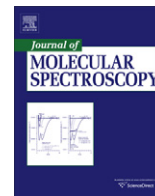




Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

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

Almost free methyl top internal rotation: Rotational spectrum of 2-butynoic acid

Vadim Ilyushin^{a,*}, Roberto Rizzato^b, Luca Evangelisti^b, Gang Feng^b, Assimo Maris^b, Sonia Melandri^b, Walther Caminati^b^a Institute of Radio Astronomy of NASU, Chervonopraporna Street 4, 61002 Kharkov, Ukraine^b Dipartimento di Chimica "G. Ciamician" dell' Università, Via Selmi 2, I-40126 Bologna, Italy

ARTICLE INFO

Article history:

Available online 29 March 2011

Keywords:

Rotational spectroscopy
Internal rotation
Large amplitude motion
Potential energy surface
Pulsed jet
Carboxylic acid

ABSTRACT

The rotational spectrum of 2-butynoic acid was measured by pulsed supersonic-jet Fourier transform microwave spectroscopy in the frequency range from 6 to 18 GHz. Rotational lines have been measured for the $m = 0$ and $m = 1$ torsional states and analyzed using the rho-axis-method. The features of the spectrum illustrate the pattern for an almost free internal rotation of the terminal methyl group that is characterized by a very low barrier $V_3 = 1.0090(4) \text{ cm}^{-1}$. The results are compared with the supporting *ab initio* calculations for this molecule.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

Conformational equilibria of carboxylic acids and their dimers have recently acquired new interest. The aim of the studies is observing and determining the potential energy surface for the concerted proton exchange between the monomers, which could be an important phenomenon in the interaction between amino acids. Intermolecular and intramolecular proton exchanges often serve as triggers for more extensive chemical or conformational changes in molecules, and systems that exhibit such phenomena are therefore of interest for molecular dynamics and biochemistry.

The 1:1 adduct between a carboxylic acid with a triple C–C bond (propionic acid) and formic acid was investigated by Daly et al. [1]. Such a heterodimer is quite similar to the formic acid dimer, which was studied extensively because of its concerted double proton tunneling phenomenon (see Ref. [2] and references therein). In their work [1] the authors observed a splitting of the rotational lines attributable to a proton transfer between the two moieties. Therefore complexes of this kind between carboxylic acids and formic acid seem to be very good candidates for observing the proton tunneling splitting. Heterodimers with 2-butynoic acid should also supply important information on proton transfer processes, and with the aim of pursuing this kind of research in the future, we report here an analysis of the rotational spectrum of the 2-butynoic acid monomer since not even the rotational spectrum of the monomer is available in the literature.

* Corresponding author. Fax: +380 57 706 1415.

E-mail address: ilyushin@rian.kharkov.ua (V. Ilyushin).

Internal large amplitude motions, such as the internal rotation of a methyl group, can complicate the rotational spectrum of carboxylic acids and their dimers. Acetic acid for example has quite a low barrier to internal rotation ($V_3 = 170 \text{ cm}^{-1}$ [3]), as has also trifluoroacetic acid ($V_3 = 241 \text{ cm}^{-1}$ [4]). Complexation of acetic acid with one or two water molecules [5] or with CF_3COOH [6] lowers the barrier to internal rotation to $V_3 = 138, 118$ and 97 cm^{-1} , respectively. The considerable decrease of V_3 with respect to the value for isolated CH_3COOH in the hydrated species and in the heterodimers was interpreted by Howard and collaborators in terms of correlation with the strength of hydrogen-bonding in the complexes [5].

It would be of interest to know how complexation will affect the barrier to internal rotation in 2-butynoic acid, since this molecule is expected to have a very low barrier to internal rotation. As was demonstrated by Olson and Papousek in their infrared work on dimethylacetylene [7], the methyl group experiences nearly free internal rotation when it is attached to a triple C≡C bond. The upper limit for the barrier to internal rotation estimated semi-quantitatively in this study for dimethylacetylene [7] is 4 cm^{-1} . Our current study shows that 2-butynoic acid has a barrier of about 1 cm^{-1} .

In this paper we report the results of our pulsed supersonic-jet microwave Fourier transform study of the 2-butynoic acid ($\text{CH}_3\text{—C}\equiv\text{C—COOH}$) spectrum in the frequency range from 6 to 18 GHz. Frequencies of the rotational lines have been measured for the $m = 0$ and $m = 1$ torsional states of the molecule. The 2-butynoic acid spectrum is analysed using the well-established rho-axis-method (RAM), which has achieved experimental accuracy (or almost so) for several internal rotation molecules

including acetic acid [3] and a molecule, acetamide [8], with a very low barrier to internal rotation ($V_3 \approx 25 \text{ cm}^{-1}$). In the present study a fit within experimental accuracy has also been achieved for the 2-butynoic acid spectrum, giving the lowest barrier height ever analyzed with an RAM Hamiltonian, $V_3 = 1.0090(4) \text{ cm}^{-1}$.

2. Experimental details

The sample of 2-butynoic acid was purchased from Aldrich and used without further purification. The rotational spectrum of 2-butynoic acid was measured in the 6–18 GHz frequency range using a COBRA-type [9] pulsed supersonic-jet Fourier-transform microwave (FTMW) spectrometer described elsewhere [10] and updated with the FTMW++ set of programs [11]. Helium at a pressure of 2 bar was flowed over a sample of 2-butynoic acid heated to about 350 K and the resulting mixture was expanded through a solenoid valve (General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry–Pérot cavity. The frequencies were determined after Fourier transformation of the 8 k data points contained in the time domain signal, recorded with 100 ns sample intervals. Each rotational transition is split by the Doppler effect due to the molecular beam expansion in the coaxial arrangement of the supersonic jet and resonator axes. The rest frequency is calculated as the arithmetic mean of the frequencies of the Doppler components. The estimated accuracy of frequency measurements is better than 3 kHz and lines separated by more than 7 kHz are resolvable.

3. Theoretical model

The Hamiltonian used in the present work is the so-called rho-axis-method internal-rotation Hamiltonian which is rather completely described in the works of Kirtman [12], Lees and Baker [13], Herbst et al. [14] and Hougen et al. [15]. In the present study we apply a RAM torsion–rotation program recently developed for molecules with a low internal rotation barrier [16]. This program has two modes: the first one, the so-called V_6 -mode, is intended for molecules with a C_{3v} top and a C_{2v} frame that possess a sixfold barrier to internal rotation; the second one, the so-called V_3 -mode, is intended for molecules with a C_{3v} top and a C_s frame that possess a threefold barrier. This program was successfully applied to fit the microwave spectra of molecules with low sixfold barriers, such as toluene [16] (light top) or benzotrifluoride [17] (heavy top). Here we decided to apply this program to the analysis of the spectrum of a molecule with a very low V_3 barrier, such as 2-butynoic acid, also in order to test the V_3 -mode of the new program on a very low V_3 barrier problem.

The V_3 -mode follows the procedure realized in the BELGI code (see Ref. [18] for details) with the main difference being the form of presentation of the Hamiltonian terms. In our program we encoded the following general expression for the Hamiltonian:

$$H = (1/2) \sum_{knpqrs0} B_{knpqrs0} \left[J_z^{2k} J_x^n J_y^p J_z^q p_x^r \cos(3s\alpha) + \cos(3s\alpha) p_x^r J_z^q J_y^p J_x^n J_z^{2k} \right] + (1/2) \sum_{knpqrt} B_{knpqrt} \left[J_z^{2k} J_x^n J_y^p J_z^q p_x^r \sin(3t\alpha) + \sin(3t\alpha) p_x^r J_z^q J_y^p J_x^n J_z^{2k} \right], \quad (1)$$

where the $B_{knpqrst}$ are fitting parameters; p_x is the angular momentum conjugate to the internal rotation angle α ; J_x , J_y , J_z are projections on the x , y , z axes of the total angular momentum \mathbf{J} . In the program, matrix elements are calculated for specific terms in the general expression of Eq. (1), which the user selects via sets of k , n , p , q , r , s , t integer indices in the input file. During input, each set of k , n , p , q , r , s , t integer indices is checked for conformity with time reversal and symmetry requirements. In the V_3 -mode only terms in the torsion–rotation Hamiltonian that are totally symmet-

ric in the group G_6 are allowed. Such an approach provides much higher flexibility in testing and fitting different Hamiltonian terms than the BELGI code which has a fixed set of Hamiltonian terms [18]. Readers are encouraged to look at Section 3 of Ref. [16] for more details on the structure of the computer program.

In the process of spectrum analysis the question of labeling the torsional states has arisen. It is well known that the internal rotation of a methyl top attached to some molecular frame should be treated as an anharmonic vibrational motion well below the top of the barrier to internal rotation, and as a nearly free internal rotation motion well above the top of the barrier. Therefore a harmonic oscillator vibrational quantum number v_t is not well defined for levels above the barrier and a free-rotor quantum number m is not well defined for levels below the barrier. The v_t labeling assumes that the spacings between degenerate and nondegenerate levels of the torsional Hamiltonian associated with given v_t are much smaller than those between levels with different v_t [19]. Since this was true for the majority of molecules with a threefold barrier treated up to now by microwave spectroscopy the harmonic oscillator vibrational quantum number v_t was traditionally used to label torsional states in the case of a threefold barrier. In the present case we deal with an extremely low threefold barrier where the E component of the ground torsional state already lies well above the barrier, and where the free-rotor quantum number m should be more appropriate. So we decided to use m quantum number for labeling torsional states in the fit of the 2-butynoic acid spectrum.

3.1. Ab initio calculations

The structural parameters of 2-butynoic acid have been optimized by *ab initio* calculations performed with the G09 suite of programs [20]. The HF, MP2 and B3LYP methods were used with the 6-311G(d,p), 6-311++G(d,p) and 6-311++G(3df,3p) basis sets. The three configurations related to the orientation of the methyl group considered here for 2-butynoic acid are shown in Fig. 1. Two of them, $C_s(\text{OH})$ and $C_s(\text{=O})$ have a C_s symmetry, while C_1 does not have symmetry elements. We optimized the structure of each configuration, and subsequently run harmonic frequency calculations. In the C_1 structure one of the methyl hydrogen atoms was forced to be orthogonal to the carboxyl group, whereas in the C_s forms one of the methyl hydrogen atoms was forced to be coplanar with the carboxyl group. For each of the optimized geometries the harmonic vibrational frequency values were found to be all positive or all positive except for the one corresponding to the methyl rotation motion. The results are given as [Supplementary material](#). The obtained relative electronic energies among the three forms vary between 0.04 and 1.6 cm^{-1} , as a result of the almost flat potential energy surface (PES) for the low barrier to internal rotation of the methyl group. Due to such flatness, it is even difficult to identify which of the forms is a minimum when calculating vibrational frequencies within the harmonic approximation. Whereas we believe that it is rather difficult to obtain an accurate V_3 value for such a flat PES it should be noted that the values obtained in our *ab initio* calculations lie below 1.6 cm^{-1} , which is in good correspondence with the V_3 value obtained from the fit (see next section).

In Table 1 the rotational constants calculated with several theoretical approaches are compared with experimental values obtained in the current study (see next section for details). One can see that for this kind of molecule the best results are obtained with the MP2/6-311++G(3df,3p) combination of method and basis set. Table 2 gives the rotational and centrifugal distortion constants calculated with this method, and Fig. 2 gives the global minimum energy configuration. The structural parameters obtained for

Download English Version:

<https://daneshyari.com/en/article/5415181>

Download Persian Version:

<https://daneshyari.com/article/5415181>

[Daneshyari.com](https://daneshyari.com)