



Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jms

1,3-Propanediol millimeter wave spectrum: Conformers I and II

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ARTICLE INFO

Article history:

Received 6 August 2013

In revised form 18 September 2013

Available online 18 October 2013

Keywords:

1,3-Propanediol

Millimeter wave spectrum

Coriolis coupling

Tunneling splittings

ABSTRACT

We present a new study of the millimeter wave spectrum of the lowest two conformers of the 1,3-propanediol ($\text{CH}_2\text{OHCH}_2\text{CH}_2\text{OH}$) molecule. The new measurements involving rotational transitions with J up to 65 and K_a up to 30 for conformer I and J up to 59 and K_a up to 29 for conformer II have been carried out between 49 and 237 GHz using the Kharkov millimeter wave spectrometer. The new data were combined with previously published measurements and fitted using a model that assumes a symmetric potential energy surface with two minima between which the system tunnels. The final fit included 19 parameters for conformer I and 23 parameters for conformer II with weighted root-mean-square deviations of 0.81 and 0.73 achieved for datasets consisting of 3384 and 2947 line frequencies belonging to the ground states of conformer I and conformer II, respectively. The millimeter wave spectra of both conformers reveal a rather strong influence of the Coriolis type perturbation, which previously was not taken into account in the analysis of the 1,3-propanediol spectrum.

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1. Introduction

Propanediols attract spectroscopic attention as possible new candidates for interstellar detection since they are the derivatives of ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$), which was detected towards the interstellar molecular cloud in Sgr B2 (N-LMH) [1]. The two forms of propanediol, namely, 1,2-propanediol and 1,3-propanediol, have been recently studied using FTMW spectroscopy methods [2,3] with the upper frequency limit of these investigations being 25 GHz. Earlier studies of both propanediol forms provide data with the upper frequencies of 40 GHz for 1,2 propanediol [4] and 78 GHz for 1,3-propanediol [5]. An interstellar search for the 1,3-propanediol conformer I was made as a part of the Green Bank Telescope (GBT) Prebiotic Interstellar Molecule Survey (PRIMOS) Legacy Project and no transitions were detected beyond the 1-sigma rms noise limit [3]. The present study is aimed at extending the investigated frequency range for 1,3-propanediol and providing a reliable basis for further interstellar searches of this molecule at higher frequencies and in hot cores.

1,3-Propanediol exists in a form of several low-energy conformers [3,5] and in the present study we concentrated our attention on the two most stable conformers I and II (see Fig. 1). Rotational spectra of both conformers show additional splittings due to tunneling between two structurally chiral forms which is associated with the concerted rotation of the two OH groups [3]. Possible pathways for such interconversions in 1,3-propanediol molecule

were analyzed in Ref. [3] based on high level ab initio calculations. Analogous interconversion between structurally chiral forms was observed for example in ethylene glycol molecule [6–8] or in conformer V of glycerol [9]. To accommodate additional splittings observed in the spectrum, a model assuming a symmetric double minimum potential surface was used where the lowest two inversion substates O^+ and O^- are split by some amount [3]. Although a considerable Coriolis interaction between the two tunneling substates may be expected from the studies of related ethylene glycol molecule [8] this coupling was not taken into account in the theoretical models used in previous studies of 1,3-propanediol spectrum. Our current results show that the Coriolis interaction between the two tunneling substates in the spectra of the two most stable conformers I and II of 1,3-propanediol is very important and may affect the results of astronomical search for this molecule.

1.1. Experimental details

1,3-Propanediol sample has been purchased from Fluka and used without further purification. To provide sufficient vapor pressure the sample was heated up to 75 °C. The new measurements for 1,3-propanediol spectrum were made in the frequency range from 49 to 149 GHz and from 202 to 237 GHz using the automated millimeter wave spectrometer of IRA NASU [10]. The synthesis of the frequencies in the millimeter wave range is carried out by a two-step frequency multiplication of the reference synthesizer in two phase-lock-loop (PLL) stages. As the reference synthesizer a computer-controlled direct digital synthesizer (DDS AD9851) is

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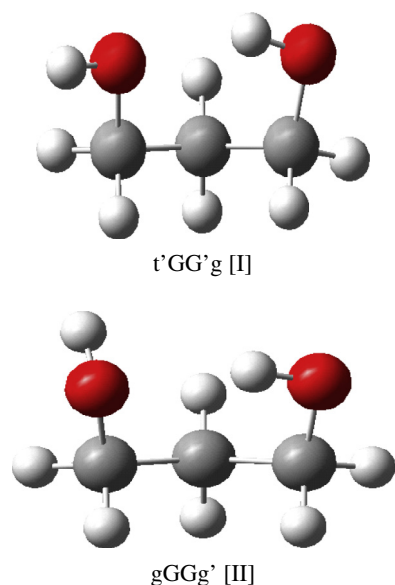


Fig. 1. The structures of conformer I and conformer II of the 1,3-propanediol molecule that were studied in our work (adapted from Ref. [3]).

employed whose output is up-converted into the frequency range from 385 to 430 MHz. At the first multiplication stage a klystron operating in the 3400–5200 MHz frequency range with a narrow-band (~ 1 kHz) PLL system is used. At the second multiplication stage, a set of Istok backward wave oscillators (BWO) locked to a harmonic of the klystron is used. The set of available BWO's covers the frequency range from 49 to 149 GHz. For the measurements from 202 to 237 GHz a self-made Shottky diode frequency doubler was used. The uncertainty of the measurements was estimated to be 10 kHz for a relatively strong isolated line ($S/N > 10$), 30 kHz for weak lines ($2 < S/N$ ratio < 10) and 100 kHz for very weak lines ($S/N < 2$).

1.2. Spectral analysis and fit

Our initial analysis was based on the results of the previous work [3] which gave an opportunity to make first tentative assignments of observed spectrum for both conformers relatively

easy. As it was already shown in Refs. [3,5] the a-type transitions of the conformer I and II are split because of tunneling between two equivalent configurations, whereas b- and c-type transitions have very little splitting or do not have it at all. Thus, a model assuming a symmetric potential energy surface with two minima between which the system tunnels was necessary for the analysis of the observed spectrum. The tunneling between two equivalent configurations is related to the concerted rotation of OH groups in the molecule [3]. Following Ref. [3] the system was modeled by two inversion substates O^+ and O^- split by some amount where b- and c-type transitions were assigned as rotational transitions within each inversion substate and a-type transitions were assigned as transitions that crossed between the inversion substates. As in Ref. [3] we used Pickett's SPFIT/SPCAT programs for spectral analysis [11] and at the initial stage of our study we used separate sets of rotational parameters for each inversion substate.

First, we decided to concentrate our efforts on conformer I since this is the lowest energy conformer of the molecule and the strongest transitions observed in the spectrum belong to this conformer. Although the results of the previous studies [3,5] made it possible to find some correspondence between predicted and observed line positions, assignment problems were encountered already for low K_a transitions. These problems are illustrated in Fig. 2, where a fragment of the recorded spectrum of 1,3-propanediol is compared with predictions obtained for conformer I using the results of Ref. [3] (Fig 2a) and our results (Fig 2c). As it can be seen from Fig. 2 there is a specific multiplet observed in the spectrum (curve 2b) that consists of two triplets of lines. At the same time the predictions based on the results of Ref. [3] (see curve 2a) assume a multiplet of somewhat different form. Whereas the shifts in line positions may be explained by extrapolation errors the distribution of intensities between the components of the multiplet posed a problem. Careful consideration of the situation showed that the source of the problem is Coriolis interaction between the two tunneling substates. In both Refs. [3,5] the Coriolis interaction was neglected and perturbed transitions were excluded from the fits [3,5]. Since the number of perturbed transitions in the datasets of [3,5] was rather small and since observed Coriolis perturbation at low frequencies gives relatively small frequency shifts such an approach seemed quite reasonable. Nevertheless, at higher frequencies, where considerable distortions in the spectrum are caused by Coriolis interaction, it was not possible to neglect this

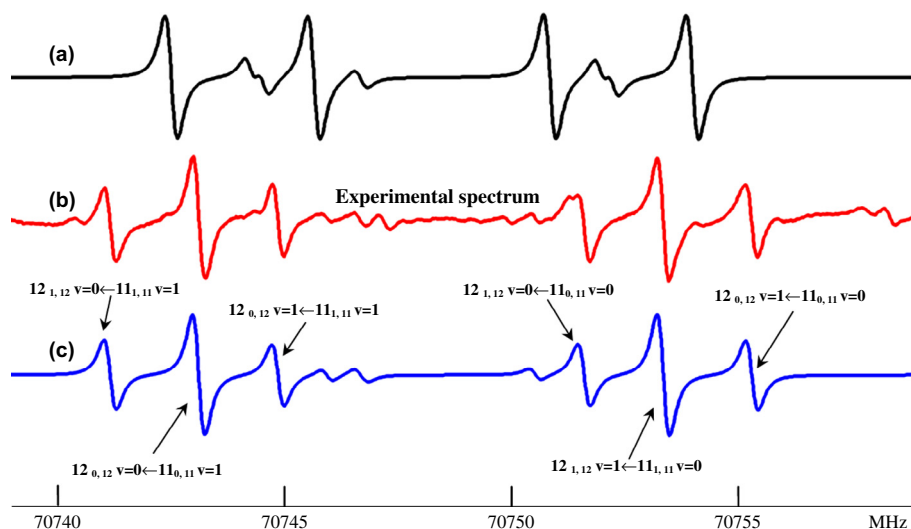


Fig. 2. Fragment of the 1,3-propanediol conformer I spectrum near 70.7 GHz. (a) Predicted spectrum based on the results of Ref. [3]; (b) experimental spectrum obtained in this work using the automated spectrometer of IRA NASU; and (c) predictions of the spectrum based on the results of our investigation. $\nu = 0$ and $\nu = 1$ stand for the two inversion substates splitted by the tunneling in the 1,3-propanediol spectrum. Note that because of the frequency modulation and first harmonic detection the form of the lines correspond to the first derivative of the actual lineshape.

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