Journal of Molecular Spectroscopy 275 (2012) 1–4

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Spectroscopy

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

Note

The rotational spectrum of perfluoropropionic acid

G.S. Grubbs II [a], Agapito Serrato III [b], Daniel A. Obenchain [a], S.A. Cooke [c], Stewart E. Novick [a], Wei Lin [b,*]

[a] Department of Chemistry, Wesleyan University, Middletown, CT 06459, United States
[b] Department of Chemistry and Environmental Science, University of Texas at Brownsville, Brownsville, TX 78520, United States
[c] School of Natural and Social Sciences, Purchase College, SUNY, 735 Anderson Hill Road, Purchase, NY 10577, United States

ARTICLE INFO

Article history:
Received 8 March 2012
In revised form 4 April 2012
Available online 21 April 2012

Keywords:
Microwave spectroscopy
Chirped pulse
Ab initio calculations
Structure
Perfluoropropionic acid

ABSTRACT

The pure rotational spectrum of perfluoropropionic acid, CF_3CF_2COOH, has been studied by a pulsed nozzle, chirped-pulse Fourier transform microwave spectrometer in the frequency range of 8–14 GHz. A total of 81 transitions, including *a*-type, *b*-type, and *c*-type transitions have been observed and analyzed. The rotational constants and the five quartic centrifugal distortion constants were determined for the first time. The rotational constants are $A = 1893.5299(4)$ MHz, $B = 1175.7031(4)$ MHz, and $C = 1118.2017(5)$ MHz. Quantum chemical calculations and the spectral analysis indicate that the observed conformer is the *gauche* form of perfluoropropionic acid with calculated dihedral angles $\angle CCCO = 106°$ and $107°$ from MP2/6-311G++(3df, 3pd) and MP2/Aug-CC-pVDZ calculations, respectively. The experimental spectroscopic constants are compared to those obtained from *ab initio* calculations.

1. Introduction

Perfluorinated compounds (PFC) have been increasingly applied in many commercial and industrial processes over the past years. Since these compounds are known to last for a very long period of time, concerns have been raised on their possible contaminations of the environment, particularly the groundwater. The short-chain PFCs including perfluoropropionic acid (PFPA) are more water-soluble and thus pose more serious contamination concerns. More detailed study on these PFCs and their interactions with water are needed in order to better understand this.

To the authors' best acknowledge, no microwave spectroscopic studies on gaseous PFPA have been reported before, but it has been the target of a series of vibrational spectroscopic studies. Crowder [1] studied the infrared and Raman spectra of PFPA and concluded that the $-CF_3CF_2$ is less electronegative than the $-CF_3$ group. Rontu and Vaida [2] reported their vibrational measurement of PFPA from $1000\ cm^{-1}$ to $11\,000\ cm^{-1}$. They also applied the B3LYP/6-311G [2d,2p] method to calculate the potential energy surface (PES) of PFPA along the O=C—O—H dihedral angle. They further reported [3] mid-IR, far-IR, and visible vibrational spectra of PFPA using Fourier transform and cavity ring down spectroscopy to explore the possibilities of using vibrational overtone-pumping to allow sunlight-initiated photochemical treatment of perfluorocarboxylic acids. Badawi et al. [4] carried out DFT-B3LYP/6-311+G** and *ab initio* MP2/6-311+G** calculations on the conformers of PFPA. They also calculated the potential energy curve and found that the *gauche* form is the most stable form. From their calculations, PFPA exits in both *gauche* and *cis* conformations at room temperature, with calculated populations of 76% and 24%, respectively.

Microwave spectroscopy is known to be an ideal technique to study molecular structures. Notably, the Howard group characterized a series of similar molecules as well as their hydrates using the FTMW technique. For example, FTMW spectroscopy of propanoic acid, CH_3CH_2COOH, and its mono- and di-hydrates have been reported [5]. The rotational constants have been improved over previous values [6]. Trifluoroacetic acid (CF_3COOH) has also been studied using microwave spectroscopy [7,8]. Grubbs et al. recently also reported the rotational study of perfluoropropionyl chloride [9] and perfluorobutyryl fluoride [10].

In order to obtain more detailed structural information on PFPA and its water complexes, a microwave study was initiated using a chirped-pulse Fourier transform microwave spectrometer. This paper will focus on PFPA monomer. The analysis of the hydrates of PFPA will be reported in a separate paper. No previous experimental structures of PFPA were available. To assist in obtaining the complete structure for PFPA, *ab initio* calculations have been carried out. The spectrum of the *gauche* form of PFPA was predicted from the calculated structural parameters. The results of this spectroscopic and theoretical study are reported herein. The spectra analysis of the PFPA monomer builds a good base for further investigations of the water complexes of PFPA.

* Corresponding author. Fax: +1 956 882 6692.
E-mail address: wei.lin@utb.edu (W. Lin).

0022-2852/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jms.2012.04.003

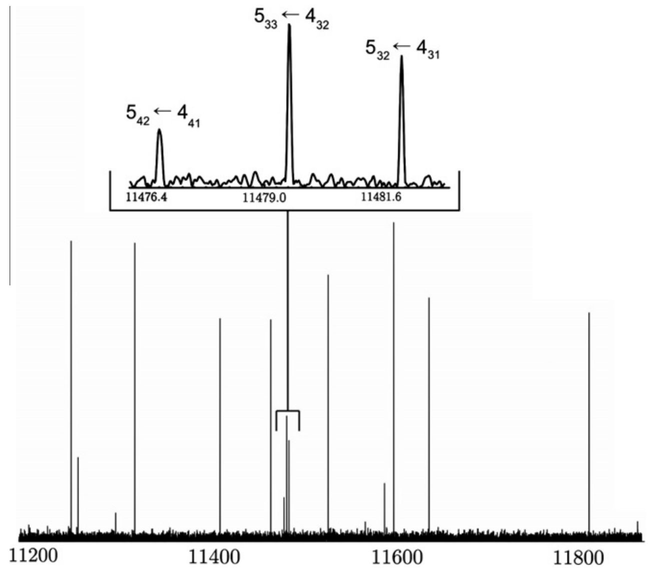

Fig. 1. A portion of spectrum for PFPA. The enlarged section of the spectrum shows several $J = 5 \leftarrow 4$ transitions.

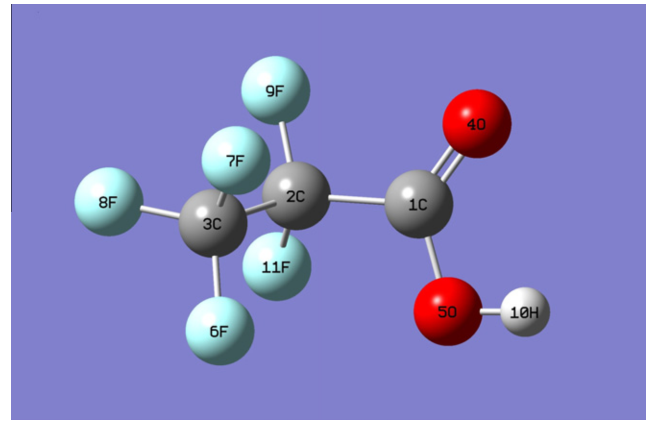

Fig. 2. The structure of the *gauche* form of PFPA.

2. Experiment and *ab initio* calculations

The PFPA sample was purchased from Aldrich Chemical Co., Milwaukee, WI with a stated purity of 97%, and the sample was used without further purification. The microwave spectra were obtained on the chirped-pulse Fourier-transform microwave spectrometer of the Southern New England Microwave Consortium located at Wesleyan University. The argon carrier gas was bubbled through the sample and pulsed through a solenoid valve (Parker–Hannefin Series 9) into a region between two horn antenna held in a vacuum at less than 10^{-4} Torr. A 4–6 μs pulse of a fast linear frequency sweep (chirp) of microwave radiation spanning a 2 GHz region was broadcast onto the supersonically expanding solution of PFPA. The spectra were recorded in three 2 GHz ranges, 8–10 GHz, 10–12 GHz, and 12–14 GHz. Macroscopic molecular polarization was achieved and, after removal of the chirped microwave pulse, the ensuing molecular free induction decay was detected, amplified, digitized and fast Fourier transformed on an

Table 1
The equilibrium structural parameters (Å and deg) and dipole moment (debye) for *gauche* PFPA.

Structural parameters	MP2/aug-pvdz[a]	MP2/6-311G++(3df, 3pd)[a]	MP2/6-311+G**[b]	B3LYP/6-311+G**[b]
Bond length (Å)				
$rC_3—C_2$	1.545	1.543	1.542	1.558
$rC_1—C_2$	1.545	1.541	1.543	1.5551
$rO_4—C_1$	1.212	1.199	1.203	1.194
$rO_5—C_1$	1.349	1.335	1.339	1.337
$rF_6—C_3$	1.343	1.325	1.330	1.335
$rF_7—C_3$	1.351	1.331	1.336	1.343
$rF_8—C_3$	1.345	1.326	1.333	1.336
$rF_9—C_2$	1.356	1.335	1.344	1.345
$rF_{11}—C_2$	1.366	1.345	1.350	1.358
$rO_5—H_{10}$	0.975	0.968	0.970	0.970
Bond angle (deg)				
$\angle C_1C_2C_3$	113.2	112.7	112.7	114.0
$\angle O_4C_1C_2$	123.3	123.2	122.8	123.1
$\angle O_5C_1C_2$	110.0	110.2	110.3	110.4
$\angle F_6C_3C_2$	110.2	109.8	110.2	110.2
$\angle F_7C_3C_2$	109.3	109.2	109.4	109.5
$\angle F_8C_3C_2$	110.8	110.8	110.4	111.1
$\angle F_9C_2C_3$	107.6	107.7	107.7	107.7
$\angle F_{11}C_2C_3$	107.9	108.2	108.0	108.2
$\angle H_{10}O_5C_1$	106.7	106.9	106.8	108.4
Dihedral angle (deg)				
$\tau F_6C_3C_2C_1$	7.4	7.8	4.6	9.2
$\tau F_7C_3C_2F_6$	119.7	119.6	119.9	119.5
$\tau F_8C_3C_2F_6$	−120.5	−120.4	−120.4	−120.5
$\tau F_9C_2C_3C_1$	120.4	120.1	120.2	120.5
$\tau F_{11}C_2C_3C_1$	−122.3	−122.1	−122.5	−122.3
$\tau O_4C_1C_2C_3$	105.9	107.0	99.6	112.4
$\tau H_{10}O_5C_1O_4$	−0.4	−0.3	−1.2	0.2
Dipole moment (debye)				
	2.40	2.35	2.46	2.44

[a] This work.
[b] Ref. [4].