

Microwave spectrum of 1-bromobutane



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ABSTRACT

The rotational spectrum of 1-bromobutane has been measured in the range of 8–18 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.

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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 QSTARK program [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 5000 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.

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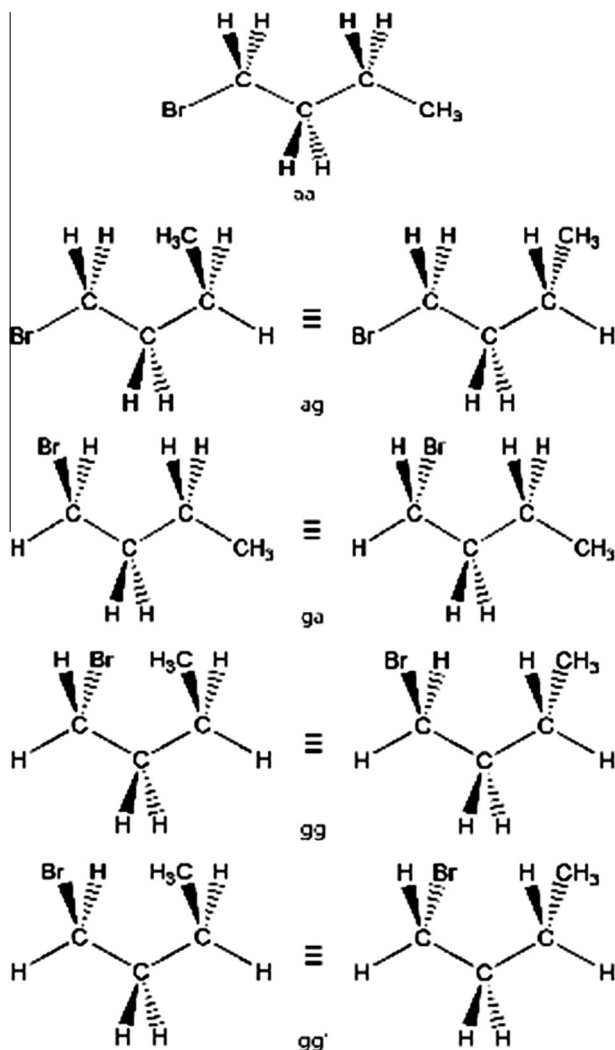


Fig. 1. Structure of the five conformers for 1-bromobutane.

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

3.1. *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 $38 \pm 34\%$, but **aa** conformer is $21 \pm 14\%$.

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

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 = 5 K | T = 10 K | T = 298 K |
| 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.

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