Hyperfine Structure in the Rotational Spectrum of GaBr

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The hyperfine structure of the rotational transition $J = 2 \leftarrow 1$ in the vicinity of 9.8 GHz was measured. The analysis yielded the following quadrupole coupling constants:

$e\,q_v\,Q\,(^{79}Br) = 105.78\,(34) + 0.92\,(38)\,(v+1/2)\,\text{MHz},$

$e\,q_v\,Q\,(^{81}Br) = 88.55\,(35) + 0.60\,(32)\,(v+1/2)\,\text{MHz},$

$e\,q_v\,Q\,(^{69}Ga) = -86.68\,(30) + 0.36\,(24)\,(v+1/2)\,\text{MHz},$

$e\,q_0\,Q\,(^{71}Ga) = -54.58\,(25)\,\text{MHz}.$

These results are consistent with systematic trends in the group of (III a/VII a)-compounds and remove some discrepencies in the literature.

The investigation of microwave spectra has provided a large amount of information about gaseous molecular species resulting in data on molecular structure. In this concern the studies of diatomic molecules are of basic interest because of the significant variations in the bonding character causing remarkable changes and trends of molecular parameters such as electric dipole moments or nuclear quadrupole coupling constants which can be measured by microwave spectroscopy.

First measurements of pure rotational transitions of gallium monohalides GaCl, GaBr, and GaI were done by Barrett and Mandel [1]. They measured one transition for each species. In case of GaBr the transition $J = 5 \leftarrow 4$ at 24 GHz has been observed. They also succeeded to resolve the hyperfine structure of this transition and could derive nuclear quadrupole coupling constants $e\,q\,Q$ of Ga and Br.

Results of former measurements [2] on diatomics of the group (III/VII)-compounds lead us to some rough extrapolations of the hyperfine parameters in GaBr which are much different from the derived constants of Barrett and Mandel [1]. In parallel Lovas and Tiemann [3] compiling microwave spectral tables of diatomic molecules made recalculations including the measurements of Barrett and Mandel [1] on GaBr. They corrected misassignments in quantum numbers of the poorly resolved hyperfine

structure. An accurate caculation of the relative intensities was necessary to determine these corrections. The new analysis resulted in more reliable hyperfine structure parameters which are in better agreement with the systematic trends in this group of molecules.

To improve these results we measured the rotational transition $J = 2 \leftarrow 1$ of GaBr at 10 GHz. By choosing such a low J transition we got larger hyperfine structure splittings and a less complicated structure by overlapping lines. In reducing the reaction temperature to get smaller line widths we were able to increase the precision of the derived coupling constants by more than one order of magnitude.

Our measurements in the X-band were mainly concerned to the ground vibrational state of the four isotopic species $^{69}Ga^{79,81}Br$ and $^{71}Ga^{79,81}Br$ with natural abundances of 30% and 20%, respectively. In addition transitions of the more abundant $^{69}Ga^{79}Br$ and $^{69}Gg^{81}Br$ in the first excited vibrational state were observed to determine the vibrational dependence of the hyperfine structure parameters. The spectrometer was a conventional 100 kHz Stark-effect spectrometer with a heated absorption cell (Type I, see [3]) using modulation fields of about 1000 V/cm. The small signal to noise ratio was increased with a signal averaging computer. All lines were measured by adding the result of 16 sweeps of 20 sec with a time constant of 100 msec (12 dB/octave) viewing a frequency region of 2 MHz. The signal to noise ratio of the strongest component was 15 : 1.

GaBr was produced directly inside of the absorption cell by reaction of $PbBr_2$ mixed with liquid gallium. The $PbBr_2$ was carefully prepared for some hours at temperatures of about 350 °C to remove residual water. Before each new run the cell was evacuated for a day to remove gases mainly water. The reaction begins at temperatures of about 220 °C. Lines were measured up to temperatures of 330 °C. At temperatures of 250 °C a total line width at half maximum intensity of 300 kHz was observed. Therefore a single line could normally be measured with an accuracy of 30 kHz.

All isotopic nuclei of gallium and bromine have spins with $I = 3/2$ resulting in double quadrupole hyperfine splittings of rotational transitions. According to the reanalysis [2] of the $J = 5 \leftarrow 4$ transition measured by Barrett and Mandel [1] one should expect nuclear coupling constants for ^{79}Br and ^{69}Ga of

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Table 1. Effective rotational constants $B_v + 8\,Y_{02}$ and the nuclear quadrupole coupling constants $e\,q_v\,Q$ of the isotopic species of GaBr derived from the analysis of the rotational transition $J = 2 \leftarrow 1$. All Parameters are given in MHz.

Molecule	v	$B_v + 8\,Y_{02}$	$(e\,q_v\,Q)_{Br}$	$(e\,q_v\,Q)_{Ga}$	
$^{69}Ga^{79}Br$	0	2477.166(2)	106.24(20)	−86.53(23)	This work
			134(3)	−74(5)	Barrett and Mandel [1]
			108.6(30)	−89.8(30)	Lovas and Tiemann [2]
	1	2467.373(3)	107.16(32)	−86.07(26)	This work
$^{69}Ga^{81}Br$	0	2448.678(2)	88.85(22)	−86.46(21)	This work
	1	2439.055(3)	89.45(23)	−86.21(27)	This work
$^{71}Ga^{79}Br$	0	2439.931(2)	106.36(23)	−54.55(27)	This work
$^{71}Ga^{81}Br$	0	2411.448(3)	88.62(22)	−54.61(29)	This work

similar magnitude. Thus an intermediate angular momentum $\boldsymbol{F}_1$ from the coupling of $\boldsymbol{I}_1$ and $\boldsymbol{J}$ is not well defined. The energy levels are characterized by J and the quantum number F of the total angular momentum and a number X, which counts the energy levels to the same F-value in order of increasing energy.

The selection of the allowed transitions between the hyperfine structure levels of two neighbouring rotation states is given by the rule $\varDelta F = 0, \pm 1$. The coupling constants are small compared to the rotational spacing. Therefore the selection rule $\varDelta J = \pm 1$ is still fulfilled. All calculations of the spectrum were performed with the programs worked out by Schenk et al. [4].

The long table showing the assignment, the measured frequencies, the calculated frequencies and relative intensities can be requested of the authors.

The $e\,q_v\,Q$-values and the constants $B_v{}'$ [Eqn (1)] were evaluated by a least square fit of the observed lines for each isotope and each vibrational state separately [4]. The mean quadratic error resulted in values between 12 and 18 kHz which is in good agreement with the experimental uncertainty of measured frequencies of 30 kHz as mentioned above.

Table 1 shows the fitted molecular constants. For comparison the coupling constants evaluated by Barrett and Mandel [1] are given. The values derived by Lovas and Tiemann [2] from the measurements of Barrett and Mandel are in sufficient agreement with our more precise results.

The Dunham coefficients Y_{01} and Y_{11} which may be calculated form $B_v{}'$

$$B_v{}' = Y_{01} + Y_{11}(v + 1/2) + \cdots + 2\,Y_{02}(J + 1)^2 \quad (1)$$

are shown in Table 2. The higher order coefficients like Y_{21} are neglected. For calculating the coefficient Y_{02} in Eq. (1) the relation [5]

$$Y_{02} \approx -4\,Y_{01}^3/\omega_e^2 \quad (2)$$

was used. The vibrational constant $\omega_e = 264.5 \text{ cm}^{-1}$ was taken from Mielscher and Wehrli [6] resulting in $Y_{02} = -0.973(2)$ kHz for $^{69}Ga^{79}Br$.

The dependence of the $e\,q\,Q$-values on the vibrational state is usually described by the following expansion [5]:

$$e\,q_v\,Q = e\,q_e\,Q + e\,q_1\,Q\,(v + 1/2) + \cdots . \quad (4)$$

With the values of $e\,q_0\,Q$ and $e\,q_1\,Q$ from this experiment $e\,q_e\,Q$ and $e\,q_1\,Q$ can be calculated. We obtain:

$$e\,q_v\,Q\,(^{69}Ga)$$
$$= -86.68(30) + 0.36(24)\,(v + 1/2)\,\text{MHz},$$
$$e\,q_v\,Q\,(^{79}Br)$$
$$= 105.78(34) + 0.92(38)\,(v + 1/2)\,\text{MHz},$$
$$e\,q_v\,Q\,(^{81}Br)$$
$$= 88.55(35) + 0.60(32)\,(v + 1/2)\,\text{MHz}.$$

The values of ^{69}Ga were calculated by averaging the results for $^{69}Ga^{79}Br$ and $^{69}Ga^{81}Br$.

From the $e\,q_e\,Q$-values of ^{79}Br and ^{81}Br the ratio of the nuclear quadrupole moments can be derived:

$$Q(^{79}Br)/Q(^{81}Br) = 1.195(9).$$

This result is in good agreement with the more precise value from a determination by Schawlow [7] using atomic beams: 1.197 07(3). The corresponding ratio of the nuclear quadrupole moments of the gallium isotopes from our experiment is

$$Q(^{69}Ga)/Q(^{71}Ga) = 1.585(8).$$

For comparison the result of a beam experiment is given [8]: 1.585 904(3). The good agreement in

Table 2. Dunham coefficients Y_{01} and Y_{11} derived from the measured effective rotational constants $B_v + 8\,Y_{02}$.

Molecule	Y_{01} (MHz)	Y_{11} (MHz)	$Y_{02} \approx -\dfrac{4\,Y_{01}^3}{\omega_e^2}$ (kHz)
$^{69}Ga^{79}Br$	2482.070(3)	−9.793(4)	−0.973(2)
$^{69}Ga^{81}Br$	2453.497(3)	−9.623(4)	−0.950(2)

these comparisons confirms our assignments of the measured hyperfine components.

The eqQ-values derived in this work are totally consistent with the systematic trends in the group of (III/VII)-compounds. In addition they verify the interpretation of the $J = 5 \leftarrow 4$ rotational transition by Lovas and Tiemann [3]. Thus the old discrepancy is removed.

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