Microwave spectrum of 1-bromobutane

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ABSTRACT

The rotational spectrum of 1-bromobutane has been measured in the range of 8 to 18 GHz using a 480 MHz bandwidth chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer. 1-bromobutane has five conformers; **aa**, **ag**, **ga**, **gg**, **gg'**. Spectra for the ⁷⁹Br isotopic species and ⁸¹Br isotopic species were observed and assigned for the three lowest energy conformers, **aa**, **ga**, and **gg**. Consequentially, the rotational constants, nuclear quadrupole coupling constants, and centrifugal distortion constants were determined and the dipole moment of the **aa** conformer with ⁷⁹Br was measured. All the experimental data are in good agreement with the *ab initio* calculations.

Keywords

1-bromobutane

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Dipole moment

Ab initio Structure

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1. Introduction

The conformational analyses of 1-haloalkanes in gas phase have been performed by Infrared and Raman spectroscopies [1], microwave spectroscopy [2–4], and electron diffraction [5,6]. In the case of 1-bromobutane, Bonham [5] first suggested five possible conformers which are **aa**, **ag**, **ga**, **gg** and **gg'** in the gas phase and reported their proportions, except for **gg'**. Also, four rotational isomers

(**aa**, **ag**, **ga**, and **gg**) of 1-halobutane except 1-fluorobutane were observed in the gas, liquid, and glass state by their infrared and Raman bands [1]. Only low resolution microwave spectroscopy (LRMW) [2] was previously applied to observing the rotational spectrum of gaseous 1-bromobutane, and it has confirmed the presence of **aa**, **ga**, and **ag** conformers, with some evidence of weak **gg** transitions also being present.

As bromine has nuclear spin $I = 3/2$, which induces hyperfine structure in the molecular spectrum, hyperfine splittings generated by bromine have been observed in the microwave spectra of bromine substituted saturated [7–15], unsaturated [16–22], and ring [23–26] compounds. In this paper, the rotational spectrum and *ab initio* calculations of 1-bromobutane have been analyzed as one of the series of the 1-bromoalkanes. The structure of 1-bromobutane is also similar with n-butylsilane [27] or n-butylgermane [28], so the same kinds of conformers are expected; **aa**, **ag**, **ga**, **gg**, and **gg'** (see Fig. 1).

The spectrum in the region of 8 GHz to 18 GHz of this molecule was measured by Chirped-pulse Fourier-transform microwave (CP-FTMW) spectroscopy at Eastern Illinois University (EIU) [29–32] and the *anti-anti* (**aa**), *gauche-anti* (**ga**), and *gauche-gauche* (**gg**) conformers were observed. Because of the nuclear spin of bromine, each rotational transition of the molecule shows nuclear quadrupole hyperfine splitting. Complete assignments were performed for the **aa**, **ga**, and **gg** conformers, and spectroscopic constants including the nuclear quadrupole coupling constants were determined. The electric dipole moments of this molecule were also determined from Stark effect measurements by resonant cavity (Balle-Flygare) Fourier-transform microwave spectroscopy at EIU [33]. The dipole moments of the most intense **aa** conformer were determined from the measurements using the QSTARKprogram [34] and compared with calculation results.

2. Experimental

The rotational spectrum of 1-bromobutane between 8 GHz and 18 GHz was measured by using the 480 MHz bandwidth CP-FTMW spectrometer at EIU [32] with most transitions having full width at half maximum height (FWHM) around 120 kHz. The samples were obtained from Aldrich Company. About 1-2 atm of Ar gas was bubbled through a liquid sample of 1-bromobutane just upstream of a pulsed gas valve. A total of 5,000 free induction decays were averaged within each 480 MHz frequency segment, with these segments later compiled into a full broadband spectrum using a LabView program.

A resonant cavity (Balle-Flygare) Fourier-transform microwave spectrometer (FTMW) at EIU [33] was used for Stark effect measurements of 1-bromobutane and also for checking the frequency precision of transitions measured on the CP-FTMW spectrometer. The nozzle is perpendicular to the microwave cavity axis and typical line widths of about 20 kHz (FTMW) resulting from Doppler broadening were observed and center frequencies were reproducible to ± 2 kHz. Two parallel plates supplied DC voltage up to 3 kV for the Stark electric field.

3. Results and discussion

Ab initio calculation

The optimization and energy calculations of 1-bromobutane were carried out at the MP2/6-311+G(2d,2p) level using the Gaussian 03 programs [35] to predict relative stability, rotational constants and dipole components of all possible conformers (Fig. 1). In addition, the calculated nuclear quadrupole coupling constants for the main isotopes (^{79}Br , $I = 3/2$, 50.5% abundance; ^{81}Br , $I = 3/2$, 49.5%) were also obtained. The results are listed in Table 1.

In our calculation results, the **gg** conformer of 1-bromobutane has the lowest energy. O. Takahashi [36] and coworkers, however, reported that the **aa** conformer has the lowest Gibbs energy in the results of calculation at the different basis set, MP2/6-311G(d,p). This is consistent with the earlier electron diffraction study on the structure of 1-bromobutane in the gas phase using sector-micro-photometer performed by Bonham [5] which suggested that the conformer percentage of **aa** form is 36 % and **gg** form is 16 % at 25°C. Another electron diffraction experiment [6] at 18°C reported that the percentages are reversed; **gg** conformer is 38 ± 34 %, but **aa** conformer is 21 ± 14 %.

As shown in Table 1, the calculated energy differences between **aa**, **ga**, and **gg** conformers are very small (~ 0.1 kJ/mol), so it is reasonable that the stability order can vary with different basis set, level of calculation and depending on whether Gibbs energies or internal energies are compared. The zero point energy (ZPE) was not included to compare the relative stability since the energy differences are relatively small and therefore the relative stabilities are uncertain with or without ZPE corrections. Experimentally, the present study utilized a supersonic expansion, so populations are not directly comparable with room temperature *ab initio* calculations. Though the most stable molecule was not obvious, quite a few lines of three conformers (**aa**, **ga**, and **gg**) in the spectrum are expected to be strong because those conformers were detected in the previous electron diffraction study [5]. Heavy atom structural parameters from the *ab initio* calculations are listed in Table 2.

Microwave spectra

The 8 GHz to 18 GHz spectrum was measured using CP-FTMW and resonant cavity FTMW at Eastern Illinois University (EIU) [32,33]. Rotational constants, centrifugal distortion constants and nuclear quadrupole coupling constants were determined and fitted by using Watson's S reduced Hamiltonian in its I' representation [37] using the SPFIT program [38].

All conformers are determined to be prolate asymmetric type rotors ($\kappa \sim -0.87$ to -0.99 for all five conformers). Due to bromine nuclear quadrupole coupling, rotational transitions exhibited hyperfine splitting [21–23]. The nuclear spin I is coupled with the molecular rotational angular momentum J to form a resultant F . The total angular momentum of the molecule with nuclear coupling is thus represented by F rather than J , which designates the total angular momentum exclusive of nuclear spin. The good quantum numbers are thus F , M_F , J and I . F is the quantum number for total angular momentum including nuclear spin, and M_F is the projection of total angular momentum including nuclear spin on space-fixed axis. The new angular momentum quantum numbers are as follows.

$$F = J + I, J + I - 1, J + I - 2, \dots, |J - I|$$
$$M_F = F, F - 1, F - 2, \dots, -F$$

Selection rules for hyperfine transitions in rotational absorption spectra are

$$J \rightarrow J + 1, F \rightarrow F, F \rightarrow F \pm 1, I \rightarrow I.$$

In brief, when the $J > I$, there are $2I + 1$ components for $F \rightarrow F + 1$, $2I$ components for $F \rightarrow F$, and $2I - 1$ components for $F \rightarrow F - 1$. The $F \rightarrow F + 1$ components are strong, while the $F \rightarrow F - 1$ components become weaker and are thus generally undetectable.

In the case of 1-bromobutane, the split lines consisted of only four strong $F \rightarrow F + 1$ transition components (see Fig. 2). The ^{13}C isotopomer spectra could not be found in the spectrum without enrichment.

For **aa** conformer, the series of the strongest a -type transitions with J from 5 to 10 were found and assigned by their relative intensity and characteristic hyperfine splitting. A total of 86 and 98 hyperfine components each for ^{79}Br and ^{81}Br were assigned. The **aa** conformer assumes C_s symmetry, so there are only three independent nuclear quadrupole coupling tensor components, including an off-diagonal component χ_{ab} (see Table 3). Fitted quadrupole coupling tensor components all agree well with the *ab initio* calculations shown in Table 1. For example, experimental χ_{aa} is 363 MHz, and it is very

consistent with the calculated value, 361 MHz. Only two distortion constants (D_I , D_{JK}) are determined for the 1-bromobutane **aa** conformer, and other conformers have three distortion constants including d_1 . All the observed transitions are listed in Table 4.

The **ga** conformer, unlike the **aa** conformer, has relatively large μ_b dipole component ($\mu_a = 1.621$ D, $\mu_b = 1.257$ D); this allows predictions of *b*-type transitions with intensities comparable to the *a*-type transitions. As a result, the series of strong *b*-type transitions with *J* from 3 to 8 were found and assigned (See Table 5 and 6).

For the **gg** conformer, only *a*-type transitions with *J* from 3 to 6 were measured and assigned. A search for *b*-type transitions, which were expected to appear at less than 10% the intensity of *a*-type transitions, was not successful because of other nearby transitions and low intensity. Interestingly, the spectrum for the **gg** conformer (Table 7) was noticeably less intense than that for the **aa** and **ga** forms. The larger μ_a for the **aa** conformer leads to stronger *a*-type transitions for that conformer, but that does not explain the **ga** conformer spectrum being more intense than **gg** since μ_a for **gg** is slightly larger than that for **ga** (See Table 1). Although making quantitative comparisons of relative abundances is challenging using the 480 MHz spectrometer due to instrumental effects on intensities during the construction of the full broadband spectrum, when we take into account the predicted dipole moment components for these three species, we must conclude that the **gg** conformer seems to be less abundant than our calculations predict, in agreement with the previous LRMW study [2] and one of the electron diffraction results [5].

The nuclear electric quadrupole coupling tensors (χ_{xx} , χ_{yy} , and χ_{zz}) in the principal axes of bromine were derived by diagonalization of experimentally determined three or five nuclear quadrupole coupling tensor components (Table 3). The χ_{zz} (MHz) for ^{79}Br are 543.4, 539.7 and 536.2 to the **aa**, **ga**, and **gg** conformers, while for ^{81}Br , it ranges from 448 to 454 MHz [34].

Those quadrupole coupling tensors for ^{79}Br and ^{81}Br were compared respectively with the values of methyl bromide (CH_3Br) [15,16], ethyl bromide ($\text{CH}_3\text{CH}_2\text{Br}$) [12,13] and n-propyl bromide ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$) [14]. They are presented in Table 8. In the case of methyl bromide, only χ_{zz} were observed and χ_{xx} and χ_{yy} are determined by symmetry. The quadrupole coupling tensors of 1-bromobutane are more similar to those of ethyl bromide rather than n-propyl bromide. Among three conformers, the **aa** conformer has the closest values to the tensors of ethyl bromide studied by Inagusa and Hayashi [12], while the other two conformers are similar to the tensors of ethyl bromide investigated by Flanagan and Pierce [13].

Dipole moment

The Stark effect shifts and splits spectral lines of atoms and molecules when the system is subjected to an electric field. It allows measurement of the electric dipole moment of gaseous molecules. The measurement for the **aa** conformer of 1-bromobutane with ^{79}Br was performed on Stark components of the $5_{1,5}-4_{1,4} F=9/2 \leftarrow 7/2$ rotational transition at 8922.5465 MHz, the $5_{1,4}-4_{1,3} F=9/2 \leftarrow 7/2$ transition at 9075.5248 MHz, and the $6_{1,6}-5_{1,5} F=9/2 \leftarrow 7/2$ transition at 10700.8613 MHz. A total of 11 components were measured with $\Delta M_F = 0$ selection rules. The Stark shifts have been measured for applied fields up to 140 V/cm. Some Stark components weren't measurable because the sublevel lines usually lose intensity quickly as more electric field is applied. The $5_{1,4}-4_{1,3} F=9/2 \leftarrow 7/2$ transition has four components, but only three components were confirmed: $M_F = 1/2, 3/2$, and $5/2$ (except for $7/2$). The **aa** conformer of 1-bromobutane has a symmetry plane (C_s symmetry). Thus, it is expected that the **aa** conformer would possess non-zero μ_a and μ_b dipole moment components, and two components of the dipole moment were determined. The resulting experimental dipole moments are listed in Table 9 with *ab initio* calculated dipole components. The experimental dipole moments are very consistent with the calculated dipole moments. The dipole moments are influenced by basis set of calculation, so further calculation applying various basis sets might predict more exact dipole moments. All the measured (points) and the calculated (continuous lines) frequency shifts of $\Delta M_F = 0$ components are plotted in Fig. 3.

4. Conclusions

The 8-18 GHz microwave spectrum of 1-bromobutane was measured using CP-FTMW, and further studies were performed using resonant cavity FTMW. The spectroscopic constants were determined by fit and compared with the *ab initio* calculated results. The rotational constants for the three stable conformers (**aa**, **ga**, and **gg**) of 1-bromobutane have been accurately determined. The centrifugal distortion constants and bromine nuclear quadrupole coupling constants were also obtained. The absence of an **ag** conformer is somewhat puzzling, particularly in light of its observation in a previous low resolution microwave study [2]. We assume that our failure to detect it in the present work is due to a small population, and/or relaxation to other conformers in the supersonic expansion since it is predicted to lie 2.5 kJ/mol above the other three conformers (See Table 1) [39].

The calculated rotational constants and nuclear quadrupole coupling constants are all in good agreement with the experimental results. The close agreement between spectroscopic parameters with the *ab initio* calculation at the MP2/6-311+G(2d,2p) level shows good credibility of the theoretical calculation at this level for 1-bromobutane.

Based on Stark effect, dipole moment components for **aa** conformer were determined and compared with *ab initio* values optimized at the level of MP2/6-311+G(2d,2p). A good agreement between experimental and calculated dipole moments suggests that the structural information of **aa** conformer also would fit with the results of calculation.

The rotational spectra indicate that the **gg** conformer is less abundant than our calculations suggested and so exact abundances of the other conformers are still unclear. Higher level calculations (including ZPE corrections, which were neglected in the current work) might lead to insight on barriers between conformers, whether conformer relaxation is significant in the supersonic expansion and how sensitive the stability order is to computational method and basis set effects. Our results appear to be consistent with electron diffraction and low resolution microwave studies performed on room temperature gas phase samples; thus, it is also unclear what effect the supersonic expansion has on relative populations of the conformers in this case.

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Fig. 1. Structure of the five conformers for 1-bromobutane.

Fig. 2. Observed $J=5_{15} \rightarrow 6_{16}$; $F \rightarrow F+1$ rotational transitions of the **ga** conformer of ^{79}Br 1-bromobutane.

Fig. 3. Observed (point) and calculated (continuous lines) frequency shifts for some of the observed $\Delta M_F=0$ Stark components in $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^{79}\text{Br}$ aa conformer.

Table 1

Ab initio calculated energy^a, dipole moments and spectroscopic constants for the five conformers of 1-bromobutane.

	E (hartree)	ΔE (kJ/mol)	Stability	Relative Abundances		
				T = 5K	T = 10K	T = 298K
gg	-2729.91262	0.000	1	1.0000	1.0000	1.0000
aa	-2729.91259	0.079	2	0.1483	0.3852	0.9685
ga	-2729.91258	0.096	3	0.0984	0.3137	0.9618
ag	-2729.91164	2.561	4	0.0000	0.0000	0.3555
gg'	-2729.90858	10.599	5	0.0000	0.0000	0.0138

	gg	aa^b	ga	ag	gg'
A (MHz)	6126.63794	16054.11243	8271.33080	12122.51662	5723.00672
B (MHz)	1508.25371	915.13169	1210.30632	1019.85790	1629.57403
C (MHz)	1385.35718	884.61391	1111.00077	984.44351	1349.47750
χ_{aa} (MHz)	151.57616	361.14646	89.08847	463.04856	116.40059
$\chi_{bb}-\chi_{cc}$ (MHz)	156.39767	174.66810	398.25101	-35.35525	318.83450
χ_{ab} (MHz)	-328.51140	-325.45810	386.29567	103.65999	381.13331
χ_{ac} (MHz)	217.66350		-70.97172	-198.55955	129.55247
χ_{bc} (MHz)	-170.37734		-85.52451	-30.64685	130.34058
κ (Kappa)	-0.948	-0.996	-0.972	-0.994	-0.872
μ_a (D)	1.705	2.179	1.621	2.278	1.671
μ_b (D)	1.041	0.744	1.257	0.041	1.246
μ_c (D)	0.478	0.000	0.216	0.391	0.291
μ_{tot} (D)	2.054	2.303	2.063	2.312	2.104

^a Calculation was carried out MP2-6-311+G(2d,2p) level in Gaussian 03.

^b The **aa** conformer has C_s symmetry, so there are only three nuclear quadrupole coupling tensor components.

Table 2Heavy atom structural parameters of 1-bromobutane from *ab initio* optimization at MP2/6-311+G(2d,2p) level. (See Fig.1 for conformer structure)

	aa	ag	ga	gg	gg'
R(Br-C ₁) (Å)	1.953	1.954	1.957	1.957	1.959
R(C ₁ -C ₂) (Å)	1.513	1.514	1.514	1.515	1.520
R(C ₂ -C ₃) (Å)	1.528	1.531	1.524	1.527	1.529
R(C ₃ -C ₄) (Å)	1.526	1.527	1.525	1.526	1.527
∠(Br-C ₁ -C ₂) (°)	111.93	111.57	112.24	112.26	113.98
∠(C ₁ -C ₂ -C ₃) (°)	111.10	111.89	114.19	114.92	115.51
∠(C ₂ -C ₃ -C ₄) (°)	111.97	113.61	111.97	113.33	115.52
τ(Br-C ₁ -C ₂ -C ₃) (°)	180.00	-177.67	-66.11	-60.39	-84.82
τ(C ₁ -C ₂ -C ₃ -C ₄) (°)	180.00	-64.77	-177.63	-55.63	65.80

Table 3
Spectroscopic constants for **aa**, **ga**, and **gg** conformers of 1-bromobutane.

	aa		ga		gg	
	⁷⁹ Br	⁸¹ Br	⁷⁹ Br	⁸¹ Br	⁷⁹ Br	⁸¹ Br
A (MHz, calc) ^a	16054.1124		8271.3308		6126.6379	
B (MHz, calc) ^a	915.1317		1210.3063		1508.2537	
C (MHz, calc) ^a	884.6139		1111.0008		1385.3572	
A (MHz)	15770.66(99)	15760.27(131)	8196.3730(66)	8183.7297(61)	6240.618(278)	6235.48(81)
B (MHz)	914.89072(63)	907.47581(61)	1207.26281(105)	1197.95218(96)	1463.8266(41)	1452.1707(44)
C (MHz)	883.90660(67)	876.95290(62)	1107.67707(78)	1099.61264(77)	1352.8742(36)	1342.6930(41)
D _J (kHz)	0.0634(32)	0.05829(301)	0.3171(77)	0.3116(64)	1.5084(278)	1.4786(282)
D _{JK} (kHz)	-3.091(115)	-3.004(85)	-5.639(111)	-5.675(97)	-12.775(238)	-13.00(101)
d _I (kHz)			-0.0511(49)	-0.0442(49)	-0.278(38)	-0.281(32)
χ _{aa} (MHz)	363.04(34)	303.67(33)	87.17(10)	73.83(93)	157.83(11)	132.69(22)
χ _{bb} -χ _{cc} (MHz)	184.90(113)	153.21(110)	420.24(6)	350.20(6)	141.98(55)	117.95(74)
χ _{ab} (MHz)	-337.81(13)	-282.01(20)	394.70(44)	329.92(43)	-336.11(28)	-280.1(36)
χ _{ac} (MHz)			-72.26(236)	-59.81(271)	221.62(31)	186.5(64)
χ _{bc} (MHz)			-87.38(18)	-74.04(149)	-172.68(76)	-144.24(68)
χ _{xx}	-269.48(48)	-225.51(48)	-264.89(197)	-220.16(242)	-264.88(54)	-221.98(182)
χ _{yy}	-273.97(59)	-228.44(58)	-274.83(154)	-230.95(210)	-271.29(39)	-226.31(393)
χ _{zz}	543.45(32)	453.95(33)	539.71(63)	451.11(84)	536.17(46)	448.29(465)
N ^b	86(23)	98(26)	99(26)	105(28)	47(14)	35(9)
Δv _{rms} (kHz) ^c	6.08	5.10	3.58	5.12	3.90	5.71
κ (Kappa)	-0.996	-0.996	-0.972	-0.972	-0.955	-0.955

^a Calculation was performed using MP2/6-311+G(2d,2p) Gaussian 03 program.

^b N is the number of fitted hyperfine components; the number in parentheses shows the number of separate rotational transitions.

^c Standard deviation of the fit in kHz.

Table 4Observed *a*-type transition frequencies for **aa** conformer of 1-bromobutane.

Transition ^a 2F' - 2F''	⁷⁹ Br		⁸¹ Br		Transition ^a 2F' - 2F''	⁷⁹ Br		⁸¹ Br	
	Observed ^b	$\Delta\nu$ ^c	Observed ^b	$\Delta\nu$ ^c		Observed ^b	$\Delta\nu$ ^c	Observed ^b	$\Delta\nu$ ^c
5 _{1,5} -4 _{1,4}					8 _{1,8} -7 _{1,7}				
13-11	8912.9115	0.0059	8842.7338	-0.0008	19-17	14264.0051	0.0067	14151.1551	0.0034
11-9	8917.2336	-0.0030	8846.3813	-0.0026	17-15	14265.0905	0.0072	14152.0650	0.0013
7-5	8917.9395	0.0000	8846.9959	-0.0015	13-11	14266.3541	0.0017	14153.1341	-0.0003
9-7	8922.5465	-0.0032	8850.8468	-0.0003	15-13	14267.4790	0.0004	14154.0781	0.0025
5 _{0,5} -4 _{0,4}					8 _{0,8} -7 _{0,7}				
11-9	8991.0185	0.0010	8919.5401	-0.0085	17-15	14381.8755	0.0016	14268.6589	0.0016
13-11	8991.1192	0.0022	8919.5946	-0.0058	13-11	14383.7798	0.0068	14270.1521	-0.0010
7-5	8999.9237	-0.0020	8926.7245	-0.0005	19-17	14385.2952	0.0006	14270.6185	0.0016
9-7	9001.9816	-0.0016	8928.2013	0.0015	15-13	14387.3523	0.0007	14272.3940	0.0002
5 _{1,4} -4 _{1,3}					8 _{2,7} -7 _{2,6}				
13-11	9068.7456	0.0017	8996.1026	0.0075	19-17			14272.9079	-0.0076
7-5	9070.5355	-0.0014	8997.7064	0.0038	13-11	14388.2632	-0.0045	14273.6113	0.0005
11-9	9072.8370	-0.0001	8999.6000	0.0081	17-15	14391.7346	-0.0023	14276.4978	0.0009
9-7	9075.5248	-0.0018	9001.8158	0.0072	15-13	14392.6912	-0.0004	14277.3003	-0.0009
6 _{1,6} -5 _{1,5}					8 _{2,6} -7 _{2,5}				
15-13	10696.9826	0.0048	10612.5414	-0.0009	19-17			14276.9245	0.0028
13-11	10699.5003	0.0071	10614.6598	0.0004	13-11			14277.6365	-0.0070
9-7	10700.8613	-0.0013	10615.8164	-0.0027	17-15			14280.3469	-0.0009
11-9			10618.0236	-0.0008	15-13			14281.1765	-0.0018
6 _{0,6} -5 _{0,5}					8 _{1,7} -7 _{1,6}				
13-11	10789.4393	0.0006	10703.5841	-0.0049	15-13	14500.2722	-0.0029	14386.8861	-0.0016
15-13	10789.6415	0.0013	10703.6948	-0.0085	19-17	14501.2965	-0.0007	14387.7496	0.0029
11-9	10791.7252	-0.0017	10705.5616	-0.0010	17-15	14512.8220	-0.0059	14396.1940	0.0010
9-7	10791.8906	-0.0039	10705.7356	-0.0024	13-11	14513.4664	0.0014	14396.6872	-0.0039
6 _{2,5} -5 _{2,4}					9 _{1,9} -8 _{1,8}				
9-7	10787.5119	0.0007			21-19	16047.1238	0.0050	15920.1131	0.0069
15-13	10787.7801	-0.0028	10702.3537	-0.0056	19-17	16047.8958	-0.0018	15920.7644	0.0038

13-11	10797.9871	0.0007	10710.9125	-0.0065	15-13	16048.9936	-0.0088	15921.6936	-0.0002
11-9	10798.1613	0.0282	10711.0252	-0.0020	17-15	16049.8097	0.0007	15922.3698	0.0019
6 _{2,4} -5 _{2,3}					9 _{0,9} -8 _{0,8}				
9-7					21-19	16182.4387	0.0017	16053.4238	-0.0003
15-13					17-15	16184.7320	-0.0055	16055.3081	-0.0026
13-11	10799.5924	-0.0045	10712.4962	0.0006	19-17	16193.5770	0.0028	16061.4810	-0.0020
11-9	10799.7604	-0.0057	10712.6157	-0.0059	15-13	16198.3961	0.0029	16065.5522	-0.0003
6 _{1,5} -5 _{1,4}					9 _{2,8} -8 _{2,7}				
15-13	10884.1662	0.0001	10796.6379	0.0082	21-19			16057.6007	0.0002
9-7	10885.2886	-0.0031	10797.7427	-0.0001	15-13			16058.2570	-0.0046
13-11	10885.9917	-0.0027	10798.3089	0.0069	19-17			16060.1069	-0.0009
11-9	10888.7740	-0.0009	10800.5068	0.0003	17-15			16060.8517	-0.0008
7 _{1,7} -6 _{1,6}					9 _{2,7} -8 _{2,6}				
17-15	12480.6457	0.0046	12381.9836	0.0004	21-19			16063.2803	-0.0006
15-13	12482.2325	-0.0049	12383.3253	-0.0007	15-13			16063.9891	-0.0055
11-9	12483.6353	-0.0022	12384.5048	-0.0027	19-17				
13-11	12485.3003	-0.0006	12385.8992	0.0013	17-15			16066.4093	-0.0016
7 _{0,7} -6 _{0,6}					9 _{1,8} -8 _{1,7}				
15-13	12587.1071	0.0011	12487.0207	0.0037	19-17	16327.2156	-0.0073	16195.8566	-0.0070
17-15	12587.6942	0.0024	12487.3716	0.0004	15-13	16327.2539	-0.0066		
11-9	12589.5177	-0.0017	12489.0808	0.0012	21-19	16329.9484	0.0063	16198.2563	-0.0036
13-11	12590.3416	-0.0005	12489.6370	-0.0025	17-15	16334.1578	-0.0036	16201.8415	0.0026
7 _{2,6} -6 _{2,5}					10 _{1,10} -9 _{1,9}				
17-15	12587.9515	0.0027	12487.9218	0.0078	23-21	17830.0280	-0.0090	17688.8823	0.0072
11-9	12588.5329	-0.0018	12488.4382	0.0048	21-19	17830.6170	-0.0054	17689.3740	0.0072
15-13	12594.3366	-0.0015	12493.2761	0.0021	17-15	17831.5682	0.0039	17690.1670	0.0019
13-11	12595.1634	-0.0026	12493.9678	0.0042	19-17	17832.1611	-0.0075	17690.6753	0.0050
7 _{2,5} -6 _{2,4}					10 _{0,10} -9 _{0,9}				
17-15	12590.7244	-0.0034	12490.5995	-0.0025	17-15	17974.3248	0.0062	17831.6180	-0.0004
11-9	12591.3318	-0.0074	12491.1389	-0.0024	21-19	17975.6474	0.0083	17832.7421	0.0001
15-13	12596.9552	0.0055	12495.8325	0.0073	23-21	17979.0837	-0.0072	17835.7582	-0.0049
13-11	12597.8098	0.0061	12496.5421	0.0071	19-17	17980.4312	-0.0077	17836.8700	-0.0233
7 _{1,6} -6 _{1,5}					10 _{1,9} -9 _{1,8}				
11-9	12699.4975	-0.0043	12597.3206	-0.0041	21-19	18140.7439	0.0304	17994.8142	0.0143
15-13	12699.7167	-0.0026	12597.4573	0.0028	23-21			17994.8622	0.0137
17-15	12701.5726	-0.0030	12598.1316	0.0016	17-15				

13-11	12704.7627	-0.0034	12600.9360	0.0004	19-17	18142.5385	-0.0045	17996.2499	-0.0127
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^a Transitions with quantum numbers ($J'K'_pK'_o - J''K''_pK''_o$) with hyperfine components.

^b Observed frequency in MHz.

^c $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ in MHz.

.

Table 5Observed *a*-type transition frequencies for **ga** conformer of 1-bromobutane.

Transition ^a 2F'-2F''	⁷⁹ Br		⁸¹ Br		Transition ^a 2F'-2F''	⁷⁹ Br		⁸¹ Br	
	Observed ^b	$\Delta\nu$ ^c	Observed ^b	$\Delta\nu$ ^c		Observed ^b	$\Delta\nu$ ^c	Observed ^b	$\Delta\nu$ ^c
4 _{1,4} -3 _{1,3}					6 _{0,6} -5 _{0,5}				
11-9	9055.6548	0.0006	8989.1287	0.0014	9-7	13850.9884	-0.0035	13748.0272	-0.0019
9-7	9058.1801	0.0044	8991.2502	-0.0048	15-13	13851.2811	0.0001		
5-3	9062.6215	-0.0044	8994.9764	-0.0083	13-11	13852.9299	-0.0019	13749.5532	0.0024
7-5	9064.9112	0.0002	8996.9363	-0.0008	11-9	13853.8919	-0.0011	13750.3480	0.0042
4 _{2,3} -3 _{2,2}					6 _{2,5} -5 _{2,4}				
5-3			9184.0724	-0.0037	9-7	13883.3884	0.0001	13779.5112	0.0027
11-9	9258.8655	-0.0005	9190.1306	0.0062	15-13	13883.7936	0.0018	13779.7895	-0.0065
7-5	9261.6461	0.0082	9191.7431	-0.0081	13-11	13886.3989	0.0027		
9-7	9266.2108	-0.0007	9196.0507	-0.0005	11-9	13886.4337	0.0022		
4 _{2,2} -3 _{2,1}					6 _{2,4} -5 _{2,3}				
5-3	9264.0017	0.0097	9195.1144	-0.0042	9-7			13816.4754	-0.0070
11-9	9265.3418	-0.0019	9196.5981	0.0053	15-13			13816.8231	0.0015
7-5	9271.6650	0.0004	9201.6075	-0.0006	13-11			13817.0231	-0.0042
9-7	9273.2314	-0.0075	9203.1945	0.0010	11-9			13817.4712	-0.0010
4 _{1,3} -3 _{1,2}					6 _{1,5} -5 _{1,4}				
5-3	9451.3218	-0.0004	9380.3553	0.0025	9-7	14175.6895	-0.0023		
7-5	9456.8867	-0.0014	9384.7055	-0.0018	11-9	14176.3396	0.0039	14068.2916	0.0061
11-9	9458.5150	-0.0010	9386.1029	-0.0005	15-13	14179.7689	-0.0012	14071.9219	-0.0005
9-7	9459.7170	0.0001	9387.2837	0.0071	13-11	14180.4958	0.0008	14072.5946	0.0008
5 _{1,5} -4 _{1,4}					7 _{1,7} -6 _{1,6}				
13-11	11319.1409	0.0034	11235.7973	0.0056	17-15	15841.0915	-0.0018	15724.3533	0.0111
11-9	11320.6016	0.0021	11237.0326	0.0014	15-13	15841.9431	0.0056	15725.0701	0.0010
7-5	11322.7591	-0.0026	11239.0001	-0.0024	11-9	15842.9293	0.0007	15725.9180	-0.0092
9-7	11323.7861	-0.0016	11239.9892	0.0038	13-11	15843.9808	0.0045	15726.7863	0.0026
5 _{0,5} -4 _{0,4}					7 _{0,7} -6 _{0,6}				
7-5	11550.4714	-0.0057	11464.9397	-0.0053	17-15	16144.0332	0.0002	16024.0561	-0.0031
13-11	11552.2756	-0.0006	11466.1096	0.0061	11-9			16024.2136	0.0031
11-9	11552.4731	-0.0015	11466.4206	0.0011	15-13	16146.2831	0.0033	16025.9452	0.0012
9-7	11554.5561	-0.0002	11468.0926	0.0006	13-11	16147.1338	0.0022	16026.6282	0.0055
5 _{2,4} -4 _{2,3}					7 _{2,6} -6 _{2,5}				
7-5	11569.6564	-0.0012	11483.2814	-0.0032	11-9	16195.2153	0.0003	16073.9886	-0.0010
13-11	11570.6959	0.0003	11484.1126	-0.0008	17-15	16195.6382	-0.0087	16074.2501	0.0036
9-7	11574.4422	0.0009	11487.3058	0.0002	15-13	16197.2177	-0.0008	16075.6493	0.0024

11-9	11575.0970	0.0018	11487.8671	-0.0010	13-11	16197.6368	0.0032	16075.9361	0.0022
5 _{2,3} -4 _{2,2}					7 _{2,5} -6 _{2,4}				
7-5	11591.8197	-0.0033	11504.7440	-0.0045	15-13			16131.9214	0.0044
13-11	11592.6139	-0.0010	11505.3668	-0.0030	11-9			16132.4952	0.0033
9-7	11594.8935	0.0067	11507.3418	0.0078	17-15			16134.0856	0.0033
11-9	11595.1040	0.0003	11507.5630	0.0034	13-11			16134.3334	0.0062
5 _{1,4} -4 _{1,3}					7 _{1,6} -6 _{1,5}				
7-5	11817.9631	-0.0079	11728.6740	-0.0023	11-9	16536.3008	-0.0039	16411.1625	-0.0067
13-11	11819.4552	-0.0026	11729.4188	0.0026	13-11	16538.2071	-0.0030	16412.6120	-0.0083
11-9	11820.4209	0.0028	11730.3054	0.0048	17-15	16538.4708	-0.0027	16412.8188	-0.0024
9-7	11822.0931	-0.0057	11732.3155	-0.0037	15-13	16538.8783	-0.0007	16413.2615	-0.0028
6 _{1,6} -5 _{1,5}					8 _{1,8} -7 _{1,7}				
15-13	13580.9637	0.0026	13480.8851	0.0036	19-17	18099.4241	0.0033	17966.0580	0.0064
13-11	13582.0098	0.0021	13481.7753	0.0024	17-15	18100.0999	-0.0024	17966.6586	-0.0012
9-7	13585.0390	-0.0020	13484.1128	-0.0001	13-11	18100.7189	-0.0062	17967.1954	-0.0086
11-9	13586.9736	0.0030	13485.5731	0.0048	15-13	18101.9086	-0.0003	17968.1290	-0.0169

^a Transitions with quantum numbers ($J'K'_pK'_o - JK''_pK''_o$) with hyperfine components.

^b Observed frequency in MHz.

^c $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ in MHz.

Table 6Observed *b*-type transition frequencies for **ga** conformer of 1-bromobutane.

Transition ^a 2F'–2F''	⁷⁹ Br		⁸¹ Br	
	Observed ^b	$\Delta\nu$ ^c	Observed ^b	$\Delta\nu$ ^c
5 _{1,4} –5 _{0,5}				
11–11	7777.7438	-0.0035	7770.1798	-0.0098
9–9	7797.3636	-0.0060	7787.3211	0.0067
13–13	7837.3200	0.0016	7819.7357	0.0079
7–7	7854.1477	0.0036	7834.3673	-0.0005
6 _{1,5} –6 _{0,6}				
13–13	8105.3067	-0.0037	8093.2313	-0.0012
11–11	8119.8144	0.0020	8105.2659	0.0099
15–15	8165.8077	0.0002	8143.5195	0.0015
9–9	8178.8477	0.0037	8154.5293	-0.0008
7 _{1,6} –7 _{0,7}				
15–15	8497.9049	-0.0048	8480.5485	-0.0043
13–13	8510.8930	0.0020	8491.2583	0.0047
17–17	8560.2492	0.0011	8532.2748	-0.0051
11–11	8571.0043	-0.0003	8541.4853	-0.0035
8 _{1,7} –8 _{0,8}				
17–17	8958.5182	0.0015	8935.9656	0.0040
15–15	8973.3489	0.0037	8947.4657	-0.0059
19–19	9025.7020	0.0019		
13–13	9031.4115	-0.0038		
1 _{1,1} –0 _{0,0}				
5–3	9295.2984	0.0089		
3–3	9328.5355	0.0000		
7 _{0,7} –6 _{1,6}				
15–13	10068.7911	0.0072	9944.8328	0.0048
13–11	10078.4091	0.0016	9953.0471	-0.0091
17–15	10110.2837	-0.0064	9979.6186	0.0006
11–9			9989.6906	-0.0068
8 _{0,8} –7 _{1,7}				
17–15	12659.1835	0.0021		
15–13	12667.0689	0.0076		
19–17	12698.8604	-0.0066		
13–11	12709.1499	0.0017		
9 _{0,9} –8 _{1,8}				
19–17			15105.1720	-0.0084
17–15			15110.6603	0.0012
21–19			15136.6024	0.0093
15–13			15143.8402	0.0061
5 _{1,5} –4 _{0,4}				
7–5			17763.3748	0.0007
13–11			17777.7998	0.0045
9–7			17806.4318	-0.0022
3 _{1,3} –2 _{0,2}				
3–1				
9–7	13656.8066	-0.0025	13608.7323	-0.0083
5–3	13668.7169	0.0011	13619.1693	0.0081
7–5	13703.1242	0.0004	13647.3021	0.0001

^a Transitions with quantum numbers ($J'K'_pK'_o - J''K''_pK''_o$) with hyperfine components.^b Observed frequency in MHz.^c $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ in MHz.

Table 7Observed *a*-type transition frequencies for **gg** conformer of 1-bromobutane.

Transition ^a 2F'-2F''	⁷⁹ Br		⁸¹ Br		Transition ^a 2F'-2F''	⁷⁹ Br		⁸¹ Br	
	Observed ^b	$\Delta\nu$ ^c	Observed ^b	$\Delta\nu$ ^c		Observed _b	$\Delta\nu$ ^c	Observed _b	$\Delta\nu$ ^c
3 _{1,3} -2 _{1,2}					5 _{1,5} -4 _{1,4}				
9-7	8277.7578	0.0070			13-11	13795.7264	0.0012	13690.7333	-0.0008
3-1					11-9	13796.1862	0.0020	13691.5099	-0.0074
7-5	8289.0313	0.0072			7-5	13796.3188	-0.0030	13691.7347	0.0027
5-3	8291.6950	-0.0048			9-7	13800.4716	-0.0005	13694.7713	-0.0063
3 _{0,3} -2 _{0,2}					5 _{0,5} -4 _{0,4}				
7-5	8436.6988	-0.0030	8372.5924	-0.0090	13-11	14043.5734	0.0018	13935.6287	-0.0014
3-1	8438.6315	-0.0007	8374.9937	0.0065	11-9	14044.2209	0.0017	13936.1994	0.0003
9-7	8440.3361	-0.0016	8375.3471	0.0075	7-5	14045.3489	-0.0062	13937.1621	-0.0050
5-3	8441.9761	-0.0014	8377.4067	-0.0082	9-7	14046.6646	-0.0006	13938.1391	-0.0042
3 _{1,2} -2 _{1,1}					5 _{2,4} -4 _{2,3}				
3-1			8538.4288	-0.0034	13-11	14074.3840	0.0058		
9-7	8612.2383	0.0034	8544.9483	-0.0080	7-5				
5-3			8549.9975	-0.0077	11-9	14083.4780	0.0041		
7-5	8620.0861	0.0093	8551.8706	0.0065	9-7	14083.9606	0.0010		
4 _{1,4} -3 _{1,3}					5 _{2,3} -4 _{2,2}				
11-9	11038.2344	0.0010	10954.3577	0.0054	7-5	14112.9621	-0.0076		
9-7			10957.8317	0.0086	13-11	14117.7835	-0.0016		
5-3					11-9				
7-5	11046.3189	-0.0045	10961.1404	-0.0081	9-7				
4 _{0,4} -3 _{0,3}					5 _{1,4} -4 _{1,3}				
11-9	11245.9385	0.0006	11159.3458	0.0045	13-11			14237.9961	-0.0034
9-7	11246.0841	0.0025	11159.5343	0.0096	9-7			14242.0012	0.0053
5-3	11248.9631	-0.0071	11162.1434	0.0058	11-9				
7-5	11250.5655	0.0010	11163.4117	-0.0049	7-5				
4 _{2,3} -3 _{2,2}	11253.6898	-0.0023			6 _{1,6} -5 _{1,5}				
5-3	11257.7104	-0.0003			15-13	16550.4585	-0.0018	16424.4900	0.0048
11-9	11263.9111	0.0055			11-9	16554.5536	0.0033	16427.8391	0.0058
7-5	11274.8513	0.0018			13-11	16557.3818	-0.0019	16429.5902	-0.0002

9-7					9-7	16560.4792	-0.0014	16431.9293	-0.0041
4 _{2,2} -3 _{2,1}					6 _{0,6} -5 _{0,5}				
5-3	11273.2148	-0.0013			15-13	16831.6794	0.0044		
11-9	11272.8792	-0.0002			13-11	16832.5083	0.0038		
7-5					9-7	16832.7757	-0.0043		
9-7	11292.7704	-0.0070			11-9	16834.3459	0.0012		
4 _{1,3} -3 _{1,2}					6 _{1,5} -5 _{1,4}				
5-3	11480.5309	-0.0074	11391.3173	-0.0014	9-7				
11-9	11482.7882	0.0028	11392.8452	0.0013	13-11				
9-7	11485.5067	0.0015	11395.3620	0.0058	15-13			17080.1688	-0.0066
7-5	11487.0037	-0.0008	11396.4026	0.0034	11-9			17080.3418	0.0051

^aTransitions with quantum numbers ($J'K'_pK'_o - J''K''_pK''_o$) with hyperfine components.

^bObserved frequency in MHz.

^c $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$ in MHz.

Table 8

Comparisons of Br quadrupole coupling tensors, in the principal axes for four alkyl bromide (R–Br) including 1-bromobutane.

Molecule	Molecular formula	⁷⁹ Br			⁸¹ Br			Ref.
		χ_{xx}	χ_{yy}	χ_{zz}	χ_{xx}	χ_{yy}	χ_{zz}	
bromomethane	CH ₃ Br	-288.5544 ^a	-288.5544 ^a	577.1088(57)	-241.0515 ^a	-241.0515 ^a	482.1030(94)	[15, 16]
bromoethane	CH ₃ CH ₂ Br	-270.32(166)	-273.71(17)	544.03(168)	-225.25(201)	-228.65(18)	453.91(203)	[12]
		-266.91	-273.55	540.46	-221.09	-228.60	449.69	[13]
1-bromopropane	CH ₃ CH ₂ CH ₂ Br (<i>gauche</i>)	-279.0	-247.4	526.4	-228.1	-206.0	434.1	[14]
1-bromobutane	CH ₃ CH ₂ CH ₂ CH ₂ Br (<i>aa</i>)	-269.48(48)	-273.97(59)	543.45(32)	-225.51(48)	-228.44(58)	453.95(33)	This work
	(<i>ga</i>)	-264.89(197)	-274.83(154)	539.71(63)	-220.16(242)	-230.95(210)	451.11(84)	This work
	(<i>gg</i>)	-264.88(54)	-271.29(39)	536.17(46)	-221.98(182)	-226.31(393)	448.29(465)	This work

^a by symmetry

Table 9

The measured and calculated dipole moment for **aa** conformer of CH₃CH₂CH₂CH₂⁷⁹Br.

	aa_{obs}	aa_{calc}	$\Delta_{\text{obs-calc}}$ ^c
μ_a (D)	2.229(13)	2.179	0.050
μ_b (D)	0.603(60)	0.744	-0.141
μ_c (D) ^a	0.000	0.000	0.000
μ_{tot} (D)	2.309	2.303	0.006
N ^b	49		

^a μ_c is not fitted because the **aa** conformer has an *ab* plane of symmetry, μ_c dipole component is zero due to symmetry.

^b The number of distinct Stark measurements.

^c $\Delta_{\text{obs-calc}}$ is observed minus calculated dipole moment value in D.

aa

Five structural isotopomers
for 1-bromobutane

ga

gg

ag

gg'