl <sup>79</sup> Br	126 311.26(25)	3.700(10)	42.80(25)	-1.66(8)	-6.33(8)
Tl <sup>81</sup> Br	105 516.78(30)	3.918(10)	41.90(30)	-1.77 <sup>b</sup>	-6.84 <sup>b</sup>

<sup>a</sup> Constants in kilohertz.<sup>b</sup> Values taken from  $J=2$ ,  $v=0$ .

and  $c_4$  do not change appreciably with  $J$  in Tl<sup>79</sup>Br. We were not able to resolve the effect of the two thallium isotopes in the  $J=3$  spectra.

The line frequencies calculated by using our hfs constants in the zero-field hyperfine Hamiltonian agreed very well with the observations. All the calculated frequencies fall within  $\pm 100$  Hz of the measured line centers, and the average fit of the most intense set of lines (those from  $J=2$ ,  $v=0$  <sup>205</sup>TlBr) is  $\pm 30$  Hz.

In the preliminary analysis of the spectra we had included in the Hamiltonian a term to account for the magnetic octupole interaction of the bromine nucleus.<sup>9</sup> Although this improved the fit slightly, the octupole contributions to the line frequencies were so small ( $< 50$  Hz) that we did not retain the octupole term for the final interpretation of the experiment.

## IV. DISCUSSION

### A. Magnetic Hyperfine Interactions

Reasonable theories for the spin-rotation interaction<sup>10</sup> in a molecule (in vibrational state  $v$ ) predict that the coupling constant for this interaction should be proportional to the nuclear gyromagnetic ratio  $g_i$  ( $i=1$  for bromine, 2 for thallium) times the rotational constant for the molecule:  $c_i \propto g_i B_v$ . The values of  $c_i(v)$  obtained from the  $J=2$  spectra of <sup>205</sup>Tl<sup>79</sup>Br and <sup>205</sup>Tl<sup>81</sup>Br are plotted as a function of  $v$  in Fig. 1; the solid lines are based on the expected relation  $c_i(v) = c_i(0)B_v/B_0$ , and we see that the agreement between results and expectations is good. In addition, we have compared ratios of the spin-rotation constants with ratios of the appropriate  $g_i B_v$  products for all isotopic combinations of thallium and bromine, and the agreement is quite satisfactory. Similarly, the spin-spin interaction constants  $c_3$  and  $c_4$  are both found to be proportional to the product of the gyromagnetic ratios of the thallium and bromine nuclei.

The coupling constants for the magnetic interactions

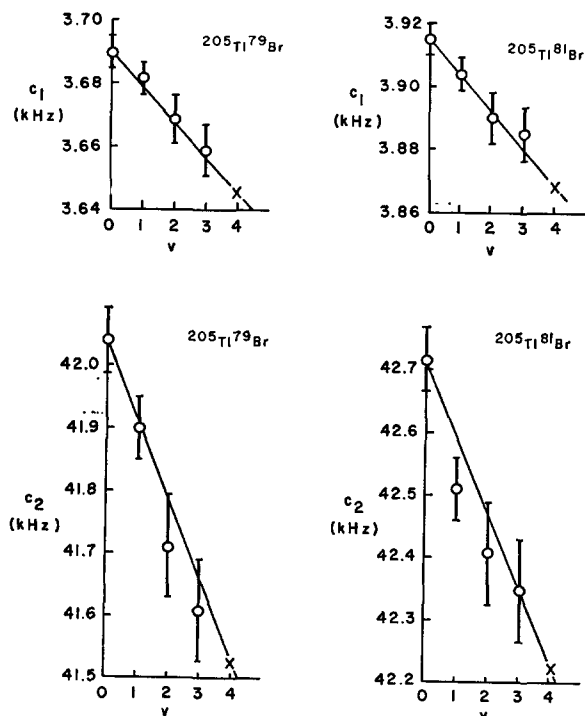


FIG. 1. Plots of  $c_i(v)$ , the  $J=2$  spin-rotation interaction constants, as functions of vibrational state  $v$ . The  $v=4$  values of  $c_1$  and  $c_2$  (Footnote b, Table I) were obtained from these plots (X) and confirmed by observations on a few  $J=2$ ,  $v=4$  lines in each of the isotopes of TlBr.

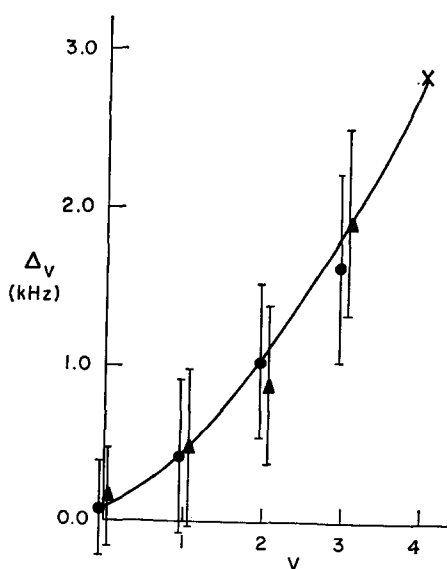


FIG. 2. Dependence of the quantity,  $\Delta_v = eqQ(^{205}\text{TlBr}) - eqQ(^{208}\text{TlBr})$ , on vibrational state  $v$ . The solid line is determined by the coefficients  $a$ ,  $b$ , and  $c$  in Table III for Tl<sup>79</sup>Br. The dots give the results for Tl<sup>79</sup>Br; the triangles are for Tl<sup>81</sup>Br.

TABLE III. Expansion coefficients for Eq. (2).<sup>a</sup>

Expansion coefficients for Eq. (2)	<sup>206</sup> Tl <sup>79</sup> Br	<sup>203</sup> Tl <sup>79</sup> Br	<sup>206</sup> Tl <sup>81</sup> Br	<sup>203</sup> Tl <sup>81</sup> Br
<i>a</i>	126 060.99	126 060.97	105 309.38	105 309.42
<i>b</i>	500.56	500.69	414.58	414.80
<i>c</i>	-1.57	-1.45	-1.33	-1.28

<sup>a</sup> Coefficients in kilohertz.

do not show a change with  $J$ , but this is not surprising since any expected changes are considerably smaller than the uncertainties in our values for these constants.

### B. Electric Quadrupole Interaction

The rotational state dependence of the quadrupole coupling constant has been discussed by Zeiger and Bolef<sup>11</sup>; they assume an anharmonic-oscillator potential for their vibrating rotor model of the molecule. From their expression for the dependence of  $eqQ$  on  $J$  we can write the change in  $eqQ$  between adjacent rotational states as

$$\Delta eqQ_{(J \rightarrow J+1)} = (2J+1)(2B_e^2/\omega_e)\xi, \quad (1)$$

where  $B_e$  is the equilibrium rotational constant of the molecule,  $\omega_e$  is the vibrational constant, and  $\xi$  is the second coefficient in the expansion of  $eqQ_v$  in powers of  $[(R-R_e)/R_e]$ ,  $R$  being the internuclear separation and  $R_e$  the equilibrium internuclear separation. In TlBr, the predicted change of  $eqQ$  between  $J=2$  and  $J=3$  is +50 Hz. The observed changes (+380±300 Hz) in Tl<sup>79</sup>Br and (+400±400 Hz) in Tl<sup>81</sup>Br are at least in qualitative agreement with the predictions.

The observed dependence of  $eqQ$  on the vibrational state  $v$  is conveniently expressed by the power series

$$eqQ_v = a + b(v + \frac{1}{2}) + c(v + \frac{1}{2})^2 + \dots, \quad (2)$$

where  $eqQ_v$  is the quadrupole interaction of the  $v$ th vibrational state and  $a$ ,  $b$ , and  $c$ , the coefficients of the expansion, are given (for  $J=2$  and all four isotopic species) in Table III. From the tabulated hfs constants we see that it is only for  $v>0$  states that changing from <sup>203</sup>Tl to <sup>205</sup>Tl produces a significant change in  $eqQ$  for a given bromine isotope. This effect is illustrated in Fig. 2. Thus we find that the coefficients  $b$  and  $c$  are more sensitive than is  $a$  to small changes in the nuclear masses, but we are not aware of a theory for the quadrupole interaction which explains this.

### C. False Quadrupole Effects

Nuclear moments of higher order than magnetic octupole cannot contribute to the hyperfine structure since the spin of bromine is only  $\frac{3}{2}$ , so the TlBr molecule

offers a good opportunity to look for false quadrupole effects.<sup>10</sup> Such effects are likely to arise from a distortion of the nucleus by the electric fields within the molecule (nuclear polarization)<sup>12,13</sup> or from a second-order paramagnetic interaction between the nuclear magnetic moment and the electron orbital moment (pseudoquadrupole effect).<sup>12,14</sup> The energies from both the nuclear polarization and the pseudoquadrupole effect vary with nuclear orientation as does the energy from the true nuclear-quadrupole interaction. The measured value of  $eqQ$  is thus the sum  $eqQ(\text{true}) + eqQ(\text{false})$ , where  $eqQ(\text{true})$  is the value from the actual nuclear electric quadrupole interaction, and  $eqQ(\text{false})$  contains the contributions from the pseudoquadrupole effect and nuclear polarization. A comparison of the ratio of values of  $eqQ$  for two isotopes of bromine, as measured in different environments, serves as a way to look for the existence of false quadrupole effects. We compare our measured values of  $eqQ$  for Tl<sup>79</sup>Br and Tl<sup>81</sup>Br, corrected for differences in vibrational motion due to the mass differences,<sup>15</sup> with the ratios of the quadrupole interaction constants in free bromine atoms as determined by Brown and King.<sup>16</sup> The differences in the ratios between TlBr and the free atom are quite small, about  $(4 \pm 4) \times 10^{-6}$ ; thus we have no evidence for pseudoquadrupole or nuclear polarization effects in TlBr.

From this experiment we see that the radio-frequency spectra from <sup>1</sup>Σ molecules, even those with large quadrupole interactions, agree with theory to within 10<sup>-6</sup>  $eqQ$  or better. Confidence in the theory to this degree is needed so that the hfs of molecules such as thallium iodide and indium fluoride may be examined in detail for evidence of a nuclear electric hexadecapole interaction.

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<sup>16</sup> H. H. Brown and J. G. King, *Phys. Rev.* **142**, 53 (1966). The ratio of quadrupole interaction constants they obtain is  $b_{79}/b_{81} = 1.1970568(15)$ .

## Hyperfine Structure of Thallium Iodide and an Upper Limit for the Electric Hexadecapole Moment of the Iodine Nucleus\*

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The hyperfine structure of thallium iodide has been studied in the  $J=3$  and  $J=4$  rotational states in an attempt to observe a nuclear electric hexadecapole effect. This study was carried out on a high-resolution molecular-beam electric resonance spectrometer at very weak electric and magnetic fields. The molecule is well described by the usual five hyperfine interaction constants which are (in kilohertz)

	$^{205}\text{Tl}^{127}\text{I}$	$^{203}\text{Tl}^{127}\text{I}$
$eqQ$	-438 916.3±0.5	-438 917.3±1.0
$c_1$	3.05±0.05	3.09±0.1
$c_2$	34.65±0.15	34.36±0.3
$c_3$	-2.48±0.1	-2.59±0.2
$c_4$	-6.67±0.05	-6.57±0.1.

No evidence for a hexadecapole interaction constant as large as 500 Hz was found; this result is interpreted as setting an upper limit of  $\sim 10^{-37}$  cm<sup>4</sup> for the nuclear electric hexadecapole moment of  $^{127}\text{I}$ .

### I. INTRODUCTION

We have measured the radio-frequency spectrum of the thallium iodide molecules  $^{203}\text{Tl}^{127}\text{I}$  and  $^{205}\text{Tl}^{127}\text{I}$  with a molecular-beam electric resonance (MBER) spectrometer. We had two motivations for this work. First, this experiment completes a series of studies on the hyperfine structure of the thallium halides. Second, the TII molecule appeared to offer a good opportunity to identify and measure a nuclear electric hexadecapole ( $2^4$ -pole) interaction. The iodine nucleus has a large electric quadrupole moment<sup>1</sup> and an observed magnetic octupole moment,<sup>2</sup> both of which suggest the existence of higher-order moments; moreover the spin of iodine ( $\frac{5}{2}$ ) is large enough to allow the nucleus to exhibit a hexadecapole interaction. In addition, we know that the quadrupole hfs of TlCl and TlBr, in which the halogen nuclear spin is less than 2, is very

well understood,<sup>3,4</sup> so any deviations from quadrupole hfs intervals in TII might be attributed with confidence to the interaction of a higher-order nuclear moment.

### II. EXPERIMENT

The important features of the MBER spectrometer used for these measurements have been described elsewhere.<sup>5,6</sup> In addition to working with single resonances, we used a microwave rf double-resonance technique to identify some of the observed radio-frequency transitions. By observing the intensity of a given rf transition (which occurs within a single rotational state) as different rotational transitions were induced with a microwave  $C$  field, we were able to determine which rotational state was involved in the rf transition.

As pointed out in the preceding paper,<sup>4</sup> electric