Bromine Spin-Rotation Coupling Constants of Cyclopropylbromide-^{79}Br and -^{81}Br

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We reinvestigated the microwave spectrum of cyclopropylbromide with the increased resolution of pulsed microwave Fourier transform spectroscopy. Because of the higher frequency precision, it was possible to determine the spin-rotation coupling constants of bromine. Global fits of rotational constants, quartic centrifugal distortion constants, quadrupole coupling constants including the off-diagonal component χ_{ac}, and spin-rotation coupling constants simultaneously to almost one hundred hyperfine components for each of the two bromine isotopomers resulted in overall standard deviations of well below 5 kHz.

Introduction

The microwave spectrum of cyclopropyl bromide was first assigned by Lam and Dailey [1], who could only detect the a-type spectrum. Recently, the c-type spectrum was assigned by Li et al. [2] who in addition reported a fairly precise value for the off-diagonal quadrupole coupling constant χ_{ac}. Unaware of this latter work, we started our investigations on this molecule mainly in order to assign the low-J a-type spectrum, which is complicated by overlapping isotopic and hyperfine patterns.

Experimental

We used our waveguide microwave Fourier transform (MWFT) spectrometers in the frequency range 4 to 18 GHz described elsewhere [3–5]. Two out of different set-ups were equipped with double-resonance facilities. The sample was provided by Aldrich Chemie, Steinheim, FRG, and used without further purification.

The first measurements were done on the $J=3-2$ a-type transitions, since they were calculated from the parameters in [1] to give only mildly overlapping hyperfine patterns of the ^{79}Br and ^{81}Br isotopomers. However, extra transitions due to molecules in high rotational and possibly in excited vibrational states made assignment sometimes difficult. (It should be noted, that MWFT spectroscopy does not normally allow the application of a Stark field.) We next studied the $J=2-1$ transitions using RF-MW double resonance [4]. An X-band Stark-cell was used with a specially designed septum, via which radiofrequencies of about 100 MHz were applied to the sample in addition to the microwave field. After having assigned most of the hyperfine components of the $J=2-1$ transitions, knowledge of the work of Li et al. allowed us, by using their A rotational constant (which had not been determined satisfactorily before), to record also a number of ^{c}Q-branch transitions; and in the following also several higher-K ^{c}P-branch and ^{c}R-branch transitions. The experimentally determined frequencies are compiled in Table 1.

Analysis

Following the suggestion of Gerry et al. [6] the analysis of the spectrum was performed by a global fit of all the relevant spectroscopic parameters (i.e., rotational, centrifugal distortion, and quadrupole coupling constants) *simultaneously* to the accumulated experimental data. Doing so, we noticed that the remaining deviations between observed and calculated frequencies showed a systematic behaviour. Since the model used in the fitting procedure was relatively elaborate in setting up the complete Hamiltonian and finding its eigenvalues by numerical diagonalisation,

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Table 1. Observed rotational transitions of cyclopropylbromide with nuclear hyperfine structure. Frequencies are in MHz, observed-minus-calculated frequencies are in kHz. ν(hfs) = observed frequency. $\Delta\nu$ = obs.-calc. frequency.

$J' K'_a K'_c - J'' K''_a K''_c$	$2F'-2F''$	^{79}Br		^{81}Br	
		ν (hfs)	$\Delta\nu$	ν (hfs)	$\Delta\nu$
[a]R-branch					
1 0 1–0 0 0	5–3	5 014.836	1	4 981.589	8
	3–3	5 131.089	−3	5 078.725	10
	1–3	4 922.251	−4	4 904.170	6
2 0 2–1 0 1	7–5	10 064.718	−1	9 992.422	−2
	5–3	10 064.014	−3	9 991.928	−1
	3–1	10 190.743	1	10 097.766	2
	5–5	10 180.273	−1	10 089.061	−2
	3–3	–	–	9 923.214	2
	1–1	10 073.692	−1	10 000.074	−1
	3–5	10 098.157	−5	10 020.345	−2
	1–3	9 864.865	8	9 825.526	3
2 1 1–1 1 0	7–5	10 168.550	−1	10 097.539	−3
	5–3	10 285.199	−5	10 194.957	−3
	3–1	10 153.955	0	10 085.201	2
	5–5	10 240.506	3	10 157.556	3
	3–3	10 234.645	2	10 152.667	−2
	1–1	10 083.123	−5	10 025.970	6
	3–5	10 189.943	1	10 115.264	1
	1–3	10 163.817	0	10 093.429	−5
2 1 2–1 1 1	7–5	9 924.127	1	9 856.956	1
	5–3	10 041.336	3	9 954.814	−2
	3–1	9 878.842	−4	9 819.187	−4
	5–5	9 970.422	1	9 895.510	0
	3–3	10 007.254	4	9 926.450	−1
	1–1	9 837.868	−1	9 784.599	−2
	3–5	9 936.336	−2	–	–
	1–3	–	–	9 891.860	0
3 0 3–2 0 2	9–7	15 104.244	0	14 994.369	−2
	7–5	15 106.198	−1	14 995.808	−3
	5–3	15 134.381	2	15 019.390	3
	3–1	15 137.770	1	15 021.928	−2
	7–7	–	–	15 092.448	−2
	5–5	–	–	14 950.672	1
	3–3	15 020.720	0	14 924.239	−2
3 1 2–2 1 1	9–7	15 282.779	0	15 171.324	−1
	7–5	15 311.381	1	15 195.276	−2
	5–3	15 315.558	1	15 198.752	−1
	3–1	15 286.197	0	15 174.264	−1
	7–7	–	–	15 255.293	3
	5–5	–	–	15 156.464	2
	3–3	–	–	15 115.031	1
3 1 3–2 1 2	9–7	14 918.587	−2	14 812.115	−3
	7–5	14 946.758	1	14 835.722	−2
	5–3	14 946.192	0	14 835.136	−1
	3–1	–	–	14 808.618	−1
	7–7	–	–	14 874.277	−2
	5–5	–	–	14 806.773	2
	3–3	–	–	14 774.028	0
3 2 1–2 2 0	9–7	15 082.837	7	14 977.346	−1
	7–5	15 199.545	4	15 074.842	14
	5–3	15 116.867	2	–	–
	3–1	–	–	14 908.550	4
	7–7	–	–	–	–
	5–5	–	–	–	–
	3–3	–	–	–	–
3 2 2–2 2 1	9–7	15 079.603	5	14 974.207	0
	7–5	15 196.149	3	15 071.567	10
	5–3	15 113.570	1	15 002.503	5
	3–1	14 997.501	0	14 905.504	1
	7–7	–	–	14 974.744	−3
	5–5	–	–	–	–
	3–3	15 114.544	−4	–	–
[a]Q-branch					
10 1 9–10 1 10	23–23	6 703.649	−1	6 606.139	4
	21–21	6 729.790	−1	6 627.953	−7
	19–19	6 726.235	−5	6 624.973	2
	17–17	6 699.549	0	6 602.733	−2
20 2 18–20 2 19	43–43	5 443.775	3	5 290.254	6
	41–41	5 454.408	−7	5 299.018	−2
	39–39	5 453.657	−1	5 298.386	−6
	37–37	5 442.947	7	5 289.566	3
[c]Q-branch					
3 1 3– 3 0 3	9– 9	13 465.967	−1	13 486.365	4
	7– 7	13 422.919	−1	13 450.441	−3
	5– 5	13 442.203	0	13 466.633	1
	3– 3	13 482.904	1	13 500.669	−1
6 1 6– 6 0 6	15–15	12 585.082	−2	12 618.676	−2
	13–13	12 564.420	1	12 601.430	0
	11–11	12 569.133	−1	12 605.565	−2
	9– 9	12 590.647	3	12 622.654	−1
9 1 9– 9 0 9	21–21	11 277.776	−1	11 328.483	−1
	19–19	11 264.133	−3	11 317.385	0
	17–17	11 265.161	0	11 317.954	−1
	15–15	11 282.343	−1	11 332.933	1
15 1 15–15 0 15	33–33	7 921.485	−2	–	–
	31–31	7 912.032	1	–	–
	29–29	7 912.911	0	–	–
	27–27	7 922.463	−1	–	–
22 1 22–22 0 22	47–47	4 196.631	2	4 282.922	3
	45–45	4 191.913	14	4 278.901	7
	43–43	4 192.200	−5	4 279.153	−3
	41–41	4 196.961	−7	4 283.200	−7
[c]P-/[c]R-branch					
5 0 5– 4 1 3	13–11	10 731.635	0	10 540.071	−3
	11– 9	10 735.248	−2	10 543.103	−3
	9– 7	10 741.832	3	10 548.605	0
	7– 5	10 738.650	1	10 545.877	−3
12 1 12–11 2 10	27–25	14 136.194	−4	13 714.407	−4
	25–23	14 130.987	−3	13 710.068	8
	23–21	14 132.614	0	13 711.398	−3
	21–19	14 138.206	2	13 716.002	−2
12 3 10–13 2 12	27–29	–	–	4 427.209	−1
	25–27	–	–	4 417.829	−2
	23–25	–	–	4 418.334	−1
	21–23	–	–	4 427.428	1
17 2 16–16 3 14	37–35	15 769.145	−7	–	–
	35–33	15 773.971	2	–	–
	33–31	15 773.841	−2	–	–
	31–29	15 769.437	8	–	–
15 4 11–16 3 13	33–35	15 886.559	2	16 605.203	2
	31–33	15 873.995	0	16 594.727	−2
	29–31	15 874.731	−1	16 595.328	−3
	27–29	15 887.081	2	16 605.654	5
15 4 12–16 3 14	33–35	15 976.076	−2	16 690.539	−5
	31–33	15 963.890	1	16 680.435	−4
	29–31	15 964.524	0	16 680.991	9
	27–29	15 976.449	−2	16 690.958	−2

we supposed the inconsistencies might be due to the effect of magnetic coupling of the bromine spin to the overall rotation. On including the appropriate matrix elements (though only to a first order approximation) [7], we found a considerable decrease in the standard deviation of the fit, with almost no systematic trends left in the actual observed-minus-calculated frequencies. Thus we are confident that indeed, the spin-rotation coupling constants (or rather the diagonal components of the spin-rotation coupling tensor) could be determined from the spectrum. It is noteworthy that, associated with the inclusion of these constants in the fit, there occurred a minor but noticeable variation in the off-diagonal quadrupole coupling constant χ_{ac}. The determined spectroscopic parameters are listed in Table 2.

Table 2. Spectroscopic parameters as determined from a global fit of all parameters simultaneously to the frequencies of the hyperfine components. I^l representation and reduction according to Van Eijck [8] used. C_{aa}, C_{bb}, C_{cc} are the bromine spin-rotation coupling constants, σ is the standard deviation of the fit. – Standard errors are given in units of the last digits in parentheses. – In addition, the calculated values for χ_{bb} and χ_{cc} are given.

	^{79}Br	^{81}Br
A'	16 334.2542(14) MHz	16 333.0458(13) MHz
B'	2 579.91939(12) MHz	2 560.54014(15) MHz
C'	2 457.71568(10) MHz	2 440.14870(12) MHz
D'_J	0.6446(8) kHz	0.6383(14) kHz
D'_{JK}	0.872(17) kHz	0.869(22) kHz
D'_K	20.178(43) kHz	20.206(72) kHz
δ'_J	−15.850(85) Hz	−15.619(109) Hz
R'_6	−1.717(24) Hz	−1.645(30) Hz
χ_{aa}	464.3403(38) MHz	388.0672(38) MHz
$\chi_{cc}-\chi_{bb}$	105.8341(65) MHz	88.2676(64) MHz
χ_{ac}	265.070(39) MHz	221.255(47) MHz
C_{aa}	6.22(99) kHz	8.91(98) kHz
C_{bb}	5.92(29) kHz	6.37(31) kHz
C_{cc}	4.10(28) kHz	4.62(30) kHz
σ	3.5 kHz	4.0 kHz
χ_{bb}	−285.086(4) MHz	−238.167(4) MHz
χ_{cc}	−179.253(4) MHz	−149.900(4) MHz

Discussion

The values of the spectroscopic parameters as determined in this work are in most cases more precise than those of [2]. This holds particularly for the constants D'_K and χ_{aa}. The reason for this is the inclusion of ^cP-/^cR-branch transitions, and of the $J, K_a = 3, 2-2, 2$ transitions in our analysis. On the other hand, the constants D'_J are less precisely determined than in [2], because the data in [2] consist almost entirely of a large number of ^aR-branch transitions. In contrast, our data contain only the lowest-J ^aR-branch lines (up to $J=3$), plus a comparatively small number of ^cP-/^cR-branch transitions.

Table 3. Comparison of principal quadrupole coupling constants and the angle between the axis systems as determined in this work with those of Li et al. [2]. z, x = axes in the symmetry plane, y = axis perpendicular to symmetry plane, θ = angle between z-axis and a-axis.

	This work		Li et al.	
	^{79}Br	^{81}Br	^{79}Br	^{81}Br
χ_{xx}/MHz	−274.369(25)	−229.207(30)	−275.01(27)	−229.72(25)
χ_{yy}/MHz	−285.086(4)	−238.167(4)	−284.88(12)	−238.24(12)
χ_{zz}/MHz	559.455(25)	467.374(30)	559.89(27)	467.96(25)
θ/°	19.739(3)	19.720(3)	19.824(19)	19.764(20)

Table 4. Comparison of bromine spin-rotation coupling constants of alkyl bromides. Note that the signs of the constants depend on the sign convention used, which is different in [9].

-bromide		^{79}Br	^{81}Br	Ref.
methyl-	$C_\perp$	−12.63(10) kHz	−13.78(19) kHz	
	$C_\parallel$	−18.8(17) kHz	−25.4(20) kHz	[9]*
ethyl-	C_{aa}	7.8(7) kHz	10.4(7) kHz	
	C_{bb}	4.7(3) kHz	5.8(3) kHz	[10]**
	C_{cc}	7.6(3) kHz	7.9(2) kHz	
cyclopropyl-	C_{aa}	6.22(99) kHz	8.91(98) kHz	
	C_{bb}	5.92(29) kHz	6.37(31) kHz	this work**
	C_{cc}	4.10(28) kHz	4.62(30) kHz	
isopropyl-	C_{aa}	2.5(14) kHz	4.2(16) kHz	
	C_{bb}	6.69(39) kHz	6.29(42) kHz	[11]**
	C_{cc}	6.12(39) kHz	5.54(43) kHz	
tert-butyl-	$C_\perp$	4.7(3) kHz	5.8(2) kHz	[12]**
	$C_\parallel$	1.0(7) kHz	0.8(5) kHz	

* Sign convention according to [13] used.
** Sign convention according to [14] used.

Because the precision of the frequency determination is much improved with microwave Fourier Transform spectroscopy, it was possible to include the spin-rotation coupling constants of bromine in the fit. Obviously (see Table 2), the constants C_{aa} are not as well determined as the other two diagonal components of the coupling tensor, but nevertheless satisfactorily. (The magnetic moment of the nucleus ^{79}Br is slightly *smaller* than that of ^{81}Br, in contrast to the quadrupole moments. Although the spin-rotation coupling constants also depend inversely on the respective moments of inertia, the isotopic variation is clearly noticeable, however hardly beyond the uncertainty of the constants.) Table 4 shows a comparison of the spin-rotation coupling constants of cyclopropylbromide with those of other alkyl bromides.

A discussion of the quadrupole coupling constants has already been given in [2] and shall not be reproduced here. Table 3 gives a comparison of the principal coupling constants, and of the derived angle between the axes systems, with those of [2]. Again, the significantly improved precision of the parameters should be noted.

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[1] F. M. K. Lam and B. P. Dailey, J. Chem. Phys. **49,** 1588 (1968).
[2] H. Li, M. C. L. Gerry, and W. Lewis-Bevan, J. Mol. Spectrosc. **144,** 51 (1990).
[3] H. Ehrlichmann, J.-U. Grabow, H. Dreizler, N. Heineking, R. Schwarz, and U. Andresen, Z. Naturforsch. **44a,** 751 (1989).
[4] N. Heineking, W. Stahl, and H. Dreizler, Z. Naturforsch. **43a,** 280 (1988).
[5] G. Bestmann and H. Dreizler, Z. Naturforsch. **37a,** 58 (1982).
[6] H. M. Jemson, W. Lewis-Bevan, N. P. C. Westwood, and M. C. L. Gerry, J. Mol. Spectrosc. **118,** 481 (1986).
[7] J. Gripp and H. Dreizler, Z. Naturforsch. **43a,** 971 (1988).
[8] B. P. van Eijck, J. Mol. Spectrosc. **53,** 246 (1974).
[9] J. Demaison, A. Dubrulle, D. Boucher, and J. Burie, J. Chem. Phys. **67,** 254 (1977).
[10] J. Gripp, preliminary results.
[11] M. Meyer and H. Dreizler, to be published.
[12] H. Harder, W. Stahl, and H. Dreizler, Z. Naturforsch. **45a,** 807 (1990).
[13] W. H. Flygare, Chem. Rev. **74,** 653 (1974).
[14] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley, New York 1984, p. 429ff.