

## STARK–ZEEMAN HYPERFINE STRUCTURE OF $\text{H}^{79}\text{Br}$ AND $\text{H}^{81}\text{Br}$ BY MOLECULAR-BEAM ELECTRIC-RESONANCE SPECTROSCOPY

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We used the molecular-beam electric-resonance (MBER) method to measure the Stark–Zeeman hyperfine structure of the molecules  $\text{H}^{79}\text{Br}$  and  $\text{H}^{81}\text{Br}$ . For the ground vibrational state ( $v=0$ ) and the rotational state  $J=1$  we obtain for both molecules the electric dipole moment and hyperfine structure constants. For the  $\text{H}^{81}\text{Br}$  molecule we also measured the magnetic molecular constants:  $g_J = 0.37122(8)$ ,  $\chi_{\parallel} - \chi_{\perp} = -0.139(7)$  kHz  $\text{kG}^{-2}$ ,  $(\sigma_{\text{av}})_{\text{Br}} = 2748(40)$  (ppm),  $(\sigma_{\parallel} - \sigma_{\perp})_{\text{Br}} = 732(14)$  (ppm), and  $(\sigma_{\parallel} - \sigma_{\perp})_{\text{H}} = 24(12)$  (ppm).

### 1. Introduction

In this experiment we used a molecular-beam electric-resonance (MBER) machine [1], with an added feature of a large homogeneous magnet in the transition region, to measure both the electric and magnetic properties of the molecules  $\text{H}^{79}\text{Br}$  and  $\text{H}^{81}\text{Br}$ . The magnet, capable of producing up to 8.5 kG in the transition region, made it possible to look at transitions between Stark and/or Zeeman shifted sublevels.

Jones and Gordy [2] and more recently Van Dijk [3] used the method of submillimeter wave spectroscopy to determine the hyperfine constants for these molecules. By fitting the observed transitions between Stark sublevels in the  $J=1$ ,  $v=0$  states of these molecules we obtain a more accurate set of constants than those obtained by Van Dijk. The constants we measured in this manner are the effective electric dipole moment  $\mu_{\text{eff}}$ , the quadrupole coupling constants  $(eqQ)_{\text{Br}}$  for the bromine nuclei ( $J_{\text{Br}} = 3/2$ ), the spin–rotation constant for the bromine ( $c_{\text{Br}}$ ), and the hydrogen ( $c_{\text{H}}$ ) nuclei, and the tensorial ( $d_T$ ) as

well as the scalar ( $d_S$ ) parts of the spin–spin interaction in both molecules [4]. Using these constants for  $\text{H}^{81}\text{Br}$  we fit the observed Stark–Zeeman transitions to determine for the first time the magnetic properties of the  $\text{H}^{81}\text{Br}$  molecule: the average shielding  $(\sigma_{\text{av}})_{\text{Br}}$  of the bromine nucleus, the anisotropy in the shielding of the bromine  $((\sigma_{\parallel} - \sigma_{\perp})_{\text{Br}})$  and the hydrogen  $((\sigma_{\parallel} - \sigma_{\perp})_{\text{H}})$  nuclei, the anisotropy in the magnetic susceptibility  $(\chi_{\parallel} - \chi_{\perp})$ , and the rotational  $g_J$  value which determines the rotational magnetic moment  $\mu_J$  of the molecule according to the formula  $\mu_J = g_J \mu_N J$ .

By combining the present Stark-field results with the results of Van Dijk [3] the anisotropy of the molecular polarizability  $(\alpha_{\parallel} - \alpha_{\perp})$  could also be determined. The molecular quadrupole moment  $\theta$  was obtained from the measured  $\chi_{\parallel} - \chi_{\perp}$  and  $\mu_J$  values.

### 2. Theory

The hamiltonian for a diatomic  $^1\Sigma$  molecule with both nuclear spins unequal to zero in an external electric and magnetic field can be written as [1, 5, 6]

$$\begin{aligned}
 H = & H_0 + AJ^2 + \sum_k Q_k \cdot V_k + \sum_k I_k \cdot M_k \cdot J_k \\
 & + \sum_{kl} I_k \cdot D_{kl} \cdot I_l - \mu_{\text{el}} \cdot E - \frac{1}{2} E \cdot \alpha \cdot E - B \cdot G \cdot J \\
 & - \frac{1}{2} B \cdot \chi \cdot B - \sum_k (\mu_k / I_k) I_k \cdot (1 - \sigma_k) \cdot B,
 \end{aligned}$$

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where the sums are over the two nuclei.

The first term  $H_0$  represents the electronic and vibrational energy of the molecule, while the second term the rotational energy with  $A$  the rotational constant and  $J$  the rotational angular momentum. The third term describes the quadrupole interaction of the bromine nucleus (both  $^{79}\text{Br}$  and  $^{81}\text{Br}$  have  $I = 3/2$ ); since  $I_H = 1/2$  the sum reduces to a single term. The fourth term represents the spin-rotation interaction, and the fifth term the sum of both the direct and the electron-coupled spin-spin interaction. The sixth and seventh terms represent the Stark energy, and the contribution of the electric polarizability. The last three terms represent the interactions of the molecule with an external magnetic field. They are in order, the molecular Zeeman effect, the magnetic susceptibility and the nuclear Zeeman effect including electronic shielding.

The matrix elements of the above hamiltonian are products of vector coupling coefficients and coupling constants representing the strength of the different interactions.

In the limit of weak external fields the quadrupole interaction is dominant. Hence the appropriate representation is  $|J I_{\text{Br}} F_1 I_H F M_F\rangle$ , while in the limit of strong external field the couplings are broken down, the appropriate representation is in that case  $|J M_J I_{\text{Br}} M_{I_{\text{Br}}} I_H M_{I_H}\rangle$ . In the hydrogen bromide molecules the quadrupole interaction splits the  $J = 1$  ( $v = 0$ ) level into three sublevels with  $F_1 = 3/2, 5/2$  and  $1/2$ . The separation between adjacent levels is of the order of 100 MHz. For the fields we use (3.3 kV cm $^{-1}$  and 8.4 kG) the Zeeman contribution is about an order of magnitude smaller, and the Stark contribution is another order of magnitude smaller. The spin-rotation and spin-spin interactions are of order of 100 kHz. For this reason we shall use a partly coupled representation to characterize the states. The representation is  $|J I_{\text{Br}} F_1 M_{F_1} I_H M_{I_H}\rangle$  abbreviated as  $|F_1 M_{F_1} M_{I_H}\rangle$ .

The matrix elements for the above hamiltonian have been reported elsewhere [1] in the high field representation, and will not be reproduced here. A computer program calculates these matrix elements and solves the secular equation to obtain the eigenvalues and the eigenvectors. The program also calculates the transition frequencies and the intensities, using the usual two-level transition probability [1].

The program varies the coupling constants of the hamiltonian to obtain a least value for the  $\chi^2$  of the fit.

Second order quadrupole interactions proportional to  $(eqQ)^2/A$  [7] due to coupling of states with  $J' = J \pm 2$  are not included in the program and are added later to the calculated frequencies. These corrections are  $-1.778$  kHz for the  $F_1 \rightarrow F_1' = 3/2 \rightarrow 1/2$  transitions are  $+2.963$  kHz for the  $3/2 \rightarrow 5/2$  transitions of  $\text{H}^{81}\text{Br}$ ;  $-2.546$  kHz and  $+4.244$  kHz for the transitions  $3/2 \rightarrow 1/2$  and  $3/2 \rightarrow 5/2$ , respectively, of  $\text{H}^{79}\text{Br}$ .

### 3. Experimental apparatus

The MBER apparatus used in this experiment has been described in detail elsewhere [1]. Hence, only relevant features will be described here. Commercial HBr gas was used for this experiment and the runs were performed with the source at room temperature. The beam machine employs a symmetric A and B fields configuration with electric quadrupoles as state selectors. The C field has two parallel plates for the application of the radio frequency and dc electric fields and a large C-type external electromagnet with pole tips 50 cm X 24 cm and 9 cm gap, which can be placed over the parallel plates, when studying Zeeman effect. The C-field plates are separated by quartz spacers 0.63632(2) cm thick. In most of the runs we used a Stark voltage of +1100 V on one plate and  $-1000$  V on the other. Hence the resulting electric field was 3300.23 V cm $^{-1}$ . Two Fluke 332 A voltage standards were used for this field. The magnetic field was measured with a NMR probe before and after the magnet was placed over the C-field chamber. Measurement of the magnetic field during the runs was not possible.

The rf voltage is obtained from a Hewlett-Packard 5105 A synthesizer, chopped at 25 Hz and amplified. The detector is a commercial mass filter with particle multiplier and phase sensitive demodulation. Signal to noise ratio was about 10 for the stronger lines at an intergration time constant of 1 sec.

### 4. Spectra and results

The constants obtained by Van Dijk for  $\text{H}^{79,81}\text{Br}$  were used to calculate the approximate Stark hyper-

fine frequencies for the  $J = 1, v = 0$  states of the molecules. The calculated frequencies were within a couple of kHz from the observed ones.

Deviations between the observed frequencies at  $3300.23 \text{ V cm}^{-1}$  and the frequencies calculated using the best-fit constants was for most lines 20 – 50 Hz. Only for a few lines the deviation was 100 – 140 Hz. For  $\text{H}^{81}\text{Br}$  18 well resolved transitions were observed, for  $\text{H}^{79}\text{Br}$  nine. The observed full line width of the spectra was 1.2 – 1.6 kHz. This is in agreement with the natural line width for the time of flight of the molecules in the transition region. For some of the observed lines the splitting of their components in the earth's magnetic field is large enough to cause them to appear as a broad symmetric or asymmetric line, or as two separate lines.

The separation of the  $(F_1, M_{F_1}, M_{JH}) \rightarrow (F_1', M_{F_1}', M_{JH}')$  =  $(3/2, \pm 1/2, \pm 1/2) \rightarrow (5/2, \mp 1/2, \pm 1/2)$  transition in  $\text{H}^{81}\text{Br}$  at 109754.32 kHz was used to measure the magnitude of the field in the C can, the value was 0.47 G. For this line the electromagnet had to be used to reduce the residual field in the C region.

Preliminary runs at 100 G and 8.4 kG were performed for  $\text{H}^{81}\text{Br}$  to obtain a starting set of the magnetic constants for the fitting procedure. As mentioned above it was not possible to establish the magnitude of the magnetic field at the beam position or during the runs. Hence we measured the magnitude of the field before placing the magnet over the C region and measured the frequencies of the transitions  $(3/2, 3/2, -1/2) \rightarrow (5/2, 1/2, -1/2)$  and  $(3/2, 3/2, 1/2) \rightarrow (5/2, 1/2, 1/2)$  whose frequencies at  $E_{dc} = 3300.23 \text{ V cm}^{-1}$  and  $B = 8397.15 \text{ G}$  were 102437.590(25) and 102410.560(25) kHz, respectively. Then we moved the magnet away and remeasured the field.

The observations of different runs were self consistent. The 102.4 MHz lines have a  $-0.916 \text{ kHz G}^{-1}$  dependence on the magnetic field and a  $+120 \text{ Hz V}^{-1} \text{ cm}$  on the electric field. Thus we measured this line regularly during the runs and all observed lines were corrected for drift and variation in the magnetic field from one run to another.

For monitoring of the electric field between the runs we used two lines at 109766.439(60) and 109757.759(60) kHz corresponding to the transitions  $(3/2, 1/2, 1/2) \rightarrow (5/2, 1/2, 1/2)$  and  $(3/2, 1/2, -1/2) \rightarrow (5/2, 1/2, -1/2)$ , respectively. These lines have a  $+0.054 \text{ kHz G}^{-1}$  and an electric field dependence of

$+1416 \text{ Hz V}^{-1} \text{ cm}$ . The above monitoring procedures indicated that the magnetic field drift was about 0.60 G, mostly due to temperature variation, and the electric field variation was within 15 ppm. The averages of the corrected values of the transition frequencies were fitted to obtain the magnetic constants.

The second order contributions to the energy due to the Stark effect and the contributions due to the electric polarizability have the same  $J, M$  dependence for a  $^1\Sigma$  molecule. Consequently they cannot be determined separately from our measurements and only an effective dipole moment  $\mu_{\text{eff}}$  defined by:

$$\begin{aligned} & -3\mu_{\text{eff}}^2/2hAJ(J+1) \\ & = -3\mu_{\text{el}}^2/2hAJ(J+1) + (\alpha_{\parallel} - \alpha_{\perp}), \end{aligned}$$

can be deduced.

The electric constants for  $\text{H}^{79}\text{Br}$  obtained from the least squares fit of the Stark hyperfine transitions of the molecule are given in table 1. In table 2 we list the electric and magnetic constants for  $\text{H}^{81}\text{Br}$ . In the evaluation of the data we used  $A = 250\,357.519 \text{ MHz}$  and  $250\,280.192 \text{ MHz}$  for  $\text{H}^{79}\text{Br}$  and  $\text{H}^{81}\text{Br}$ , respectively [3]. For the Planck's constant we used the value  $6.626196(50) \times 10^{-34} \text{ J sec}$ .

The errors quoted on the electric and magnetic dipole moments and on  $(\sigma_{\text{av}})_{\text{Br}}$  are due to uncertainties in the electric and magnetic field, respectively. The uncertainty in the value of the magnetic field is of the order of  $1 \times 10^{-4}$ . When the magnetic field is changed by +1 G the magnetic constants  $(\sigma_{\text{av}})_{\text{Br}}$  and  $g_J$  change by +20 ppm and  $-4 \times 10^{-5}$ , respectively; all the other constants do not change within the experimental errors. Hence the values for these quantities should be  $g_J = 0.37122(8)$  and  $(\sigma_{\text{av}})_{\text{Br}} = 2748(40)$ . The errors of the other quantities are three times their standard deviation.

## 5. Discussion

In tables 1 and 2 we list also the results of Van Dijk's work as well as those of others for comparison with the results of the present investigation. The agreement between ours and Van Dijk's results seems to be better for  $\text{H}^{79}\text{Br}$  than it is for  $\text{H}^{81}\text{Br}$ .

The values for the effective electric dipole moments

Table 1  
Molecular constants of H<sup>79</sup>Br ( $J=1, v=0$ )

Constant	Present work	Van Dijk [3]	Other measurements
$\mu_{el}$ (D)	0.82657(8) <sup>a)</sup>	0.8272(3)	0.834(8) [10]
$(eqQ)_{Br}$ (kHz)	532305.90(24)	532304.1(8)	535400(1400) [2]
$c_{Br}$ (kHz)	290.796(28)	290.83(8)	290(200) [2]
$c_H$ (kHz)	-41.97(26)	-41.27(31)	-43(3) [8]
$d_T$ (kHz)	10.296(70)	10.03(21)	
$d_S$ (kHz)	-0.145(159)		

a) Effective dipole moment, see text.

for the HBr molecules, despite the increased accuracy of our measurement, still do not reflect the effects of isotopic substitution. Hence we can take an average value for this quantity as 0.82656(6) D. Other measurements of the electric dipole moment are by Zahn [9] 0.788 D and by Robinette and Sanderson [10] 0.834(8) D. Tipping and Herman [11] calculated the electric dipole moment for this molecule using the vibration rotation data of Babrov et al. [12], to be 0.824(6) D. Van Dijk using his DBr, HBr isotopic substitution data, obtained for the dipole moment in the equilibrium configuration a value 0.8165(5) D. The measurements of Van Dijk of HBr involved Stark transitions for which the effect of the polarizability was zero. Using Van Dijk's average value of  $\mu_{el}$  for H<sup>79</sup>Br and H<sup>81</sup>Br and our effective dipole moment

$\mu_{eff}, \alpha_{\parallel} - \alpha_{\perp}$  can be calculated for HBr. The obtained value for  $\alpha_{\parallel} - \alpha_{\perp}$  fits nicely in the list of polarizabilities for the different hydrogen halides as shown in table 3.

From the measured magnetic constants of H<sup>81</sup>Br we calculated the molecular quadrupole moment of the ground vibrational state. The method is described by De Leeuw and Dymanus [1] for HF and HCl. The result for HBr is  $\langle \theta \rangle_{v=0} = 4.14(13) \times 10^{-26}$  esu cm<sup>2</sup>. The values for the electronic and nuclear contribution to the molecular quadrupole moment are listed in table 4 in comparison with those for HF and HCl as obtained by De Leeuw and Dymanus [1]. The trend of the various contributions to the molecular quadrupole moment of the investigated hydrogen halides confirms qualitative expectations. Quantitative considera-

Table 2  
Molecular constants of H<sup>81</sup>Br ( $J=1, v=0$ )

Constant	Present work	Van Dijk [3]	Other measurements
$\mu_{el}$ (D)	0.82654(8) <sup>a)</sup>	0.8275(3)	0.834(8) [10]
$(eqQ)_{Br}$ (kHz)	444680.66(15)	444679.3(8)	447900(1400) [2]
$c_{Br}$ (kHz)	313.370(21)	313.25(8)	310(100) [2]
$c_H$ (kHz)	-42.14(12)	-41.23(31)	-43(3) [8]
$d_T$ (kHz)	11.138(51)	10.89(21)	
$d_S$ (kHz)	-0.063(72)		
$(\sigma_{av})_{Br}$ (ppm)	2748(20)		
$(\sigma_{\parallel} - \sigma_{\perp})_{Br}$ (ppm)	732(14)		
$(\sigma_{\parallel} - \sigma_{\perp})_H$ (ppm)	24(12)		
$\chi_{\parallel} - \chi_{\perp}$ (kHz kG <sup>-2</sup> )	-0.139(7)		
$g_J$	0.37122(8)		

a) Effective dipole moment, see text.

Table 3  
Polarisability anisotropy of hydrogen halides

Molecule	$\alpha_{\parallel} - \alpha_{\perp} (\text{\AA}^3)$	Reference
HF	0.22(2)	[13]
HCl	0.31	[14]
HBr	0.58(14)	Present result

Table 4  
Molecular quadrupole moment of hydrogen halides

Quantity ( $10^{-26}$ esu cm <sup>2</sup> )	HF [1]	HCl [1]	HBr <sup>a)</sup>
$\langle \theta^e \rangle_{v=0}$	-1.52(3)	-3.95(12)	-5.54(13)
$\langle \theta^n \rangle_{v=0}$	3.88	7.69	9.68
$\langle \theta \rangle_{v=0}$	2.36(3)	3.74(12)	4.14(13)

<sup>a)</sup> Present results.

tive considerations have to await ab initio calculations on HBr.

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#### References

- [1] F.H. de Leeuw, Ph.D. Thesis, University of Nijmegen, The Netherlands (1971);  
F.H. de Leeuw and A. Dymanus, *J. Mol. Spectry.* (1973), to be published.
- [2] G. Jones and W. Gordy, *Phys. Rev.* 136 (1964) A1229.
- [3] F.A. van Dijk, Ph.D. Thesis, University of Nijmegen, The Netherlands (1971).
- [4] F.H. de Leeuw, R. van Wachem and A. Dymanus, *J. Chem. Phys.* 50 (1969) 1393.
- [5] Ch. Schlier, *Fortschritte der Physik* 9 (1961) 455.
- [6] W. Hüttner and W.H. Flygare, *J. Chem. Phys.* 47 (1967) 4137.
- [7] C.H. Townes and A.L. Scharlow, *Microwave spectroscopy* (Mc Graw-Hill, New York, 1955) p. 517.
- [8] N.F. Ramsey, *Am. Scientist* 49 (1961) 509.
- [9] C. Zahn, *Phys. Rev.* 24 (1924) 400.
- [10] W.H. Robinette and R.B. Sanderson, *Appl. Opt.* 8 (1969) 711.
- [11] R.H. Tipping and R.M. Herman, *J. Mol. Spectry.* 36 (1970) 404.
- [12] H.J. Babrov, A.L. Shabott and B.S. Rao, *J. Chem. Phys.* 42 (1965) 4124;  
B.S. Rao and L.H. Lindquist, *Can. J. Phys.* 46 (1968) 2739;  
B.P. Gustafson and B.S. Rao, *Can. J. Phys.* 48 (1970) 330.
- [13] J.S. Muentzer, *J. Chem. Phys.* 56 (1972) 5409.
- [14] E.W. Kaiser, *J. Chem. Phys.* 53 (1970) 1686;  
N.J. Bridge and A.D. Buckingham, *Proc. Roy. Soc.* A295 (1966) 334.