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Microwave spectra and structure of the cyclopropanecarboxylic acid-formic acid dimer

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The rotational spectrum of the cyclopropanecarboxylic acid–formic acid doubly hydrogen bonded dimer has been measured in the 4–11 GHz region using a Flygare-Balle type pulsed-beam Fourier transform microwave spectrometer. Rotational transitions were measured for the parent, four unique singly substituted ¹³C isotopologues, and a singly deuterated isotopologue. Splittings due to a possible concerted double proton tunneling motion were not observed. Rotational constants (*A*, *B*, and *C*) and centrifugal distortion constants (*D_J* and *D_{JK}*) were determined from the measured transitions for the dimer. The values of the rotational (in MHz) and centrifugal distortion constants (in kHz) for the parent isotopologue are *A* = 4045.4193(16), *B* = 740.583 80(14), *C* = 658.567 60(23), *D_J* = 0.0499(16), and *D_{JK}* = 0.108(14). A partial gas phase structure of the dimer was derived from the rotational constants of the measured isotopologues, previous structural work on each monomer units and results of the calculations. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4931923>]

I. INTRODUCTION

There has been recent growing interest in doubly and triply hydrogen bonded complexes. These complexes are simple prototypes of the doubly and triply hydrogen bonded DNA base pairs, adenine–thymine and guanine–cytosine. The dynamics of hydrogen bonding is also involved in the intricate formation of protein secondary structures as well as in the most basic proton transfer within solutions. Some of the doubly hydrogen bonded dimers studied previously¹ do not have static structures in the gas phase. Spectral splittings may be observed caused by the concerted proton tunneling motion between the two molecules. The dynamics of this proton tunneling process are best characterized through the analysis of the rotational spectrum. These tunneling motions may be associated with point mutations, causing genetic mutations and disease.^{2,3} Studying these carboxylic acid doubly hydrogen bonded dimers may allow for more insight and better quantitative predictions for these tunneling phenomena.

The simplest of these doubly hydrogen bonded systems is the formic acid (FA) homodimer.⁴ The two equivalent forms of this dimer were found to interconvert through the concerted tunneling motion of the two acidic protons. The potential energy surface for this system has a classic double-minimum potential, similar to that for ammonia and the systems of single proton tunneling in malonaldehyde^{5–8} and tropolone.^{9,10} Microwave spectroscopy is the most suitable technique to study the molecular structure and dynamics of many systems but is restricted to molecules and complexes with permanent electric dipoles. Several heterodimers of carboxylic acids that maintain *C*_{2vM} symmetry have shown to exhibit the concerted double proton tunneling dynamics in the gas phase, such as the propionic acid–formic acid dimer,^{1,11,12} benzoic acid–formic acid dimer,¹³ acetic acid–formic acid dimer,¹⁴ and the nitric acid–formic acid dimer.¹⁵

One of the interesting features of this work is to determine if tunneling splittings can be observed in doubly H-bonded heterodimers without the *C*_{2vM} symmetry that is present for the propionic acid–formic acid dimer. So far these tunneling splittings have only been seen in dimers with the *C*_{2vM} symmetry. We recently studied the monoenoic tautomer of 1,2-cyclohexanedione–formic acid, a heterodimer without the *C*_{2vM} symmetry, and no proton tunneling was observed.¹⁶

The cyclopropanecarboxylic acid (CPCA) monomer has been studied by microwave spectroscopy previously and gas phase structural information was determined.^{17,18,20} The microwave spectrum of trifluoroacetic acid–cyclopropanecarboxylic acid dimer was also measured and no tunneling splittings were observed.¹⁹ One criterion for observing the tunneling splittings would be if the energies of the two minima in the double well potential are very close. The present work will be another benchmark system to further understand the dynamics of proton tunneling.

In this paper, we report the experimentally derived gas phase structure of the cyclopropanecarboxylic acid–formic acid dimer from the rotational spectrum using structural results for the monomers and some parameters from the calculations. *Ab initio* calculations predicted two low energy conformers of the dimer, separated by only 219 cm^{−1}, making it likely that these two conformers could be observed. We recently continued to measure isotopologue transitions of the CPCA monomer and were able to assign unknown transitions that corresponded to this high energy conformer of the CPCA monomer.²⁰ It may be possible to observe the dimer conformer corresponding to this high energy state; however, these transitions may be considerably weaker and more difficult to observe because of the low abundance of this higher energy structure under the present experimental conditions. These transitions have not yet been observed.

II. MICROWAVE MEASUREMENTS

The rotational spectrum was measured in the 4–11 GHz region for the doubly hydrogen bonded dimer CPCA-FA. Microwave measurements were made using a Flygare-Balle type pulsed-beam Fourier transform (PBFT) microwave spectrometer described previously.^{21,22} The CPCA (95%) and FA (98%) samples were purchased from Sigma Aldrich and the FA-d₁ (99.2% d) was purchased from CDN isotopes; each sample was used without further purification. The samples were transferred to separate glass sample cells. The glass sample cell containing the CPCA was connected directly to the pulsed-valve (General Valve series 9) and was heated to ~70 °C. The cell containing the FA was placed in the Ne gas line leading to the CPCA sample and the pulsed-valve, seeding the FA vapor into the vacuum chamber. The FA sample (and also FA-d₁) was first cooled to about –8 °C before connecting to the gas line and the temperature was maintained using a Peltier cooling device. The pressure inside the microwave cavity was maintained at 10^{–6} to 10^{–7} Torr prior to the molecular beam pulse into the cavity. The Ne carrier gas backing pressure was maintained at ~1 atm.

The valve was set to pulse at ~2 Hz. All measured transitions of the CPCA-FA dimer are given in Table I and examples of observed transitions from the ¹³C isotopologues are shown in Figure 1.

Rotational transitions from five ¹³C isotopologues of the CPCA-FA dimer were measured under natural abundance, and these include the parent and four single ¹³C substitutions at all unique carbon atom positions within the dimer. The ¹³C substitutions at carbon atoms 3 and 6 were calculated to be equivalent, which would result in an increased intensity in the observed transitions. These two positions are indeed equivalent and a comparison of the signal to noise ratios of some isotopologue transitions are shown in Figure 1. The labeling scheme used for the atoms in the dimer is shown in Figure 2. There were 51 total rotational transitions measured for the lower energy conformer shown in Figure 2 (top); 28 a-type transitions and 3 b-type transitions were measured for the parent isotopologue and 7 a-type transitions were measured for each of the four uniquely substituted ¹³C and deuterated isotopologues. The small splittings observed in the transitions shown in Figure 3 were determined to be a result of the Doppler splitting and

TABLE I. Spectral assignment and frequencies for parent and ¹³C isotopologues of the cyclopropanecarboxylic acid-formic acid dimer.

J'	K _a '	K _c '	J''	K _a ''	K _c ''	Parent	o-c ^a	¹³ C(16)	o-c ^a	¹³ C(3 and 6)	o-c ^a	¹³ C(1)	o-c ^a	¹³ C(9)	o-c ^a	D(17)	o-c ^a
<i>a</i> -type transitions																	
3	0	3	2	0	2	4191.421	0										
3	2	2	2	2	1	4197.447	1										
3	2	1	2	2	0	4203.475	1										
3	1	2	2	1	1	4319.526	5	4261.910	2	4262.330	1	4291.032	1	4316.691	4		
4	1	4	3	1	3	5429.595	0	5361.166	0	5362.955	–1	5394.770	1	5425.831	0	5305.745	12
4	0	4	3	0	3	5581.547	0	5509.598	1	5510.783	2	5545.365	–1	5577.765	1	5451.427	–1
4	2	3	3	2	2	5595.418	1										
4	3	2	3	3	1	5599.555	6										
4	3	1	3	3	0	5599.648	–5										
4	2	2	3	2	1	5610.463	0										
4	1	3	3	1	2	5757.559	3	5680.834	0	5681.396	0	5719.599	–2	5753.775	0		
5	1	5	4	1	4	6784.273	–1	6698.874	–1	6701.116	0	6740.787	0	6779.566	0	6629.704	3
5	0	5	4	0	4	6965.732	0	6876.372	0	6877.861	0	6920.702	1	6960.994	0	6804.090	–1
5	2	4	4	2	3	6992.377	0										
5	3	3	4	3	2	7000.724	–1										
5	3	2	4	3	1	7001.087	–2										
5	2	3	4	2	2	7022.376	0										
5	1	4	4	1	3	7193.992	0	7098.244	–1	7098.947	–2	7146.600	1	7189.260	–3		
6	1	6	5	1	5	8137.229	–3									7952.096	–10
6	0	6	5	0	5	8342.650	–2									8150.128	1
6	2	5	5	2	4	8388.072	–5										
6	3	4	5	3	3	8402.670	2										
6	2	4	5	2	3	8440.285	0										
6	1	5	5	1	4	8628.358	–2										
7	1	7	6	1	6	9488.217	2										
7	0	7	6	0	6	9711.186	0									9488.486	1
8	1	8	7	1	7	10837.018	3										
8	0	8	7	0	7	11070.533	–1										
<i>b</i> -type transitions																	
1	1	1	0	0	0	4703.986	0										
6	0	6	5	1	5	5569.666	0										
2	1	2	1	0	1	6021.120	0										

^aObserved-calculated frequencies in kHz.

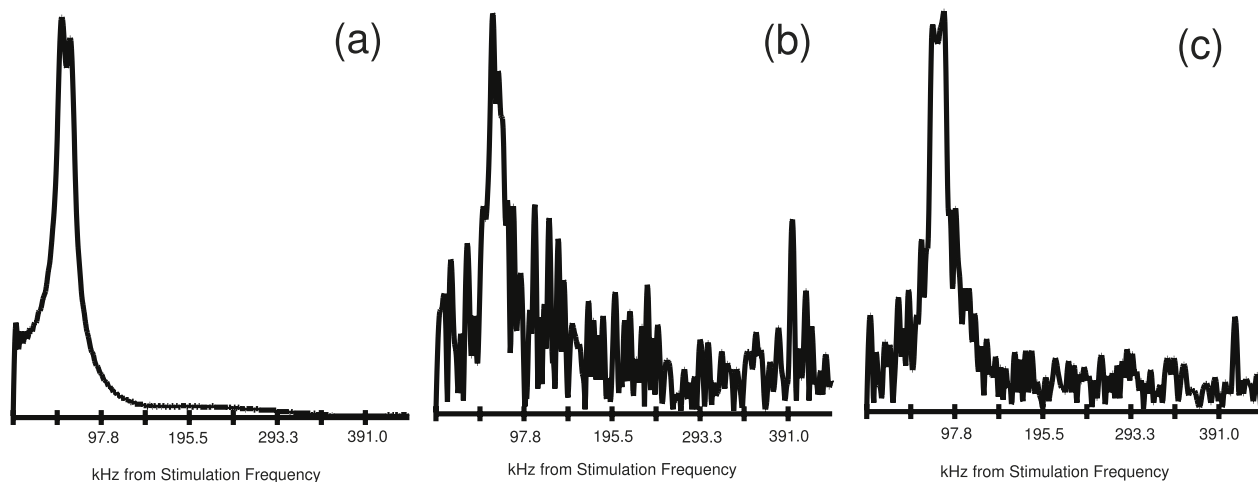


FIG. 1. Example transitions of the parent isotopologue (6965.580 MHz stimulation) (a), the ^{13}C isotopologue at the C16 position (6876.240 MHz stimulation) (b), and the ^{13}C isotopologue at the equivalent positions of C3 and C6 (6878.020 MHz stimulation) (c) of the 404–505 transition (from left to right) taken at 300 pulsed-beam cycles for each transition shown.

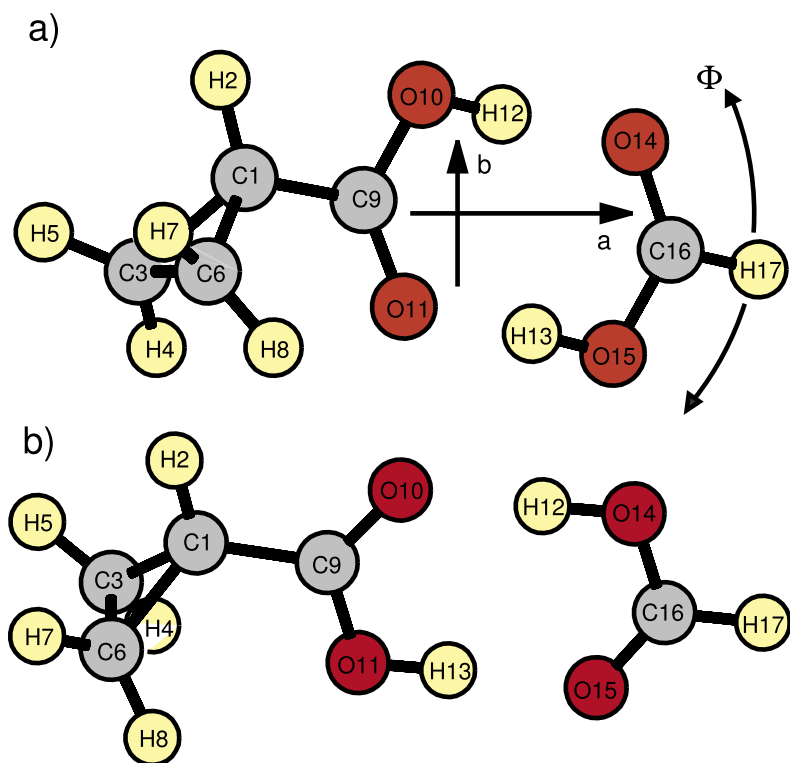


FIG. 2. Calculated structures of the low energy (a) and higher energy (b) CPCA-FA conformers using B97D with aug-cc-pVTZ basis. Also shown superimposed on the low energy conformer are the a and b principle axes and the visualization of the parameter φ (phi) used in the structure fit.

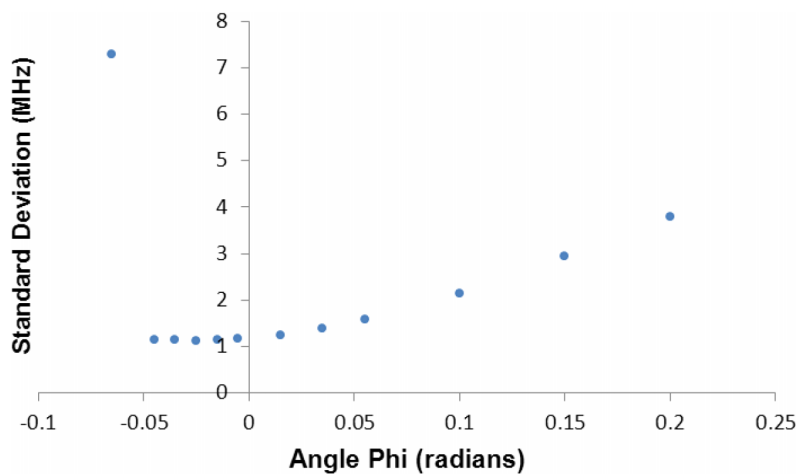


FIG. 3. Plot showing the variation of the “best-fit” standard deviation for the nonlinear least squares structure fit with the angle φ . The variation of the angle φ represents the rotation of the FA moiety in the x-y Cartesian plane and changes the relative lengths of the two hydrogen bonds.

not the proton tunneling motion. Rotational transitions were searched for corresponding to the high energy conformer in Figure 2 (bottom); however after significant scanning, we were unable to observe or measure any transition from this higher energy conformer.

III. CALCULATIONS

Ab initio calculations for an optimized structure of the low energy CPCA-FA conformer were performed using the Gaussian 09 suite²³ using B97D/aug-cc-pVTZ and MP2/aug-cc-pVTZ methods to obtain initial values of rotational constants. The calculated a and b dipole moments for this conformer shown in Figure 2 (top) were 1.4 and 0.2 D, respectively, from the MP2 calculation, so it was expected that the a-type transitions would be the strongest. The calculated rotational constants from the optimized Gaussian structure for this conformer were used in the Pickett program, SPCAT,²⁴ to calculate the a and b-type rotational transitions. The calculated values of the rotational constants are shown in Table II, along with the experimentally fit constants determined from the measured transitions. A Kraitchman analysis using the Kisiel KRA program²⁵ was performed on each of the isotopically ¹³C substituted and deuterium substituted atoms in the CPCA-FA dimer. These Kraitchman coordinates are shown in Table III, compared with the best fit gas phase structure coordinates.

A separate B97D/aug-cc-pVTZ calculation was performed to optimize the high energy conformer's geometry. Comparing two B97D calculations of each of the conformers of the dimer, the energy separation of the two was calculated to be 219 cm⁻¹, less than what was calculated to be the energy separation of the CPCA monomers. The energy separation between the two conformers of the CPCA monomer was small enough so these transitions from this other conformer were observed previously.²⁴ Based on these calculations and previous results, we expected to observe the high energy CPCA-FA conformer. After performing the predictive calculations for rotational constants and transitions, no transitions were observed after significantly scanning for these high energy conformer transitions.

IV. ROTATIONAL CONSTANTS

The experimental rotational and centrifugal distortion constants for the parent low energy conformer of the dimer,

TABLE II. *Ab initio* (MP2/aug-cc-pVTZ and B97D/aug-cc-pVTZ) spectroscopic constants and dipole moments of the cyclopropanecarboxylic acid-formic acid dimer.

Type	B97D/aug-cc-pVTZ	MP2/aug-cc-pVTZ	Experiment
A(MHz)	4068.66	4038.00	4045.42
B(MHz)	732.32	747.56	740.58
C(MHz)	652.25	663.19	658.57
μ_a (D)	1.7	1.4	
μ_b (D)	0.2	0.2	
μ_c (D)	0.0	0.0	

TABLE III. Structural coordinates of the CPCA-FA (low energy) dimer in Å from the nonlinear least squares fit with a standard deviation of 1.13 MHz. Also shown are the Kraitchman determined coordinates for each of the isotopically ¹³C substituted atoms.

Atom	a	b	c	Krait- a	Krait- b	Krait- c
C1	2.154	0.509	0.021	2.1464(11)	0.5447(42)	0.03*(8)
H2	2.478	1.537	0.053			
C3	2.972	-0.587	0.745	2.9923(8)	0.4674(53)	0.7440(34)
H4	2.433	-1.394	1.218			
H5	3.827	-0.215	1.289			
C6	3.012	-0.483	-0.748	2.9923(8)	0.4674(53)	0.7440(34)
H7	3.880	-0.083	-1.251			
H8	2.485	-1.263	-1.276			
C9	0.701	0.299	-0.002	0.661(5)	0.3354(97)	0.04(9)
O10	0.027	1.474	0.022			
O11	0.139	-0.767	-0.037			
H12	-4.022	0.506	0.006	4.1468(13)	0.476(12)	0.282(20)
H13	-0.915	1.258	0.005			
O14	-2.840	-1.325	-0.001			
O15	-2.209	0.833	-0.001			
C16	-3.022	0.085	0.001	3.08253(72)	0.190(12)	0.02(13)
H17	-1.935	-1.645	0.012			

Figure 2 (top), were determined using the Pickett's program SPFIT²⁴ and are given in Table IV. A similar analysis was carried out for all remaining singly substituted ¹³C and deuterium substituted isotopologues. The centrifugal distortion constants obtained from the parent were held fixed in the fits for the ¹³C and D isotopologues. These results are also given in Table IV. The rotational constants from the calculations and the experiment are compared in Table II. The MP2 calculation with the aug-cc-pVTZ basis yielded rotational constants within 1% of the experimental results.

V. MOLECULAR STRUCTURE

A nonlinear least squares fit was performed to obtain a best fit gas phase structure of the low energy conformer of the CPCA-FA dimer using the rotational constants of each of the measured ¹³C isotopologues and the deuterated isotopologue. This program was written in Fortran by members of the lab. The input is the set of Cartesian coordinates of the atoms within the structure of the dimer. These Cartesian coordinates of the atoms are varied to produce a structure with moments of inertia closest to the experimental results, so the derived structure assumes a rigid rotor approximation in the ground vibrational state. The standard deviation for this structure fit on the CPCA-FA dimer was 1.13 MHz. In the fit, the coordinates of all atoms for each monomer unit were held fixed to previously obtained structural values.^{18,26} Following the results from the *ab initio* calculations, all atoms of formic acid had their z Cartesian coordinates fixed to the previously determined values. The z-coordinates were not set to be varied from these fixed positions from previous structural work. There were only two variable parameters used in the structure fit, which represented the movement of the fixed structure of the FA moiety in the x-y Cartesian plane (a-b plane) relative to the fixed center of mass of CPCA. A third parameter, φ , is the angle

TABLE IV. Spectroscopic constants for the parent and ^{13}C isotopologues of the CPCA–FA dimer.

	Parent	$^{13}\text{C}(16)$	$^{13}\text{C}(3 \text{ and } 6)$	$^{13}\text{C}(1)$	$^{13}\text{C}(9)$	D(17)
A(MHz)	4045.419 3(16)	4044.16(21)	4021.03(25)	4035.98(22)	4041.76(37)	4035.84(66)
B(MHz)	740.583 80(14)	730.454 55(16)	730.447 65(18)	735.636 79(17)	740.110 49(30)	722.3152(32)
C(MHz)	658.567 60(23)	650.513 44(17)	650.813 82(20)	654.403 57(19)	658.098 39(33)	643.9651(12)
ΔJ (kHz)	0.049 9(16)	0.0499 ^a	0.0499 ^a	0.0499 ^a	0.0499 ^a	0.0499 ^a
ΔJ_K (kHz)	0.108 (14)	0.108 ^a	0.108 ^a	0.108 ^a	0.108 ^a	0.108 ^a
N	31	7	7	7	7	7
σ (kHz)	2	1	1	1	2	6

^aFixed at the values for the parent isotopologue.

of rotation in the x-y plane for the FA coordinates using the standard rotation matrix. Figure 2 shows the relative motion the angle φ invokes on the FA moiety. The angle φ was not a variable parameter in the fit, but different trial values were tested. The structure with the smallest standard deviation is reported and is referred to as the “best fit” structure. Figure 3 shows a plot of the fit standard deviation obtained with different values of the angle φ . The minimum observed in the plot represents the “best fit” structure. The standard deviation of the structure fit significantly increases after a value of $\varphi = -0.05$ radians as the FA moiety is rotated to an unreasonable position relative to the CPCA molecule and clearly does not correspond with experimental results as seen with the standard deviation. The actual value of φ is less important than the differences in hydrogen bond lengths which are directly correlated with φ . Comparing the calculated Gaussian structure with the best fit structure obtained from the nonlinear least squares fit, the hydrogen bond lengths and center of mass separation of each monomer can be seen in Table V. The hydrogen bond lengths became very asymmetric in the best fit structure and the center of mass separations of the monomers only increased by 0.02 Å.

VI. DISCUSSION

The pure rotational spectrum of the doubly hydrogen bonded dimer formed between CPCA and FA has been measured using a PBFT microwave spectrometer and all the measured rotational transitions were assigned to be associated with the low energy conformer. Scans for the high energy conformer transitions for the dimer were unsuccessful. The predicted energy difference between the two conformers was only $\sim 200 \text{ cm}^{-1}$ but may be larger as these high energy conformer transitions were not observed. The steric interactions of the FA hydrogen bonding to CPCA may prevent the CPCA molecule from rotating about the $\text{C}_1\text{--C}_9$ bond to the high energy form, which may be why we were unable to

observe this high energy conformer of CPCA–FA, even though this conformer of CPCA was observed with the monomer.²⁰

The Kraitchman determined coordinates of the ^{13}C atoms and the D are in fair agreement with the best fit coordinates, with the exception of some coordinates varying by $\sim 0.1 \text{ \AA}$ and more for the D substituted atom. The errors in some of the substituted coordinates are large, a result of the substituted atoms lying close to the principle axes or center of mass within the dimer. If we exclude the cyclopropane ring, the backbone structure of the dimer is planar. The hydrogen bond lengths in the best fit structure became very asymmetric compared with the theoretical calculation and the separation of each of the monomers changes very little with the rotation angle φ . The asymmetry of the hydrogen bonds in the “best fit” structure may confirm these steric interactions of FA with the cyclopropane ring, explaining why the high energy conformer was not observed as previously proposed. A smaller asymmetry of the hydrogen bond lengths was found for the more symmetric doubly hydrogen bonded complex propiolic acid-formic acid and 1,2-cyclohexanedione-formic acid.^{16,27}

For each of the measured rotational transitions of the parent isotopologue of the CPCA–FA dimer, as well as many of the ^{13}C transitions, there appeared to be a small splitting within each transition and an example of this splitting can be observed in Figure 1. This is due to Doppler Effects commonly observed in spectra using PBFT spectrometers and likely not due to proton tunneling as was observed in other carboxylic acid dimers. The magnitude of the splitting increased with increasing frequency of the transitions, typical of Doppler type splittings. To confirm that these splittings were indeed Doppler splittings, a 50/50 argon/neon mixture was used as the carrier gas and, as expected with the presence of argon, these Doppler splittings decreased slightly. In the study of the monomer of CPCA, there were no signs of splittings caused by internal rotation of the cyclopropane group^{17,18,20} and the same seemed to hold true for the CPCA–FA dimer. Tunneling splittings were not observed, most likely because the dimer lacks the C_{2vM} symmetry, which may be necessary to create the symmetric double well potential with similar energies at the minima, allowing for the protons to tunnel through the energy barrier. Because this dimer lacked C_{2vM} , it may have resulted in a more asymmetric double well potential, “locking” the dimer in the lower of the tunneling states. The doubly hydrogen bonded dimers that exhibit this proton tunneling seem to have this symmetry or very close to it. The asymmetric hydrogen bond lengths obtained in the “best fit” structure may also contribute to why these tunneling splittings were not observed.

TABLE V. Interatomic distances obtained by fitting the experimental rotational constants for six isotopologues in a nonlinear least squares fit. Hydrogen bond lengths and COM separations are in Å.

Interatomic distance	Microwave fit value	Calculated (MP2) value
$r(\text{H}_{12}\text{--O}_{14})$	1.36	1.67
$r(\text{O}_{11}\text{--H}_{13})$	2.25	1.62
COM separation	4.11	4.09

VII. CONCLUSIONS

The microwave spectrum was measured for the CPCA–FA doubly hydrogen bonded dimer and all measured transitions were assigned for the first time. From the experimentally determined values of the rotational constants of each of the isotopologues, a nonlinear least squares fit was performed to obtain a “best fit” gas phase structure of this dimer. The best fit hydrogen bond lengths became asymmetric when compared with the calculations, $r(\text{H}_{12}\text{-O}_{14})$ changing from 1.67 Å to 1.36 Å and $r(\text{O}_{11}\text{-H}_{13})$ from 1.62 Å to 2.25 Å. To further refine the structure of this dimer, deuterium substitution isotopologues would need to be measured. *Ab initio* calculations predicted another higher energy conformer of this dimer, but after significant scanning, the higher energy conformer was not observed. No proton tunneling was observed for this dimer, most likely due to the asymmetry of the dimer introduced by the cyclopropane ring, which may have been the case with the CPCA hydrogen bonded dimer with trifluoroacetic acid. This asymmetry results in two inequivalent potential wells that tend to quench the proton tunneling. This work can add another benchmark to help further understand the dynamics of proton tunneling.

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