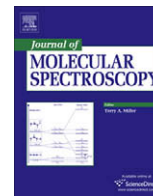




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Microwave spectrum of 1,2-propanediol

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ABSTRACT

The microwave spectrum of the sugar alcohol 1,2-propanediol ($\text{CH}_3\text{CHOHCH}_2\text{OH}$) has been measured over the frequency range 6.5–25.0 GHz with several pulsed-beam Fourier-transform microwave spectrometers. Seven conformers of 1,2-propanediol have been assigned and ab initio electronic structure calculations of the 10 lowest energy forms have been calculated. Stark effect measurements were carried out on several of the lowest energy conformers to provide accurate determinations of the dipole moment components and assist in conformer assignment.

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1. Introduction

Recently, the simplest sugar, glycolaldehyde (CH_2OHCHO) [1], and its diol derivative, ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$) [2], were detected towards the interstellar molecular cloud, Sgr B2 (N-LMH). The identification of sugar alcohols and sugar acids in the Murchinson and Murray meteorites [3] has also increased the interest in investigating interstellar sugars and their derivatives in astronomical environments. 1,2-Propanediol is one of two forms of propanediol, the other being 1,3-propanediol, and is related to ethylene glycol by the addition of a methyl group to one of the carbon atoms in place of an H atom. Because of its structural similarity to ethylene glycol, 1,2-propanediol is of interest as a potential interstellar molecule.

1,2-Propanediol is an asymmetric top molecule with numerous low energy conformers. Vázquez et al. [4] reported optimized geometries for 23 conformers from Pulay's gradient optimized ab initio calculations [5] using the 4-21G basis set with eight conformers having relative energies below 560 cm^{-1} . Since this is a rather small basis set, the current ab initio calculations were carried out at the MP2 level [6] with the augmented correlation consistent triple zeta basis set, aug-cc-pVTZ, [7] beginning with the eight lowest energy structures reported in [4]. We use the conformer labeling scheme employed in Ref. [4] as well as their atom numbering for easier

comparisons. This labeling scheme provides a three character label, xXx, where X (capital for the OCCO dihedral angle orientation and lower case for the hydroxyl hydrogens) can be G, or G', depending on the *gauche* position of the atom considered with respect to a reference bond. G and G' indicate an anticlockwise or a clockwise rotation from the *cis* (*syn*) position of O2–C3–C4–O5 dihedral angle for the X values and similarly for the HOCC dihedral angles represented by x whose values may be g, g', t, or t'. The first x represents the position of the hydroxyl hydrogen H1 with respect to C4, the second x the position of H6 with respect to C3.

The microwave spectra of two low energy conformers of 1,2-propanediol, labeled as g'Gt (conformer 1 here) and gG't (conformer 2), were previously investigated in the frequency range from 26.5 to 40 GHz using a conventional Stark-modulated microwave absorption spectrometer [8]. The gG't (conformer 2) was assigned to be the most stable. We have expanded the data obtained in Ref. [8] by a new series of measurements in the 6.5–25 GHz frequency range using a National Institute of Standards and Technology (NIST) cavity spectrometer and the broadband instrument at University of Virginia. Since seven of the eight low energy conformers were assigned from the surveys, we extended the structure calculations to cover conformers 9 to 12 reported by Vázquez et al. [4]. However, only conformers 9 and 12 were stable forms with conformers 10 and 11 relaxing to other conformer structures.

2. Experimental details

At NIST, measurements were carried out using a Fabry–Perot cavity, pulsed nozzle Fourier-transform microwave (FTMW)

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spectrometer of the Balle–Flygare type [9] designed by Lovas and Suenram [10,11]. This design employs a co-axially oriented nozzle [12] and PC based system for timing, mirror movement, nozzle control, synthesizer tuning and signal processing and uses the FTMW++ software system designed by Grabow [13]. Under ambient conditions, 1,2-propanediol has a very low vapor pressure. Therefore, in order to obtain a sufficient vapor pressure of 1,2-propanediol, the sample was heated up to 60 °C in a nozzle equipped with a reservoir. The jet-cooled expansion was produced by mixing the vapor with a 20% helium and 80% neon by volume carrier gas at a total pressure of 100 kPa (1 bar) and then injecting it into the cavity through 1 mm nozzle orifice along the axis of the Fabry–Perot cavity and parallel to the microwave field. Molecular transitions, observed as Doppler doublets, had line widths of 5 kHz, and the frequency measurement uncertainties were estimated to be 2.5 kHz in most cases.

Measurements at the University of Virginia were performed with a broadband chirped-pulse FTMW spectrometer [14]. The “B” configuration described in Ref. [14] was used with an additional upgrade of the arbitrary waveform generator (AWG) to a 24 Gs/s sample rate (Tektronix AWG7122B) [15]. The chirped microwave excitation pulse was created by mixing a linear sweep pulse generated by the AWG with a 18.95 GHz phase-locked dielectric resonator oscillator (PDRO). The AWG pulse sweeps the frequency range of 12–0.5 GHz with a duration of 1 μ s creating a microwave pulse that covers the 6.95–18.45 GHz frequency range following frequency up-conversion with the PDRO.

The two strategies to reduce sample consumption described in Ref. [14] were implemented. Sample introduction into the vacuum chamber used two pulsed valve sources operated with 700 μ s pulse duration. The nozzles inject the sample perpendicular to the microwave propagation. For each sample injection cycle, 10 separate broadband rotational spectra were acquired. The individual broadband chirped pulses were separated by 25 μ s. The rotational free induction decay was acquired for 20 μ s following each 1 μ s excitation pulse. The repetition rate for the sample injection was 0.6 Hz and is limited by the data processing rate of the digital oscilloscope. A total of 288 000 rotational spectra of 1,2-propanediol were acquired in 28 800 injection cycles with a total measurement duration of approximately 14 h. The sample conditions for the broadband FTMW measurements were the same as the cavity FTMW measurements described above.

3. Ab initio calculations

Previously Vázquez et al. [4] reported optimized geometries for 23 conformers from ab initio calculations with a 4-21G basis set. We have re-examined 10 of the lowest energy forms whose calculated energies were below 12.6 kJ/mol (1056 cm^{-1}). The theoretical study of the ten conformers of 1,2-propanediol was initially performed at the MP2/6-311G(d) [16] level using the GAUSSIAN 03 Quantum Chemistry Package [15,17]. Each of the geometric isomers was fully optimized at the MP2/aug-cc-pVTZ level and shown in Figs. 1 and 2. All geometries were at true energy minima as verified in calculations of the analytical second derivatives. The relative energies of the 10 conformers with and without zero-point-energy (ZPE) corrections are summarized in Table 1. The predicted rotational constants and dipole moment components are also reported in the Table 1 and used below to aid the identification of the experimentally observed forms. The structural parameters of the six lowest energy forms observed are given in Tables 2 and 3 according to the labeling given in Fig. 1. Structural parameters of the remaining four conformers may be found in the supplementary material. The conformer labels used in Table 1 and subsequent

tables use those from Vázquez et al. [4] for conformers 1 to 9. Conformer 10 here is conformer 12 in Ref. [4].

Rather interestingly, in Ref. [4] conformer 1 was found to be the lowest energy conformation, while in the higher level calculations presented here, conformer 3 is the lowest in energy. On the other hand in the laboratory study by Caminati [8], where only conformers 1 and 2 were assigned, it was concluded that conformer 2 was the lower energy form.

4. Results and analysis

The analysis was started using rotational constants reported in the previous study by Caminati [8]. Predictions based on these data allowed us to readily assign new spectral lines for the two conformers identified by Caminati. For conformer 1 (g'Gt), 32 new transitions were assigned and for conformer 2 (gG't), 41 new transitions were assigned over the frequency range of 6.4–25 GHz. These transitions were fitted together with the data from Ref. [8] with a fit deviation of about 2 kHz for the currently measured data. The measurements, assignments and residuals of the fits for conformers 1 and 2 are shown in the supplementary tables. The improved values of rotational and centrifugal distortion constants are given in Table 4.

Once the two previously known conformers were completely assigned, we examined the remaining spectral lines for evidence of any of the other conformers based on the ab initio results in Table 1. Conformer 3 was easily assigned since its a-type transitions were the same intensity as those of conformer 2 and only offset in frequency by 10's of MHz and conformer 3 was calculated to be the lowest energy form. We also managed to assign a rather weak set of spectral lines found in the NIST FTMW scan to conformer 4, which has the highest calculated energy of conformers 1 to 4. The assigned spectral lines for conformer 3 are shown in Table 5 and those for conformer 4 are listed in Table 6 along with the residuals of the fits. Table 7 lists the fitted molecular constants for both conformers 3 and 4 and compares them with the theoretical rotational constants.

In order to determine if any other higher energy conformers might be assigned as well as ^{13}C isotopologues of the low energy forms, deep integration scans were carried out using the University of Virginia spectrometer. In addition, since this instrument has no cavity or waveguide to make relative intensity measurements difficult, this spectrum can give the best experimental determination of the relative energies of the various conformers when coupled to the theoretical or experimental dipole moments (described in Section 5). From the new deep integration data shown in Fig. 3, three more spectra were assigned. Two were easily identified as belonging to the conformers 5 and 6 based on agreement with the rotational constants as listed in Table 8. The remaining conformer has rotational constants very similar to those calculated for conformers 4, 7 and 8. The rotational analysis of this last (7th conformer) is shown in Table 9 along with a comparison to the theoretical values calculated for conformers 7 and 8. In order to provide a more definitive assignment of these two spectra for conformers “4” and “7”, the calculated dipole moment components squared were used to simulate the relative intensities and compared to the observed spectra. For conformer 4 observed we find relative intensities of 69%, 14% and 17% for the a-type, b-type and c-type transitions, respectively, by normalizing the relative intensities to 100%. Comparing these to the ratio of the calculated dipole moment squared and total dipole moment squared, which are 72%, 24% and 15%, we find good agreement with the a- and c-type and a bit poorer agreement with the b-type. For conformer 7 observed we find relative intensities of 24%, 10% and 66% for the a-type, b-type and c-type transitions, respectively, by normalizing

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