

# Microwave spectrum of perfluoropentanoic acid



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## ABSTRACT

The pure rotational spectrum of perfluoropentanoic acid,  $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{COOH}$ , has been measured using a pulsed beam Fourier transform Flygare–Balle type microwave spectrometer in the frequency range of 4–7 GHz. A total of 34 transitions, including *a*-type and *b*-type transitions were observed and analyzed. The three rotational constants and two quartic centrifugal distortion constants were determined for the first time. The rotational constants are  $A = 1063.0518(5)$  MHz,  $B = 374.8849(1)$  MHz, and  $C = 359.2965(1)$  MHz. Theoretical predictions from *ab initio* calculations using MP2/6-311G++(2d, p) and MP2/cc-pVTZ were performed and the results are in reasonably good agreement with experimental values.

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## 1. Introduction

Perfluorinated carboxylic acids (PFCA) are a series of synthesized compounds that have been increasingly applied in industrial processes. They are widely used as surfactants and surface protectors. For example, perfluorooctanoic acid (PFOA) has long been used to manufacture prominent industrial and household products which include a teflon coating. These PFCAs are believed to be toxic and associated with several adverse health effects on animals [1]. Because these compounds are highly stable and easily associate with water, there are concerns over their contamination in both the air and groundwater. In 2006, the U.S. Environmental Protection Agency initiated the PFOA Stewardship Program to work toward elimination of PFOA and related chemicals before 2015. It was proposed that the toxicity of PFCA is dependent upon the carbon chain length, the longer chain acids are more toxic than the shorter chain ones [2]. More information on the structures of these compounds from microwave work and other sources may be helpful to better understand the toxicity and other interactions within the body and with other molecules. Perfluoropentanoic acid (PFPeA), or nonafluoropentanoic acid/nonafluorovaleric acid, is considered to be one of the short chain PFCAs. A recent freshwater hazard assessment study reported PFPeA as ‘low to medium concern’ based on its possible acute aquatic hazard [3].

Since these compounds are volatile, microwave spectroscopy is an excellent technique to provide gas phase structural information.

Leopold [4] recently reviewed the hydrated acid clusters and many excellent studies that use microwave spectroscopy methods to characterize the acid–water intermolecular interactions. Ouyang et al. [5,6] reported studies of a series of carboxylic acids as well as their hydrates using the Fourier transform microwave spectroscopy (FTMW) technique. For example, the mono- and di-hydrates of acetic acid were studied [5]. FTMW spectroscopy of propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , and its mono- and di-hydrates mono- and di-hydrates have also been reported [6]. The rotational constants of propanoic acid have been improved over previous values [7]. For the perfluorinated carboxylic acid, several short chain PFCAs have been studied. Trifluoroacetic acid ( $\text{CF}_3\text{COOH}$ ) has been studied using microwave spectroscopy [8,9]. Grubbs et al. recently reported the rotational study of perfluoropropionic acid [10] and its monohydrate [11]. Thomas et al. studied the microwave spectra of perfluorobutyric acid and its monohydrate [12]. When these acids form the monohydrates with water, they tend to form two hydrogen bonds: the oxygen atom from water molecule interacts with the hydrogen atom from the hydroxyl group of the acid and one hydrogen atom from the water molecule interacts with the oxygen atom on the carbonyl group of the acid. It will be very interesting and beneficial to obtain geometrical information of these PFCAs and their hydrates to determine if the length of the carbon chain plays a role in the observed interactions.

In this work, we extend the spectroscopic study of the PFCAs to PFPeA, the next short chain PFCA in the series. To the authors’ best knowledge, no spectroscopic studies on gaseous PFPeA have been previously reported. In order to obtain more detailed structural information on PFPeA and to aid the study of the hydrate of PFPeA, a microwave study was carried out using the pulsed

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beam Fourier transform Flygare–Balle type [13] microwave spectrometer at the University of Arizona. This instrument has been successfully applied on several hydrogen bonded systems including formamide–formic acid dimer [14], and formic acid–propionic acid dimer recently [15–17]. To assist in obtaining the complete structure for PFPeA, *ab initio* calculations were performed using MP2/6-311G++(2d, p) and MP2/cc-pVTZ. The microwave spectrum of PFPeA was predicted from the calculated moments of inertia to aid the search for the rotational transitions. The results of this spectroscopic and theoretical study are reported herein.

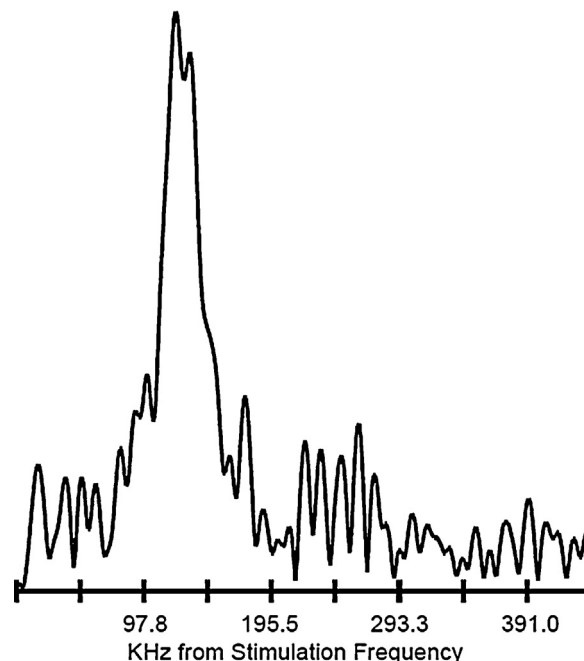
## 2. Experiment and *ab initio* calculations

The PFPeA sample was purchased from Aldrich Chemical Co., Milwaukee, WI with a stated purity of 97%. The sample was used without further purification. The microwave data were obtained using the pulsed beam Fourier-transform microwave spectrometer in the Kukulich lab at the University of Arizona. Neon carrier gas was passed through the sample and pulsed through the pulsed valve (General Valve series 9) with the backing pressure of neon maintained at about 600 Torr. The pressure inside the spectrometer chamber was kept at  $10^{-6}$  to  $10^{-7}$  Torr prior to the valve opening. The homodyne detector used measured the difference of the stimulating frequency generated by the frequency generator and the true molecular resonance frequency, which produced a free induction decay (FID) signal with a frequency corresponding to the difference between the stimulating and molecular resonance frequencies. A more detailed explanation of signal acquisition can be found in an earlier paper [18]. The spectrometer has been described more fully elsewhere [19]. An example *b*-type  $7_{07}-6_{16}$  transition is shown in Figure 1.

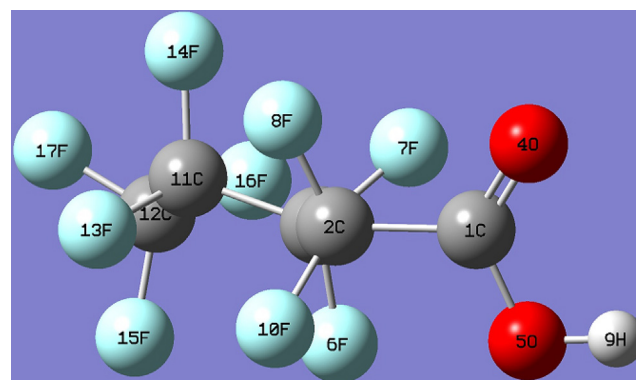
The *ab initio* calculations were performed with the GAUSSIAN-09 suite [20] using MP2/6-311G++(2d, p) and MP2/cc-pVTZ. Calculations were carried out at the University of Texas at Brownsville with full electron correlation by the perturbation method [21] to second order and 6-311G++(2d, p) basis sets were utilized for predicting the structural parameters. The objective of these calculations was to determine a predicted structure of the target molecule to aid in searching for rotational transitions and spectral assignment of each observed transition. The calculated structure using MP2/6-311G++(2d, p) is shown in Figure 2. Further calculations using MP2/cc-pVTZ were performed on the University of Arizona htc and smp multiprocessor high performance computing clusters.

## 3. Results and discussion

Because of the relatively larger size and smaller rotational constants of PFPeA, only high rotational energy levels are expected to be observed in the Flygare–Balle type FTMW spectrometer. A few MHz of uncertainty in the predicted rotational constants will represent a much wider range of frequency scanning due to the error in



**Figure 1.** The *b*-type  $J=7 \leftarrow 6$  transition ( $7_{07}-6_{16}$ ) of PFPeA after 1811 pulsed beam cycles. The stimulating frequency for this measurement is 4578.06 MHz.



**Figure 2.** The calculated structure of PFPeA from the MP2/6-311G++(2d, p) calculation.

the predicted microwave spectrum. To aid the spectroscopic search, MP2/6-311G++(2d, p) calculations for PFPeA as well as several other short chain PFCAs were performed. The calculated results and comparisons to the experimental values are listed in Table 1. As shown in Table 1, the calculated values agree with experimental values reasonably well for the studied molecules. The calculated rotational constants of PFPeA were then scaled based on the comparisons of

**Table 1**

The comparison of calculated and experimental rotational constants in MHz for a series of short chain PFCAs. Some of these were used to aid the spectral search. 'Change' is the ratio of experimental to calculated parameters.

Rotational constants Molecules	A			B			C		
	Cal. <sup>a</sup>	Exp.	Change	Cal. <sup>a</sup>	Exp.	Change	Cal. <sup>a</sup>	Exp.	Change
CF <sub>3</sub> COOH	3837.27	3865.13 <sup>b</sup>	100.73%	2506.16	2498.79 <sup>b</sup>	99.71%	2073.15	2075.20 <sup>b</sup>	100.10%
CF <sub>3</sub> CF <sub>2</sub> COOH	1884.50	1893.53 <sup>c</sup>	100.48%	1178.76	1175.70 <sup>c</sup>	99.74%	1130.68	1118.20 <sup>c</sup>	98.90%
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> COOH	1394.39	1398.68 <sup>d</sup>	100.31%	628.84	624.64 <sup>d</sup>	99.33%	604.14	598.42 <sup>d</sup>	99.05%
CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COOH	1059.94	1063.05 <sup>e</sup>	100.29%	378.79	374.88 <sup>e</sup>	98.97%	363.57	359.29 <sup>e</sup>	98.82%

<sup>a</sup> Calculated constants from MP2/6-311++G(2d, p) calculations.

<sup>b</sup> Reference [9].

<sup>c</sup> Reference [10].

<sup>d</sup> Reference [12].

<sup>e</sup> This work.

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