Rotational spectroscopy of 2H,3H-perfluoropentane

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Abstract

The structure of 2H,3H-perfluoropentane, $\text{CF}_3\text{CHFCHFCF}_2\text{CF}_3$, has been determined by a combination of Chirp-pulsed Fourier transform microwave (CP-FTMW) spectroscopy and cavity FTMW spectroscopy. Of the four possible stereoisomers, only the enantiomeric pair (R,R)/(S,S) were observed experimentally; there was no spectroscopic evidence for the enantiomeric pair (R,S)/(S,R). The conformational structure of the (R,R)/(S,S) stereoisomer(s) was that of partial helices with C–C–C–C dihedral angles of 12° (helical) and 1° (staggered).

Introduction

Previous structural studies of alkanes and perfluoroalkanes have concluded that alkanes have staggered structures where the hydrogen atoms along the chain have C–C–C–C dihedral angles of 180° , while perfluoroalkanes with four or more carbons along the carbon chain display a helical C_2 geometry with the C–C–C–C dihedral angles of approximately 15 – 17° .¹ The staggered structure of C_5H_{12} and the helical structure of C_5F_{12} are shown in Figure 1. These results have led to an interest in identifying the structure of fluorinated alkane chains with various substituents. In this study, the rotational spectrum of all carbon-12 2H,3H-perfluoropentane (H_2PFP), and all five singly-substituted ^{13}C isotopologues were observed and assigned.

A racemic sample of 2H,3H-perfluoropentane contains a mixture of four stereoisomers labeled as either “R” or “S” about each of the chiral centers, carbons “2” and “3”.² Since both carbon-2 and carbon-3 are chiral centers in H_2PFP , there are four possible stereoisomers, (S,S), (R,R), (R,S), and (S,R). The (S,S) and (R,R) structures are enantiomers of each other, as are the (R,S) and (S,R) isomers. This means that they have the same conformeric form and energies, but are mirror images of each other. Since (S,S) and (R,R) are mirror images, they will have identical moments of inertia tensors and thus identical microwave spectra. The same holds true for the (R,S)/(S,R) pair. Only in an achiral environment will enantiomers be distinguishable. Recently, it has been shown that this can be achieved by microwave spectroscopy,^{3,4} but not in the current experiments.

Experimental

A racemic mixture of 2H,3H-perfluoropentane (H_2PFP) was purchased from SynQuest Laboratories. Approximately 2 ml of the racemic mixture was injected into a polyethylene tube and isolated from air to prevent contamination of the spectra due to atmospheric gases. Argon carrier gas was then bubbled through the sample at a pressure of approximately 50 psi. In this study, the rotational spectrum of all carbon-12 H_2PFP , was observed and assigned using a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer.⁵ An average of 10,000

gas pulses for every 2 GHz section from 7-15 GHz was collected on the Chirp. All five ^{13}C isotopologues were observed and characterized on a Balle-Flygare type cavity spectrometer.⁶ Given a racemic sample of 2H,3H-perfluoropentane with four available structural isomers, only the (S,S)/(R,R) structure was observed in the broadband spectrum, and it is the ^{13}C isotopologues of these enantiomers that were observed in the cavity spectrometer.

Calculations

An *ab initio* scan of the C₁-C₂-C₃-C₄ dihedral angle of 2H,3H-perfluoropentane was performed using a low-level MP2/3-21g method and basis set from Gaussian 09⁷ to identify potential minima as the starting point for full optimizations. Two minimum energy conformations were found in the scan for the (R,R)/(S,S) enantiomers but only one minimum energy conformation was found in the scan for the (R,S)/(S,R) enantiomers. These structures from the low-level calculations were then fully optimized using an MP2/6-311++g(2d,2p) method and basis. These structures are shown in Figure 2 and the relative energies, rotational constants, and dipole moments from the calculation are given in Table 1.

Results and Discussion

The observed transitions and their assignments for the six isotopologues are given in Supplementary Tables S1 - S6. Only *c*-type transitions were observed and assigned. Some very weak unassigned transitions are perhaps *b*-type transitions. Table 2 gives the spectroscopic constants of the normal isotopologue of 2H,3H-perfluoropentane and of its five singly-substituted ^{13}C isotopologues. From comparisons of the predicted and observed rotational constants, it is clear that we are only observing the lowest energy trans conformation of the (R,R)/(S,S) enantiomer. The cis conformer was not observed on the CP-FTMW spectrometer, probably because its energy is $\sim 160\text{ cm}^{-1}$ above that of the trans conformer (see Table 1). Without a high energy barrier between the two conformers, the supersonic expansion cools the molecules only into the low energy conformation. The fact that we only observe strong *c*-type spectra is consistent with our assignment of the observed conformer to the trans (R,R)/(S,S)

structure, but is not definitive. Since our chemical sample of H₂PFP is purported to be a racemic mixture, we should also have observed the lowest energy conformation of the (R,S)/(S,R) enantiomeric pair, but we did not. We can conclude that the (R,S)/(S,R) isomers, given the small values of the dipole moments for the low energy trans conformation, as given in Table 1, were not present in sufficient quantity in our sample for us to observe in the Chirp experiment. While the higher energy cis conformation of the (R,S)/(S,R) enantiomers, at 794 cm⁻¹ relative to 180 cm⁻¹, has a large *c* dipole, it is not populated in our jet.

From the rotational constants from the six isotopologues of H₂PFP as given in Table 2, we are able to calculate the *r_s*, or Kraitchman coordinates of the five carbon atoms in the chain. Since the Kraitchman calculation only yields the absolute value of the coordinates, we give the signs of the coordinates from the MP2/6-311++g(2d,2p) calculation. In those two cases where the coordinates are so close to a principal axis that the Kraitchman calculation gives an imaginary value, the coordinate from the *ab initio* calculation is given. These *r_s* and *ab initio* coordinates of H₂PFP, in the principal axis system of the all carbon-12 isotopologue, are given in Table 3. The structure of the all-trans (R,R) enantiomer, found in the experiment, is presented in Figure 2. Since we have not measured the fluorine or the hydrogen positions, the structure presented in Figure 2 is the *ab initio* calculated structure, adjusted to the experimentally measured C–C–C–C dihedral angles of 11.74° and 1.04° from 180° for dihedral angles C₁–C₂–C₃–C₄ and C₂–C₃–C₄–C₅, respectively. The first of these angles is consistent with a helical geometry and the second angle is consistent with a staggered structure.

So, this answers the question we set out to ask: is the structure of 2H,3H-perfluoropentane helical like that of a fluorocarbon, or staggered like that of a hydrocarbon. Answer: both.

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Table 1. 2H,3H-perfluoropentane, *ab initio*^a relative energies, rotational constants, and dipole moments

(R,R)/(S,S)	Energy/ cm ⁻¹ ^b	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	μ _a /D	μ _b /D	μ _c /D
trans conformer	0	1204.73	339.94	332.81	0.10	0.56	1.84
cis conformer	163	1108.10	381.24	365.07	0.26	0.90	1.56
(R,S)/(S,R)							
trans conformer	180	1221.02	350.95	322.89	0.13	0.27	0.14
cis conformer	794	1140.22	396.41	369.87	0.64	0.27	2.19

a. At the MP2/6-311++g(2d,2p) level of theory and basis

b. Energy relative to the lowest energy conformation

Table 2. Spectroscopic constants ^a of 2H,3H-perfluoropentane and its isotopologues

Parameter	Parent	¹³ C(1)	¹³ C(2)	¹³ C(3)	¹³ C(4)	¹³ C(5)
<i>A</i> / MHz	1208.3387(2)	1208.06482(4)	1207.30327(6)	1208.10028(8)	1207.55696(7)	1208.01824(6)
<i>B</i> / MHz	336.90086(5)	335.35038(5)	336.50271(8)	336.91668(10)	336.59260(7)	335.54300(8)
<i>C</i> / MHz	329.24675(6)	327.76299(6)	328.80708(11)	329.24601(10)	328.91641(13)	327.92397(10)
Δ_J / kHz	0.00550(6)	0.0049(2)	0.0052(3)	0.0049(2)	0.0048(4)	0.0049(3)
Δ_K / kHz	0.063(4)	[0.063]	[0.063]	[0.063]	[0.063]	[0.063]
Δ_{JK} / kHz	0.0167(3)	[0.0167]	[0.0167]	[0.0167]	[0.0167]	[0.0167]
δ_J / kHz	-0.00011(2)	[-0.00011]	[-0.00011]	[-0.00011]	[-0.00011]	[-0.00011]
δ_K / kHz	0.148(7)	[0.148]	[0.148]	[0.148]	[0.148]	[0.148]
 N	 182	 11	 12	 20	 12	 12
RMS / kHz	6.0	0.3	0.6	1.0	0.6	0.6

a. values in square brackets are not fitted, but are held fixed. This is the case for four of the five quartic centrifugal distortion constant for the C-13 isotopologues, whose values are held to those of the normal isotopologue.

Table 3. Positions of the carbon backbone atoms from Kraitchman analysis^a from ¹³C substitution and *ab initio* calculations^b, in Å, in the principal axis system of the all-¹²C isotopologue.

Atom	from Kraitchman			from ab initio		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
C ₁	-2.6265(6)	-0.233(6)	-0.203(7)	-2.630	-0.256	-0.202
C ₂	-1.317(1)	0.564(3)	-0.202(7)	-1.346	0.566	-0.198
C ₃	[-0.113]	-0.280(5)	0.06(2)	-0.113	-0.289	0.070
C ₄	1.150(1)	0.468(3)	-0.228(7)	1.178	0.455	-0.265
C ₅	2.4655(6)	-0.342(4)	[-0.007]	2.471	-0.344	-0.007

a. The signs of the Kraitchman coordinates are those of the *ab initio* calculated values. In those cases where the Kraitchman coordinates are calculated to be imaginary, the values given in square brackets are from the *ab initio* calculation.

b. MP2/6-311++g(2d,2p) using Gaussian 09.

Figure 1. The staggered structure of C_5H_{12} and the helical structure of C_5F_{12} as given by a hf/6-311++g(d,p) and b3lyp/3-21g *ab initio* calculations, respectively.

Figure 2. The structure of 2H,3H-perfluoropentane.

Figure caption. On the left is the view along the chain with C(5) in the foreground; in the middle is the view along the chain with C(1) in the foreground; on the right is the view displaying the chain of this trans-trans conformation of the (R,R) isomer. The structures presented are the *ab initio* calculated structures, but with the C–C–C–C dihedral angles adjusted to the experimentally determined values.

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