Microwave Measurements of Cyclopropanecarboxylic Acid and -OD Isotopologue

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Abstract

The microwave spectrum of cyclopropanecarboxylic acid has been measured in the 5-15 GHz region using a Flygare-Balle type, pulsed-beam Fourier-transform microwave spectrometer. These lower-frequency measurements are at a much higher resolution than the previous waveguide studies. The experimental rotational constants obtained in this study were $A=7625.0432(17)$ MHz, $B=2724.7672(8)$ MHz, and $C=2382.0755(5)$ MHz. The centrifugal distortion constants determined were $\Delta_J=0.4010(25)$ kHz, $\Delta_{JK}=3.04(17)$ kHz, $\delta_J=0.0434(72)$ kHz, and $\delta_K=-11.32(24)$ kHz.

1. Introduction

Derivatives of cyclopropanes are versatile compounds in many organic syntheses and are found in many natural compounds¹. Specifically, cyclopropanecarboxylic acid (CPCA) is an important biologically active compound due to the hypoglycemic metabolic effects shown in experiments by Duncombe and Rising in several animal species, including humans². CPCA can be synthesized using chiral copper carbenoids³ and due to the versatility of the cyclopropane ring, geminal dihalides of CPCA can be easily derivatized using a Ni induced reductive carbonylation⁴. Other syntheses of CPCA utilize other transition metal catalyzed reactions, cycloaddition of alkenes, sulfoxides and other metal carbenoids¹.

The crystal structure of CPCA was determined by Boer and Stam⁵. IR and Raman spectroscopic techniques were then utilized by Maillols, Tabacik, and Sportouch⁶ to determine gaseous structural parameters of CPCA, as there are packing effects in crystal structures that distort the structure. To extend the study on gaseous CPCA and obtain more accurate structural parameters, Marstokk, Møllendal, and Samdal⁷ performed an electron diffraction experiment, waveguide microwave measurements (in the 26.5-38 GHz regime), and *ab initio* calculations to further understand the stable rotamers of CPCA.

In this study, high resolution pulsed-beam Fourier-transform (PBFT) microwave spectroscopy was used to measure lower frequency transitions (in the 5-15 GHz regime) of the parent and –OD isotopologues. The basic structure of this compound, as obtained from our calculations, is shown in Figure 1. The lowest energy structure is the

cis, or Z conformer with an angle of 120° between the C1-C9 bond and the plane of cyclopropane. The C2 and C3 carbon atoms are staggered relative to O2.

Figure 1. Calculated structure for the cyclopropane carboxylic acid cis conformation, showing the a and b principal axes.

2. Microwave Measurements

Microwave transitions were measured for the parent isotopologue and the –OD isotopologue in the 5-15 GHz range using a PBFT Flygare-Balle type microwave

spectrometer^{8,9}. 16 new transitions have been measured for the parent and 9 for the –OD isotopologue.

The CPCA sample was purchased from Sigma Aldrich (95%) and was used as received. The deuterated CPCA sample was prepared by mixing equimolar quantities of CPCA (Sigma Aldrich, 95%) and MeOD (Cambridge Isotope Lab, Inc., 99%) and letting them exchange overnight. The MeOH was removed from the mixture under vacuum, leaving the less volatile CPCA-OD behind. Each sample was then loaded into a glass sample cell. The sample and pulsed-valve (General Valve series 9) were heated to 45 °C to obtain vapor pressure sufficient to provide a single shot signal of a parent isotopologue test line. The pressure within the microwave cavity was maintained at 10^{-6} to 10^{-7} Torr prior to the pulsed injection of the sample and Ne carrier gas. The Ne backing pressure was maintained at ~1 atm during microwave measurements. The new measured rotational transitions for the parent and –OD isotopologue are given in Tables 1 and 2 respectively.

3. Calculations

The calculated rotational constants for the parent isotopologue, using Gaussian MP2, B97D functional with augmented quadruple zeta basis are: $A = 7661.0$, $B = 2758.7$, $C = 2405.2$ (MHZ), about 5% higher than the measured values. These deviations are much higher than those obtained for similar size molecules at this level of calculations. Calculated cartesian coordinates of atoms in the principal axis system are given in Table 3.

4. Rotational Constants

Since previous microwave work was already performed by Marstokk *et. al.*⁷, the rotational constants obtained in the previous study were used to predict the lower frequency microwave transitions to be measured. Measurements of the new experimental transitions were in agreement with the predictions. The OD transitions were predicted by changing the mass of the H atom in the initial structure to that of deuterium, from which preliminary rotational constants of the OD structure were obtained. The differences between the previously determined rotational constants and the new experimentally determined rotational constants of the parent isotopologue were applied to the preliminary OD rotational constants, providing a more accurate set of rotational constants for the OD isotopologue and these were used to predict the rotational transitions.

Experimental rotational and centrifugal distortion constants for the parent and –OD isotopologues which were determined using a least squares fitting program, FITSPEC,¹⁰ are given in Table 4. The rotational constants obtained for the –OD isotopologue lines were obtained with similar least squares fits, fixing distortion constant values to those obtained for the parent. The differences between the observed (o) and calculated (c) frequencies for the transitions are also given in Table 3. The rotational and distortion constants from Marstokk *et al.*⁷ are also provided for comparison of results.

5. Discussion

The rotational spectrum for CPCA has been extended to the 5-15 GHz regime, with new higher resolution measurements using a PBFT microwave spectrometer. The experimental rotational transitions are shown in Tables 1 and 2 and the rotational constants obtained from this study and from the work of Marstokk *et. al.*⁷ are given in Table 3. The new rotational and distortion constants obtained are in very good agreement with values obtained previously. Singly substituted ¹³C transitions were searched for, but could not be conclusively assigned due to signals being very weak, as well as much overlap with transitions from other vibrational states. We believe that the gas phase structure obtained by Marstokk is reasonably accurate, but could be even more accurately determined with the further measurements of the singly substituted ¹³C transitions. No splittings attributable to possible internal rotation were observed in these measurements.

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Table 1. Parent isotopologue measured transitions (ν_{obs}). Frequencies are given in MHz. ν_{0-c} are the deviations from the least squares fit to the line frequencies.

$J'_{Ka' Kc'}$	$J''_{Ka'' Kc''}$	ν_{obs}	ν_{0-c}
6 ₂₅	5 ₃₂	5039.365	0.000
1 ₀₁	0 ₀₀	5106.835	-0.006
1 ₁₀	1 ₀₁	5242.984	0.001

2 ₀₂	1 ₁₁	5296.063	-0.001
2 ₁₁	2 ₀₂	5603.069	0.001
3 ₁₂	3 ₀₃	6175.152	-0.001
6 ₂₄	5 ₃₃	6210.009	0.000
4 ₁₃	3 ₂₂	6878.550	-0.001
4 ₁₃	4 ₀₄	6995.124	-0.001
5 ₁₄	5 ₀₅	8104.475	0.000
2 ₁₂	1 ₁₁	9870.926	0.002
1 ₁₁	0 ₀₀	10007.086	-0.002
2 ₀₂	1 ₀₁	10196.314	0.003
2 ₁₁	1 ₁₀	10556.397	0.002
3 ₀₃	2 ₁₂	10676.475	0.001
3 ₁₃	2 ₁₂	14795.766	-0.002

Table 2. –OD isotopologue transitions. Frequencies are given in MHz.

J' K _{a'} K _{c'}	J'' K _{a''} K _{c''}	ν_{obs}	$\nu_{\text{0-c}}$
1 ₀₁	0 ₀₀	4938.008	0.009
1 ₁₀	1 ₀₁	5311.345	0.001
2 ₁₁	2 ₀₂	5647.302	-0.009
3 ₁₂	3 ₀₃	6178.926	0.005
4 ₁₃	4 ₀₄	6937.507	0.003
5 ₁₄	5 ₀₅	7960.020	0.001
2 ₁₂	1 ₁₁	9555.002	0.012
2 ₀₂	1 ₀₁	9860.989	-0.002
2 ₁₁	1 ₁₀	10196.945	-0.014

Table 3. Calculated Cartesian coordinates (Å) of atoms in the principal axis system.

Atom	a	b	c
C1	0.533559	-0.649653	-0.000043
H2	0.482682	-1.725334	-0.000093
C2	1.669178	0.019034	-0.742815
H3	1.418795	0.944425	-1.236181
H4	2.353250	-0.634593	-1.258665
C3	1.669161	0.018942	0.742843
H5	2.353223	-0.634762	1.258607
H6	1.418786	0.944274	1.236334
C4	0.750291	0.068824	-0.000012
O1	1.802783	-0.781371	-0.000006
O2	0.881611	1.272240	0.000024
H1	2.591883	-0.220804	0.000029

Table 4. Rotational constants (MHz) and centrifugal distortion constants (kHz) of parent and –OD isotopologues. Centrifugal distortion constants from parent were held fixed during least squares fit of the –OD transitions. Calculated values obtained using B97D aug-cc-QZ basis are provided of the parent.

	Parent		OD	Parent ^a	-OD ^a	Calculated
<i>A</i>	7625.0432(17)	7619.8580(67)		7625.000	7619.8344	7661.86
<i>B</i>	2724.7672(8)	2629.4700(14)		2724.7530	2629.4620	2758.68
<i>C</i>	2382.0755(5)	2308.5301(14)		2382.0630	2308.5222	2405.16
Δ_J	0.410(25)			0.3794		
Δ_{JK}	3.04(17)			3.178		
δ_J	0.0434(72)			0.04581		
δ_K	-11.32(24)			-11.317		

^aValues are taken from Marstokk *et. al.*⁷

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