Hyperfine Structure in the Rotational Spectrum of tert-Butyl Bromide

H. Harder, W. Stahl, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

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We reinvestigated the rotational spectra of tert-butyl bromide $(CH_3)_3C^{79}Br$ and $(CH_3)_3C^{81}Br$, with the high precision of microwave Fourier transform spectroscopy. The rotational and quadrupole coupling constants were improved, the centrifugal distortion and bromine spin-rotation constants were determined.

Introduction

The microwave spectrum of $(CH_3)_3CBr$ was investigated for the first time by Williams and Gordy [1]. Zeil et al. [2] measured the $J=5-4$ transition and determined the quadrupole coupling constants. Later Legon et al. [3] analyzed the hyperfine structure of the $J=4-3$ transition. Conventional Stark spectroscopy was used.

We reinvestigated the spectra and measured the low J transitions up to $J=5-4$ in order to improve rotational and quadrupole coupling constants and to determine centrifugal distortion constants. The higher resolution of waveguide and pulsed molecular beam microwave Fourier transform (MWFT) spectrometers compared with Stark spectrometers enabled us to determine spin-rotation coupling constants of the bromine nucleus.

Experimental

We used commercial tert-butyl bromide (Aldrich Chemie, Steinheim). First we remeasured the $J=4-3$ transition with our Ku-band MWFT spectrometer [4]. With improved constants we predicted transitions in lower bands, which were recorded by means of our X- and G-band MWFT spectrometers [5, 6]. The $J=5-4$ transition was recorded with our K-band molecular beam spectrometer [7] in order to suppress transitions of excited vibrational states. Components of $J=2-1$ and $J=3-2$ transitions were additionally measured with our X-band beam spectrometer because of better signal/noise ratio and resolution. The measurements with the waveguide spectrometers were made at temperatures in the range from 220 to 240 K and pressures around 6.5 mTorr (0.9 Pa).

The frequencies were determined by a least-squares fit of the time domain signal [8].

With the beam spectrometer a stagnation pressure of 1 to 2 atm was used. The injected Ar contained 1 to 3% tert-butyl bromide. Frequencies of the transitions are given in Tables 1 and 2.

Analysis

All molecular constants were fitted simultaneously with our program SYM2QS.FOR [9], which is based on the diagonalization of the Hamiltonian matrix including elements off-diagonal in J [10]. Only diagonal bromine spin-rotation coupling elements were included [11]. The results are given and compared with data of Legon et al. [3] in Table 3.

The rotational constant B and the quadrupole coupling constant eQq could be improved considerably. The difference between the quadrupole coupling constants eQq of this work and [3] results from the lower precision of measurements used in [3].

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Reprint requests to Prof. Dr. H. Dreizler, Abteilung Chemische Physik, Institut für Physikalische Chemie, Christian-Albrechts-Universität, Ludewig-Meyn-Str. 8, D-2300 Kiel, FRG.

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Table 1. Observed, ν_{obs}, and calculated, ν_{calc}, frequencies of $(CH_3)_3C^{79}Br$. $\Delta\nu = \nu_{obs} - \nu_{calc}$. * Molecular beam measurements.

Transition				Frequencies		
$J'-J$	K	F'	F	$\nu_{calc.}$ (MHz)	$\nu_{obs.}$ (MHz)	$\Delta\nu$ (kHz)
1–0	0	0.5	1.5	3 961.806	3 961.813	7
	0	1.5	1.5	4 191.916	4 191.916	0
	0	2.5	1.5	4 063.455	4 063.456	1
2–1	0	0.5	0.5	8 176.941	8 176.955	14
	0	1.5	0.5	8 306.280	8 306.280	0
	0	0.5	1.5	7 946.831	7 946.834	3
	0	2.5	1.5	8 165.991	8 165.989	−2
	0	2.5	2.5	8 294.452	8 294.450	−2
	0	3.5	2.5	8 166.229	8 166.231	2
	1	0.5	0.5	8 051.991	8 051.988	−3
	1	1.5	0.5	8 115.116	8 115.120	4
	1	0.5	1.5	8 176.039	8 176.038	−1
	1	1.5	1.5	8 230.164	8 230.168	4
	1	2.5	1.5	8 275.559	8 275.555	−4
	1	2.5	2.5	8 211.388	8 211.385*	−3
	1	3.5	2.5	8 146.362	8 146.367	5
3–2	0	1.5	1.5	12 161.951	12 161.950	−1
	0	2.5	1.5	12 290.436	12 290.437	1
	0	2.5	2.5	12 200.616	12 200.612	−4
	0	3.5	2.5	12 259.348	12 259.337	−11
	0	3.5	3.5	12 387.571	12 387.570	−1
	0	4.5	3.5	12 259.449	12 259.444	−5
	1	1.5	0.5	12 251.802	12 251.789	−13
	1	1.5	1.5	12 188.677	12 188.683	6
	1	2.5	1.5	12 284.387	12 284.385	−2
	1	2.5	2.5	12 238.992	12 238.993	1
	1	3.5	2.5	12 283.397	12 283.397	0
	1	4.5	3.5	12 251.925	12 251.920	−5
	2	1.5	0.5	12 138.714	12 138.712	−2
	2	1.5	1.5	12 268.043	12 268.033	−10
	2	2.5	1.5	12 266.373	12 266.372	−1
	2	3.5	2.5	12 357.757	12 357.759	2
	2	4.5	3.5	12 229.073	12 229.075	2
4–3	0	2.5	1.5	16 364.797	16 364.792	−5
	0	3.5	2.5	16 364.568	16 364.565	−3
	0	4.5	3.5	16 349.996	16 350.002	6
	0	4.5	4.5	16 478.119	16 478.128	9
	0	5.5	4.5	16 350.050	16 350.041	−9
	1	2.5	1.5	16 352.639	16 352.637	−2
	1	2.5	2.5	16 256.929	16 256.931	2
	1	3.5	2.5	16 365.641	16 365.638	−3
	1	4.5	3.5	16 358.969	16 358.972	3
	1	4.5	4.5	16 455.467	16 455.480	13
	1	5.5	4.5	16 346.401	16 346.403	2
	2	2.5	1.5	16 316.734	16 316.740	6
	2	3.5	2.5	16 368.717	16 368.718	1
	2	4.5	3.5	16 386.184	16 386.184	0
	2	5.5	4.5	16 335.393	16 335.395	2
	3	2.5	1.5	16 258.704	16 258.705	1
	3	2.5	2.5	16 419.631	16 419.630	−1
	3	3.5	2.5	16 373.382	16 373.384	2
	3	3.5	3.5	16 447.322	16 447.323	1
	3	4.5	3.5	16 432.562	16 432.561	−1
	3	4.5	4.5	16 273.033	16 273.040	7
	3	5.5	4.5	16 316.832	16 316.833	1

Table 1 (continued)

Transition				Frequencies		
$J'-J$	K	F'	F	$\nu_{calc.}$ (MHz)	$\nu_{obs.}$ (MHz)	$\Delta\nu$ (kHz)
5–4	0	3.5	2.5	20 448.302	20 448.310*	8
	0	3.5	3.5	20 320.046	20 320.045*	−1
	0	4.5	3.5	20 448.210	20 448.204*	−6
	0	4.5	4.5	20 404.049	20 404.045*	−4
	0	5.5	5.5	20 567.659	20 567.660*	1
	1	3.5	2.5	20 443.021	20 443.022*	1
	1	3.5	3.5	20 334.310	20 334.306*	−4
	1	4.5	3.5	20 449.494	20 449.497*	3
	1	4.5	4.5	20 411.760	20 411.760*	0
	1	5.5	4.5	20 443.862	20 443.861*	−1
	1	5.5	5.5	20 552.927	20 552.924*	−3
	1	6.5	5.5	20 437.576	20 437.577*	1
	2	3.5	2.5	20 427.290	20 427.290*	0
	2	3.5	3.5	20 376.977	20 376.972*	−5
	2	4.5	3.5	20 453.298	20 453.295*	−3
	2	4.5	4.5	20 435.025	20 435.023*	−2
	2	5.5	4.5	20 456.746	20 456.747*	1
	2	5.5	5.5	20 508.662	20 508.663*	1
	2	6.5	5.5	20 431.418	20 431.420*	2
	3	3.5	2.5	20 401.432	20 401.430*	−2
	3	4.5	3.5	20 459.490	20 459.511*	21
	3	4.5	4.5	20 474.251	20 474.246*	−5
	3	5.5	4.5	20 478.451	20 478.450*	−1
	3	5.5	5.5	20 434.652	20 434.653*	1
	3	6.5	5.5	20 421.090	20 421.090*	0
	4	3.5	2.5	20 365.965	20 365.962*	−3
	4	3.5	3.5	20 545.824	20 545.819*	−5
	4	4.5	3.5	20 476.855	20 476.857*	2
	4	4.5	4.5	20 530.125	20 530.121*	−4
	4	5.5	4.5	20 509.336	20 509.334*	−2
	4	5.5	5.5	20 330.539	20 330.540*	1
	4	6.5	5.5	20 406.492	20 406.492*	0

Table 2. Observed and calculated frequencies of $(CH_3)_3C^{81}Br$. See Table 1.

Transition				Frequencies		
$J'-J$	K	F'	F	$\nu_{calc.}$ (MHz)	$\nu_{obs.}$ (MHz)	$\Delta\nu$ (kHz)
1–0	0	0.5	1.5	3 950.752	3 950.758	6
	0	1.5	0.5	4 143.025	4 143.032	8
	0	2.5	1.5	4 035.777	4 035.781	4
2–1	0	1.5	0.5	8 113.489	8 113.488*	−1
	0	1.5	0.5	8 221.364	8 221.362*	−1
	0	0.5	1.5	7 921.217	7 921.214*	−3
	0	2.5	1.5	8 104.345	8 104.343*	−2
	0	1.5	2.5	8 136.339	8 136.338*	−1
	0	2.5	2.5	8 211.593	8 211.592*	−1
	0	3.5	2.5	8 104.516	8 104.514*	−2
	1	0.5	0.5	8 008.698	8 008.697*	−1
	1	1.5	0.5	8 061.555	8 061.555*	0
	1	0.5	1.5	8 104.829	8 104.825*	−4
	1	1.5	1.5	8 157.687	8 157.684*	−3
	1	2.5	1.5	8 195.653	8 195.652*	−2
	1	1.5	2.5	8 104.096	8 104.094*	−2
	1	2.5	2.5	8 142.064	8 142.063*	−1
	1	3.5	2.5	8 087.886	8 087.884*	−2

Table 2 (continued)

Transition				Frequencies		
$J'-J$	K	F'	F	$\nu_{calc.}$ (MHz)	$\nu_{obs.}$ (MHz)	$\Delta\nu$ (kHz)
3–2	0	1.5	0.5	12 191.815	12 191.813*	−2
	0	1.5	1.5	12 083.940	12 083.941	1
	0	2.5	1.5	12 191.217	12 191.216*	−1
	0	2.5	2.5	12 115.963	12 115.963	0
	0	3.5	2.5	12 165.168	12 165.168	0
	0	3.5	3.5	12 272.245	12 272.245*	0
	0	4.5	3.5	12 165.242	12 165.240	−2
	1	1.5	1.5	12 106.113	12 106.111	−2
	1	2.5	1.5	12 186.113	12 186.114	1
	1	2.5	2.5	12 148.146	12 148.146	0
	1	3.5	2.5	12 185.301	12 185.301	0
	1	3.5	3.5	12 239.479	12 239.479*	0
	1	4.5	3.5	12 158.943	12 158.942	−1
	2	1.5	0.5	12 064.211	12 064.211	0
	2	2.5	1.5	12 170.904	12 170.901	−3
	2	2.5	2.5	12 246.683	12 246.681*	−2
	2	3.5	2.5	12 247.254	12 247.254*	0
	2	4.5	3.5	12 139.847	12 139.846	−1
4–3	0	2.5	1.5	16 236.094	16 236.092	−2
	0	2.5	2.5	16 128.817	16 128.830	13
	0	3.5	2.5	16 235.936	16 235.935	−1
	0	3.5	3.5	16 186.731	16 186.736	5
	0	4.5	3.5	16 223.729	16 223.728	−1
	0	5.5	4.5	16 223.769	16 223.775	6
	1	2.5	1.5	16 225.972	16 225.974	2
	1	2.5	2.5	16 145.972	16 145.967	−5
	1	3.5	2.5	16 236.808	16 236.804	−4
	1	3.5	3.5	16 199.653	16 199.654	1
	1	4.5	3.5	16 231.241	16 231.246	5
	1	4.5	4.5	16 311.778	16 311.779	1
	1	5.5	4.5	16 220.714	16 220.714	0
	2	2.5	1.5	16 196.002	16 196.007	5
	2	2.5	2.5	16 197.171	16 197.167	−4
	2	3.5	2.5	16 239.327	16 239.326	−1
	2	3.5	3.5	16 238.756	16 238.764	8
	2	4.5	3.5	16 253.987	16 253.989	2
	2	5.5	4.5	16 211.506	16 211.505	−1
	3	2.5	1.5	16 147.329	16 147.328	−1
	3	2.5	2.5	16 281.641	16 281.641	0
	3	3.5	2.5	16 243.201	16 243.201	0
	3	3.5	3.5	16 305.063	16 305.068	5
	3	4.5	3.5	16 292.613	16 292.616	3
	3	4.5	4.5	16 159.279	16 159.277	−2
5–4	0	3.5	2.5	20 288.686	20 288.694*	8
	0	3.5	3.5	20 181.568	20 181.566*	−2
	0	4.5	3.5	20 288.624	20 288.615*	−9
	0	4.5	4.5	20 251.626	20 251.624*	−2
	0	5.5	5.5	20 388.368	20 388.366*	−2
	1	3.5	2.5	20 284.285	20 284.283*	−2
	1	3.5	3.5	20 193.448	20 193.447*	−1
	1	4.5	3.5	20 289.685	20 289.687*	2
	1	4.5	4.5	20 258.097	20 258.096*	−1
	1	5.5	4.5	20 284.979	20 284.977*	−2
	1	5.5	5.5	20 376.043	20 376.045*	2
	1	6.5	5.5	20 279.716	20 279.712*	−4
	2	3.5	2.5	20 271.160	20 271.161*	1
	2	3.5	3.5	20 229.004	20 229.005*	1
	2	4.5	3.5	20 292.835	20 292.836*	1
	2	4.5	4.5	20 277.604	20 277.600*	−4
	2	5.5	4.5	20 295.753	20 295.749*	−4
	2	5.5	5.5	20 339.017	20 339.018*	1
	2	6.5	5.5	20 274.562	20 274.567*	5
	3	3.5	2.5	20 249.538	20 249.537*	−1
	3	3.5	3.5	20 287.978	20 287.973*	−5
	3	4.5	3.5	20 297.982	20 297.981*	−1
	3	4.5	4.5	20 310.432	20 310.435*	3
	3	5.5	4.5	20 313.872	20 313.873*	1
	3	5.5	5.5	20 277.143	20 277.147*	4
	3	6.5	5.5	20 265.926	20 265.925*	−1
	4	3.5	2.5	20 219.785	20 219.784*	−1
	4	3.5	3.5	20 369.948	20 369.945*	−3
	4	4.5	3.5	20 304.973	20 304.974*	1
	4	4.5	4.5	20 357.064	20 357.060*	−4
	4	5.5	4.5	20 339.589	20 339.594*	5
	4	5.5	5.5	20 190.169	20 190.168*	−1
	4	6.5	5.5	20 253.738	20 253.736*	−2

Table 3. Molecular constants: Rotational constant B; centrifugal distortion constants D_{JK}, D_J; quadrupole coupling constant eQq; spin-rotation constant C_N, C_K.

Constant		$(CH_3)_3C^{79}Br$		$(CH_3)_3C^{81}Br$	
		this work	[3]	this work	[3]
B	(MHz)	2044.2400(2)	2044.237(7)	2028.3777(1)	2028.369(9)
D_{JK}	(kHz)	0.89(2)		0.89(1)	
D_J	(kHz)	0.31(1)		0.30(1)	
eQq	(MHz)	511.987(4)	513.7(8)	427.708(3)	432(2)
C_N	(kHz)	4.7(3)		5.8(2)	
C_K	(kHz)	1.0(7)		0.8(5)	
Standard deviation (kHz)		5.1		3.4	

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