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Microwave measurements of proton tunneling and structural parameters for the propiolic acid–formic acid dimer

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Microwave spectra of the propiolic acid-formic acid doubly hydrogen bonded complex were measured in the 1 GHz to 21 GHz range using four different Fourier transform spectrometers. Rotational spectra for seven isotopologues were obtained. For the parent isotopologue, a total of 138 a-dipole transitions and 28 b-dipole transitions were measured for which the a-dipole transitions exhibited splittings of a few MHz into pairs of lines and the btype dipole transitions were split by \sim 580 MHz. The transitions assigned to this complex were fit to obtain rotational and distortion constants for both tunneling levels: A^{0+} $= 6005.289(8), B^{0+} = 930.553(8), C^{0+} = 803.9948(6) \text{ MHz}, \Delta^{0+}{}_{\text{J}} = 0.075(1), \Delta^{0+}{}_{\text{JK}} = 0.71(1), \text{ and } \delta^{0+}{}_{\text{J}} = -0.010(1) \text{ kHz} \text{ and } A^{0-} = 6005.275(8), B^{0-} = 930.546(8), C^{0-}$ = 803.9907(5) MHz, $\Delta^{0-}{}_{J}$ = 0.076(1), $\Delta^{0-}{}_{JK}$ = 0.70(2), and $\delta^{0-}{}_{j}$ = -0.008(1) kHz. Double resonance experiments were used on some transitions to verify assignments and to obtain splittings for cases when the b-dipole transitions were difficult to measure. The experimental difference in energy between the two tunneling states is 291.428(5) MHz for proton-proton exchange and 3.35(2) MHz for the deuterium-deuterium exchange. The vibration-rotation coupling constant between the two levels, F_{ab} , is 120.7(2) MHz for the proton-proton exchange. With one deuterium atom substituted in either of the hydrogen-bonding protons, the tunneling splittings were not observed for a-dipole transitions, supporting the assignment of the splitting to the concerted proton tunneling motion. The spectra were obtained using three Flygare-Balle type spectrometers and one chirpedpulse machine at the University of Virginia. Rotational constants and centrifugal distortion constants were obtained for HCOOH ··· HOOCCCH, H¹³COOH ··· HOOCCCH, HCOOD ··· HOOCCCH, HCOOH ···· DOOCCCH, HCOOD ···· DOOCCCH, DCOOH ··· HOOCCCH, and DCOOD ···· HOOCCCH. High-level *ab initio* calculations provided initial rotational constants for the complex, structural parameters, and some details of the proton tunneling potential energy surface. A least squares fit to the isotopic data reveals a planar structure that is slightly asymmetric in the OH distances. The formic OH···O propiolic hydrogen bond length is 1.8 Å and the propiolic OH···O formic hydrogen bond length is 1.6 Å, for the equilibrium configuration. The magnitude of the dipole moment was experimentally determined to be $1.95(3) \times 10^{-30}$ C m (0.584(8) D) for the 0⁺ states and $1.92(5) \times 10^{-30}$ C m (0.576(14) D) for the 0⁻ states. © 2011 American Institute of Physics. [doi:10.1063/1.3643720]

I. INTRODUCTION

Hydrogen bonding interactions have substantial effects on phase transition temperatures and conformations and interactions of proteins and nucleic acids. In DNA the hydrogenbonded base pair recognition is the key to the transcription and translation of the genetic messages. This recognition relies on specific doubly and triply hydrogen-bonded base pairing interactions. Calculations of concerted proton tunneling in hydrogen-bonded base pair interactions are reported by Scheiner and Kern¹ where they describe the concerted proton tunneling as "a simultaneous and synchronous motion of two protons" in a double-well potential. The suggestion that the tunneling of the hydrogen bonded protons may play an important role in mutagenesis has been discussed by Löwdin² and Catalán and Kasha.³

This concerted proton tunneling has been studied experimentally for the formic acid dimer by Havenith *et al.*^{4–6} and recently the formic acid–acetic acid complex has been shown to exhibit simultaneous proton transfer⁷ with a barrier to exchange of 8000 cm⁻¹. High resolution IR spectroscopy of the formic acid–formic acid dimer reveals that (DCOOH)₂ has a spectrum that can be fit to four sets of rotational constants. It

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FIG. 1. Structure of the Pro-FA complex from the calculations using MP2/6- $311++G^{**}$.

has been proposed that two pairs are for the upper and lower levels of splittings due to tunneling in the double well potential for both the ground and first excited vibrational state. The propiolic acid–formic acid dimer (Pro-FA) is a similar system that exhibits tunneling effects similar to those of the formic acid dimer. The microwave spectrum of the gas phase dimer, Pro-FA, has been measured from 1 to 21 GHz using pulsed beam microwave spectroscopy and since observed lines were split into two components, we can report two sets of rotational constants for the ground vibrational state for both the parent and carbon-13 substituted formic acid with propiolic acid.

The Pro-FA complex has a permanent electric dipole and is predicted to be a prolate top with an a-dipole moment of 0.82 D and a b-dipole of -0.10 D. A preliminary account of some parts of this work was published earlier.⁸ The basic structure of the complex is shown in Fig. 1. There are many calculations on double well potentials in the literature,⁹⁻¹¹ but to our knowledge no published results on Pro-FA are available. Calculations of the proton tunneling rates have yielded widely varying results. The present measurements of the energy level splittings for the concerted proton exchange for both the double proton and double deuterium hydrogen bonding for Pro-FA provides benchmark experimental data for the theoretical work.

Analysis of the tunneling-rotation spectra is further complicated by a vibration-rotation interaction term F_{ab} , which is significant because the acetylinic group of propiolic acid does not lie along the a-axis of the complex. Various choices for the axis systems used to evaluate vibration-rotation interactions were presented by Herb Pickett¹² and the reduced axis system analysis was incorporated into his program SPFIT.¹³ The formalism and analysis have been extended by Baughcum *et al.*¹⁴ and applied to malonaldehyde and to tropolone by Tanaka *et al.*¹⁵ This analysis can be used to fit the parameters ΔE_{01} and F_{ab} , the difference in energy between the ground and first excited state, and the coefficient of the vibrationrotation interaction.

II. DFT AND AB INITIO CALCULATIONS

Density functional theory (DFT) and MP2 calculations were performed to estimate the binding energy, gas phase structure, and energy barrier to proton exchange for Pro-FA. Table I gives the results for the predicted rotational constants and key structural parameters obtained. The calculated structural parameters are shown in Fig. 1. The calculations were done using the GAUSSIAN 03 (Ref. 16) suite running on the University of Arizona ICE high performance computing cluster.

MP2/6-311++G**(Gaussian) was used to calculate the binding energy and the counterpoise correction was included in calculations to help remove the basis set superposition error. The value obtained for the (HCOOH)₂ was -56.9 kJ/mol. For the Pro-FA dimer the calculated binding energy is -58.1 kJ/mol using this method. In addition, rotational constants and key structural parameters were estimated using the monomer gas phase structures for additional constraints. Density functional theory methods B3LYP,¹⁷ B3PW91,¹⁸ HCTH407,¹⁹ and TPSSTPSS (Ref. 20) were also used to compute gas phase structures, vibrational frequencies, and the energy barrier to proton exchange, and the structural parameters are given in Table I. To obtain an estimate for the energy barrier to proton exchange, the transition state parameters were calculated using the GAUSSIAN program with the results ranging from 2000 cm⁻¹ to 4000 cm⁻¹. Using the ab initio values for barrier heights and the equilibrium coordinates for the tunneling proton along with the experimental difference in energy between vibrational states, a relatively simple model can be used to estimate the reduced mass for the proton transfer.

	MP2 6-311++G**	MP2 aug-cc-pVDZ	HCTH407 6-311++G**	B3PW91 6-311++G**	B3LYP 6-311++G**	TPSSTPSS 6-311++G**	Expt. ^a
A (MHz)	5962	5880	5952	6024	5991	5903	5988.7
B (MHz)	910	914	896	934	920	933	927.782
C (MHz)	789	791	779	809	797	805	803.72
R(O1H-O3) (Å)	1.73	1.69	1.77	1.66	1.70	1.64	1.76 ^b
R(O2-HO4) (Å)	1.71	1.67	1.76	1.64	1.68	1.63	1.60 ^b
<(O3CO4) (°)	126.3	126.3	126.6	126.2	126.2	126.3	125.9 ^b
<(O1CO2) (°)	125.4	125.5	125.4	125.3	125.1	125.4	124.4 ^b
$ \mu_a $ (D)	0.88	0.77	0.80	0.78	0.81	0.84	0.584(8) ^c

TABLE I. Summary of calculated and experimental key molecular and structural parameters.

^aRotational constants from fit of the ground vibrational state 0⁺.

^bValues obtained from Fit I.

 $^{c}|\mu_{a}| = 0.584(8)D$ for 0^{-} .

III. EXPERIMENTAL METHODS

Formic acid (99%) and propiolic acid (96%) were purchased from Aldrich and were used without purification. Isotopically enriched formic acid, DCOOD, HCOOD, and H¹³COOH were purchased from Cambridge Laboratories. DCOOH was made with equal amounts of DCOOD and HCOOH. DOOCCCH was made with equal amounts of HOOCCCH and HCOOD. Certain commercial products are identified in this paper in order to adequately specify the experimental or theoretical procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

A. Experiments at the University of Arizona

Measurements in the frequency range of 1-14 GHz were done using two pulsed beam Fourier transform microwave (FTMW) spectrometers. Measurements in the 4-14 GHz range were performed using a conventional microwave Fourier transform spectrometer discussed previously.²¹ Measured frequencies for the normal isotopologue are listed in Table II. In the Obs. - calc. column are listed the deviations of the "best fit" calculated frequencies from the experimental frequencies. To prepare the samples, the sample cell was loaded onto the spectrometer sample chamber and subsequently placed into a liquid nitrogen bath to freeze the liquid sample. This cell was then evacuated, charged to 1.2 atm with neon, and allowed to come to -10 °C. The temperature of -10° C was then maintained by placing the cell in a bath with an ethanol/water mixture and dry ice. Propiolic acid and formic acid seeded in neon were introduced into the spectrometer cavity transverse to the microwave cavity axis at a 2 Hz pulse rate, using a pulsed valve (General Valve series 9). The pressure inside the spectrometer chamber was maintained at 10^{-6} - 10^{-7} Torr prior to the valve opening, and the backing pressure of neon was kept at about 0.9-1.2 atm during the frequency scanning. Following the molecular pulse (about 1 ms delay), a $\pi/2$ microwave excitation pulse (1 μ s duration) was injected into the resonator to coherently excite the molecules, using a Herley SPDT microwave switch. The molecular free induction decay (FID) signal was transmitted via the same SPDT switch, passed to a Miteq 6-18 GHz low noise amplifier, and sent to the RF circuit for further signal processing. Initially, the samples were kept in separate cells and each monomer spectrum was observed while the other was frozen out with an optimum signal observed for both $\sim -10^{\circ}$ C. Given the similar properties of the acids, we added both samples to the same cell and obtained all the isotopic data using a single sample cell.

Measurements in the 1–4 GHz range were performed using a new Flygare-Balle spectrometer that was constructed at the University of Arizona.²² Designed for the frequency range between 1 and 6 GHz, it has unusual dimensions with mirror diameters of 48" and is housed in a vacuum system weighing 2 tons. The diffusion pump (Varian NHS-35) has a throat diameter of 35". The mirrors have a radius of curvature of

TABLE II. The measured transitions of Pro-FA from 1.7 GHz to 21.3 GHz.

J' _{KaKc}	v′	J″ _{KaKc}	v″	Frequency (MHz)	Obs. – calc. (kHz)
10,1	1	00,0	1	1731.493	-0.6
10,1	0	00,0	0	1731.834	0.1
21,2	1	11,1	1	3339.166	-1.6
21,2	0	11,1	0	3340.174	-0.4
20,2	1	10,1	1	3460.747	-0.5
20,2	0	10,1	0	3461.44	-0.1
21,1	1	$1_{1,0}$	1	3586.851	1.1
21,1	0	$1_{1,0}$	0	3587.202	-0.1
31,3	1	21,2	1	5007.364	-1.2
31,3	0	21,2	0	5008.881	-0.6
30,3	1	20,2	1	5185.527	-0.1
30,3	0	20,2	0	5186.594	0.1
32,2	1	22,1	1	5194.49	1.3
32,1	1	22,0	1	5203.43	-1
31,2	1	21,1	1	5378.861	1.8
31,2	0	21,1	0	5379.394	-0.4
11,1	0	00,0	1	6520.902	4.7
41,4	1	31,3	1	6673.937	1
41,4	0	31,3	0	6675.966	-1.3
40,4	1	30,3	1	6903.622	0
40,4	0	30,3	0	6905.096	-0.8
42,3	1	32,2	1	6924.239	0.4
43,2	0	33,1	0	6931.678	-0.3
43,1	0	33,0	0	6931.827	-1.7
42,2	1	32,1	1	6946.562	-0.4
1 _{1,1}	1	00,0	0	7103.387	-18.5
41,3	0	31,2	0	7169.857	-2.4
21,2	0	10,1	1	8129.58	1.5
5 _{1,5}	1	4 _{1,4}	1	8338.397	2.1
5 _{1,5}	0	41,4	0	8340.95	0.8
50,5	1	40,4	1	8612.895	-0.4
50,5	0	40,4	0	8614.821	0.5
5 _{2,4}	1	42,3	1	8652.493	2
52,4	0	42,3	0	8654.204	-1.6
52,3	1	42,2	1	8697.007	2.1
21,2	1	$1_{0,1}$	0	8710.748	9.1
51,4	1	41,3	1	8957.035	-1.4
5 _{1,4}	0	4 _{1,3}	0	8957.967	1.8
31,3	0	$2_{0,2}$	1	9677.711	-2
31,3	0	20,2	1	9677.719	6.3
61,6	1	5 _{1,5}	1	10 000.3	-2.7
61,6	0	5 _{1,5}	0	10 003.39	-0.2
31,3	1	20,2	0	10256.67	5.2
60,6	1	50,5	1	10311.37	-2.1
60,6	0	50,5	0	10313.8	-1.8
60,6	0	50,5	0	10313.8	0.7
8 _{0,8}	1	7 _{1,7}	0	10319.46	-0.8
62,5	1	52,4	1	10378.87	-0.3
62,5	1	5 _{2,4}	1	10378.88	1.4
62,5	0	52,4	0	10380.95	0.5
63,4	1	5 _{3,3}	1	10400.5	0.7
63,3	1	53,2	1	10401.91	-0.2
63,4	0	53,3	0	10402.46	0
63,3	0	53,2	0	10403.86	-0.4
6 _{2,4}	1	52,3	1	10456.35	-1
6 _{2,4}	1	5 _{2,3}	1	10456.36	1.7
6 _{2,4}	0	52,3	0	10458.02	-7.1
6 _{2,4}	0	52,3	0	10458.02	-1.1
615	1	514	1	10741.88	-0.9

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TABLE II. (Continued.)

9_{4,5}

94,6

9_{4,5}

1

0

0

84,4

84,5

84,4

1

0

0

15604.73

15607.42

15607.61

J' _{KaKc}	\mathbf{v}'	J″ _{KaKc}	v″	Frequency (MHz)	Obs. – calc. (kHz)	J' _{KaKc}	\mathbf{v}'	J″ _{KaKc}	v″	Frequency (MHz)	Obs. – calc (kHz)
61.5	0	51.4	0	10743.02	0.1	93.7	1	83.6	1	15614.92	3.1
41.4	0	30.3	1	11 168.16	4.9	93.7	0	83.6	0	15617.75	-1.4
7 _{1.7}	1	6 _{1.6}	1	11659.3	-1.2	9 _{3.6}	1	83.5	1	15 626.49	0.9
71.7	0	61.6	0	11 662.92	-3.9	9 _{3.6}	0	83.5	0	15 629.24	-1.8
4 _{1.4}	1	30.3	0	11744.01	3.6	9 _{2.7}	1	82.6	1	15798.35	-2.8
-,. 20.9	0	81.8	1	11782.18	0.4	927	0	82.6	0	15 800.28	-2.5
70.7	1	60.6	1	11 997.36	-2	717	1	60.6	0	15908.29	0.9
70.7	0	60,6	0	12,000.35	0.9	9 _{1.8}	1	81.7	1	16070.07	-0.7
70.7	0	60,6	0	12,000,35	1.2	9 _{1.8}	0	81.7	0	16072.0	-2.7
726	1	62.5	1	12 103.02	3.1	101 10	1	9 _{1.9}	1	16616.03	2.6
2,0 72,6	0	62,5	0	12 105 46	2.3	101,10	0	9 _{1,9}	0	16 621 37	-3
2,0 12 5	1	6 _{2,3}	1	12 137 38	-0.1	81.0	0	707	1	16 669 43	58
5,5 125	0	63,4	0	12 139.55	0.5	100.10	1	90,7	1	16 971 46	0.2
3,5 Io 4	1	63,4	1	12 139.05	0.5	100,10	0	9 _{0,9}	0	16 976 49	0.2
3,4 7	0	63,3	0	12 140.50	07	100,10	1	90,9 90.0	1	17 258 38	8
7	1	6.	1	12 172.77	-0.7	102,9	0	9 _{2,8}	0	17 250.50	7
2,5 7	1	0 _{2,4}	1	12 223.91	-2.7	102,9	1	92,8	1	17201.98	0.1
2,5	1	02,4	1	12 227.72	-5.1	104,7	1	94,6	1	17 342.97	0.1
1,6	1	01,5	1	12 522.9	1.5	104,6	1	94,5	1	1/343.3/	-1.9
1,6	0	61,5	0	12 524.28	0.3	104,7	0	9 _{4,6}	0	17346.13	1.5
) _{1,5}	0	40,4	1	12605.45	-25.5	10 _{4,6}	0	9 _{4,5}	0	17346.53	l
0 _{1,5}	0	40,4	1	12 605.48	4.5	10 _{3,8}	1	9 _{3,7}	1	17 355.4	3.6
51,5	1	40,4	0	13 177.31	3.4	10 _{3,8}	0	9 _{3,7}	0	17 358.51	-1.7
51,5	1	40,4	0	13 177.31	3.4	$10_{3,7}$	0	9 _{3,6}	0	17 378.12	-1.7
31,8	1	7 _{1,7}	1	13 315.06	1	$10_{2,8}$	1	9 _{2,7}	1	17 600.84	-4.4
31,8	0	7 _{1,7}	0	13 319.24	-2.5	$10_{2,8}$	0	9 _{2,7}	0	17 602.79	-4.9
80,8	1	7 _{0,7}	1	13 669.64	-1	$10_{1,9}$	1	9 _{1,8}	1	17 834.28	-1
80,8	0	70,7	0	13 673.25	-0.6	$10_{1,9}$	0	9 _{1,8}	0	17 836.53	-1
32,7	1	7 _{2,6}	1	13 824.56	2.2	$11_{1,11}$	1	$10_{1,10}$	1	18 261.01	4.4
32,7	0	7 _{2,6}	0	13 827.38	5.2	$11_{1,11}$	0	$10_{1,10}$	0	18 266.97	-2.8
33,6	1	7 _{3,5}	1	13 875.54	1.5	$11_{0,11}$	1	$10_{0,10}$	1	18 602.12	0
33,6	0	73,5	0	13 878.09	-0.7	$11_{0,11}$	0	$10_{0,10}$	0	18 607.92	-0.1
33,5	1	7 _{3,4}	1	13 881.87	2.9	$11_{2,10}$	1	102,9	1	18969.96	10.8
3 _{3,5}	0	7 _{3,4}	0	13 884.38	-0.4	$11_{2,10}$	0	102,9	0	18973.97	8.9
5 _{1,6}	0	50,5	1	13 995.98	0.5	113,9	1	103,8	1	19096.78	3
32,6	1	72,5	1	14 006.52	0.6	113,9	0	103,8	0	19100.17	2.1
82,6	0	7 _{2,5}	0	14008.41	1.4	113,8	1	103,7	1	19128.71	-1.4
6 _{2,4}	0	61,5	1	14014.39	-2.7	113,8	0	103,7	0	19131.85	-2.9
7 _{2,5}	1	7 _{1,6}	0	14 289.43	-4.6	11 _{2,9}	1	102,8	1	19412.6	-8.2
5 _{2,3}	0	5 _{1,4}	1	14 298.25	-0.7	112,9	0	102,8	0	19414.54	-6.3
81,7	1	71,6	1	14 299.28	1.7	$11_{1,10}$	1	101,9	1	19 590.76	2.6
81,7	0	71,6	0	14 300.92	0.1	$11_{1,10}$	0	101,9	0	19 593.38	-0.8
100.10	1	91.9	0	14 327.19	-2.3	121.12	1	$11_{1.11}$	1	19902.28	-8.9
42.2	0	41.3	1	14 556.79	-3.5	121.12	0	111.11	0	19908.91	-4.1
51.6	1	50.5	0	14 562.79	-0.9	120.12	1	110.11	1	20221.26	2.5
62 A	1	61.5	0	14,587.8	-3.8	120.12	0	110.11	0	20227.87	-1
3 _{2 1}	0	31.2	1	14778.12	-7	121.11	1	11, 10	1	21 338 3	1.6
5 _{2,1}	1	51.4	0	14 874 47	-1.2	121.11	0	11,10	0	21 341 34	2.9
91.0	1	81.0	1	14 967 35	0.9			11,10		21011101	2.,
91,9 91.0	0	81.0	0	14 972 11	_1						
-1,9 90.0	1	80.0	1	15 307 60	_2 1						
20,9 0	0	8	0	15 331 01	-2.1	10	nd +1'			mind hat-	10// on 1 60//
-0,9 7	0	0 _{0,8}	1	15 247 54	-3.2	1.0 m a		r spacing ca	an de va	ined between	42° and 60° ,
/ 1,7 2	0	2	1	15 510 04	1.0	providi	ng betw	een 3 and 1	2 TEM_0	$_0$ modes and the	e same num-
3 _{2,2}	1	3 _{1,3}	1	15 524 40	11./	ber of T	EM ₁₀ r	nodes (high	er order	r modes are pro	esent, but are
-2,0	1	21,1 o	1	15 542 12	7.5	not suit	able fo	r measuren	nents).	The cavity Q	values range
^{2,8}	1	8 _{2,7}	1	15 545.15	2.9	from 15	5000 to	40 000 for	various	different mode	s. The cavity
2,8	0	8 _{2,7}	0	15 546.33	5	resonan	ces are	very sharp	, usually	y between 40	and 300 kHz
4,6	1	84,5	1	15 604.54	-4.1	FWHM	render	ing the snee	ctromete	er very narrow	-banded The
945	1	8	1	1560473	_1.6	1 11111	,	mg uie sper	- u o mou	a very narrow	canaca. The

sample mixture is injected by a pulsed valve (General Valve

series 9) in a transverse geometry. The studied molecules are

-1.6

0.2

1.2

TABLE III. Measured transitions for the dipole moment determination of the 0^+ and 0^- states of the formic acid–propiolic acid complex, performed with an electric field strength of 464 V/cm. All frequencies are reported in MHz.

				Frequency	Frequency			
J" _{KaKc}	J'_{KaKc}	$M^{\prime\prime}$	\mathbf{M}'	(zero-field)	(Stark field)	Experimental shift	Calculated shift ^a	Obs calc
					0 ⁺ state			
414	313	0	0	6675.966	6675.890	-0.076	-0.061	-0.015
414	313	1	1	6675.966	6676.068	0.102	0.108	-0.006
404	303	3	3	6905.096	6905.370	0.274	0.252	0.022
413	312	0	0	7169.857	7169.814	-0.043	-0.059	0.016
413	312	1	1	7169.857	7169.694	-0.163	-0.164	0.001
413	312	2	2	7169.857	7169.392	-0.465	-0.480	0.015
5 ₁₅	414	2	2	8340.950	8341.070	0.120	0.111	0.009
5 ₁₅	414	3	3	8340.950	8341.246	0.296	0.296	0.000
5 ₁₅	414	4	4	8340.950	8341.502	0.552	0.555	-0.003
514	413	4	4	8957.967	8957.662	-0.305	-0.295	-0.010
					0 ⁻ state			
414	313	0	0	6673.937	6673.886	-0.051	-0.058	0.007
414	313	1	1	6673.937	6674.060	0.123	0.106	0.017
404	3 ₀₃	3	3	6903.622	6903.882	0.260	0.245	0.015
413	312	0	0	7169.121	7169.088	-0.033	-0.058	0.025
413	312	1	1	7169.121	7168.970	-0.151	-0.160	0.009
413	312	2	2	7169.121	7168.678	-0.443	-0.468	0.025
5 ₁₅	414	2	2	8338.397	8338.516	0.119	0.108	0.011
5 ₁₅	414	3	3	8338.397	8338.704	0.307	0.288	0.019
514	413	4	4	8957.035	8956.738	-0.297	-0.287	-0.010

^aCalculated assuming pure second-order Stark shifts, and the best fit dipole moment value for 0⁺ state: 0.584(8) D (1.95(3) × 10⁻³⁰ C m) and 0⁻ state: 0.576(14) D (1.92(5) × 10⁻³⁰ C m) (2σ error limits).

diluted (fractions of a percent) in a neon carrier gas at 1.1 atm. Amounts of about 7 μ l of the mixture are injected at the rate of 3–8 Hz. In the case of the propiolic–formic acid complex the acids were kept at 0 °C.

The spectrometer uses homodyne detection,²¹ and the configuration is shown in Fig. 2. The microwave signals are generated by a HP 8665B synthesizer (position 1 in Fig. 2) and divided into two arms by a power splitter (position 2). The lower arm constitutes the local oscillator signal for the mixer, while the upper arm provides the excitation power that enters the Fabry–Perot cavity (position 4) through a switch (pos.3, CMCS8553). The width of the excitation pulse is 2 μ s, and the power is chosen to produce the optimum excitation of the

molecules (between -20 dBm and +10 dBm). The molecular signal is routed by the same switch through a low noise amplifier (position 5, Miteq AFS2-00010600-25-S6-4) into the mixer (position 6, RHG DM4-8SS23). The down-converted signal is amplified by a low noise video amplifier (position 7, HP 08640-60506) and digitized by the acquisition board (position 8, pico ADC-212/50).

The measured lines of the propiolic-formic complex below 5 GHz (see Table II) are required between 25 and 3200 molecular pulses to reach the signal-to-noise ratio of S/N = 3, but usually many more pulses are recorded to better see the details. The line widths are around 10 kHz and have been attributed to the Doppler shift caused by the angular spread



FIG. 2. Diagram of the large-cavity, pulsed-beam Fourier transform spectrometer (Arizona). (1) Microwave synthesizer hp 8665B, (2) power divider, (3) SPDT microwave switch, (4) microwave cavity, 48" diameter mirrors, (5) low-noise microwave amplifier MITEQ, (6) microwave mixer, (7) Stanford Research Systems preamplifier, (8) multichannel digitizer PICO ADC-212/50.

TABLE IV. Propiolic acid–formic acid (¹³C) data showing the tunneling splitting pairs. Units are Obs. (MHz), Obs. – calc. (kHz).

		Pro-FA	$^{13}C(0^{+})$	$Pro-FA^{13}C(0^-)$		
J' _{KaKc}	$J^{\prime\prime}{}_{KaKc}$	Frequency	Obs. – calc.	Frequency	Obs. – calc.	
30,3	20,2	5120.198	-8	5121.209	-8	
31,2	$2_{1,1}$	5308.486	4	5308.989	<1	
41,4	31,3	6592.647	-2	6594.586	2	
40,4	30,3	6817.054	-3	6818.453	-3	
41,3	31,2	7075.435	<1	7076.122	-2	
51,5	41,4	8236.985	-1	8239.428	3	
50,5	40,4	8505.529	-2	8507.359	<1	
5 _{1,4}	4 _{1,3}	8840.141	<1	8841.025	3	
61,6	51,5	9878.904	6	9881.850	-2	
60,6	50,5	10183.744	2	10 186.052	1	
61,5	51,4	10601.948	1	10 603.039	1	

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FIG. 3. The 1731.834 MHz line of the propiolic–formic acid complex (average of 35 000 pulses), data taken with the large-cavity, FTMW spectrometer (Arizona).

of the molecular jet. Line positions can be measured with uncertainties of 0.2–1.5 kHz. An example spectrum is given in Fig. 3. The frequency scale is MHz relative to 1731.730 MHz. More details on the new spectrometer can be found in Ref. 22.

B. Experiments at the University of Virginia

The experimental setup used for some measurements and the double-resonance work consisted of a Balle-Flygare type Fourier transform microwave spectrometer²³ based on the recent NIST (Ref. 24) design. The carrier gas (80/20 Ne/He) was passed through a steel sample cell placed outside the vacuum chamber which contained 4:1 mixture of propiolic acid to formic acid. The nozzle (General Valve series 9, 1mm orifice) was heated to 50 °C.

Double resonance spectroscopy measurements of the type described by Nakajima et al.25 were performed. This technique was essential to making confident transition assignments due to the large number of species present in the expansion and the weak b-type transition intensities for the ProOD-FAOD complex. The cavity FTMW spectrometer was tuned to the frequency of an a-type transition of the complex. The double resonance pulse was generated by a microwave synthesizer and amplified to 1 W with a transistor-transistor logic-controlled solid-state amplifier. A microwave horn antenna was placed orthogonal to the microwave cavity axis, through which the double resonance pulse was broadcast. The double resonance pulse immediately followed the cavity excitation pulse and had a duration of 4 μ s. The double resonance source was then scanned in frequency in discrete steps of 50 kHz while recording the intensity of the monitored transition. Any significant depletion in this monitored signal intensity was attributed to coherence destruction due to the double resonance pulse being resonant with a transition sharing a quantum state with the monitored transition. It should be noted that 100% modulation was not possible in this experiment because the a-dipole 0^+ and 0^- transitions for this species are not resolved at the resolution of this spectrometer, and only one of the component transitions was resonant with the double resonance pulse at any single frequency. Search scans were started from the origin of the predicted transition frequency without tunneling splitting until such depletion was



FIG. 4. The FTMW-pulsed-MW double resonance spectra are shown for the pure rotational transition 7_{07} - 6_{06} 0⁻ centered at 11 997.3572 MHz (black) and the tunneling-rotation transition 7_{17} 0⁺- 6_{06} 0⁻ centered at 15 347.5405 MHz (grey). The center frequency of each double resonance spectrum was subtracted to put both double resonance peaks at 0 frequency. This was done to directly compare the linewidths of the two measurements. The linewidth is an indicator of line strength. These measurements were performed by monitoring the amplitude of 6_{06} 0⁻- 5_{05} 0⁻ (10 311.3665 MHz) rotational transition with the FTMW cavity, while the pump frequency of a second microwave source, radiated from a standard gain horn, was scanned across the desired rotational transition with 10 averages at each step and 10 kHz step size for tunneling-rotation transitions. For both spectra the double resonance pulse had a duration of 5 μ s and a power level of 7.3 W.

found. Representative double resonance spectra are shown in Fig. 4.

The dipole moment was determined using a chirpedbroadband spectrometer²⁶ with a stark cage²⁷ that was calibrated with OCS (0.1% in H₂/Ar) at 12 kV giving a field of 464.4 V/cm. The propiolic acid–formic acid sample was the same as described above and the measured transition frequencies with electric field on and off are given in Table III.

IV. DATA ANALYSIS AND RESULTS

A. Microwave spectrum

The propiolic acid–formic acid heterodimer is a nearprolate asymmetric top which exhibits splittings of the rotational transitions due to proton tunneling effects. The a-dipole spectrum consists of pairs of transitions that are separated between 1 and 3 MHz that can be fit to two sets of rotational constants which have been assigned to the tunneling states, 0⁺ and 0⁻. There were 138 a-type transitions and 28 b-type assigned to the normal isotopologue, HCOOH… HOOCCCH and consist of $0^+ \rightarrow 0^+$, $0^- \rightarrow 0^-$, $0^+ \rightarrow 0^-$, and $0^+ \rightarrow 0^-$ transitions as shown in Fig. 5. These transitions provide information on the A, B, and C rotational constants and centrifugal distortion constants for the upper and lower tunneling states.

The intensities of the a-type transitions must follow the spin statistics that result from having a pair of hydrogen nuclei which is equivalent with respect to a 180° rotation about the symmetry axis. Tunneling followed by a 180° rotation results in exchange of the H nuclei in the propiolic–formic acid dimer. The hydrogen atoms obey Fermi-Dirac statistics which require the total wave function to be anti-symmetric. The total wave function is comprised of the electronic, vibrational, rotational, and spin wave functions and P is the permutation



FIG. 5. The 0^- (a) and 0^+ (b) tunneling doublets for the $7_{07}-6_{06}$ pure rotational transitions and the (c) $6_{06}0^-$ and $7_{17}0^+$ tunneling-rotation transition observed by FTMW spectroscopy are shown. The spectra were recorded with 400 signal averages at a 10 Hz repetition rate. Panels (a) and (b) illustrate the 3:1 intensity ratio for changing vibrational state only.

operator which exchanges the hydrogen atoms (x and y).

$$\mathbf{P}_{\mathbf{x}\mathbf{y}}\Psi = \psi_e \psi_v \psi_r \psi_s = -\Psi. \tag{1}$$

For two hydrogen atoms there are three symmetric spin functions (+) and one anti-symmetric spin function (-). This results in a 3:1 intensity ratio between 0⁺ and 0⁻ doublets when K_a is odd and 1:3 when K_a is even as shown in Fig. 6. In the prolate rotor limit, K_a (even or odd) determines whether the rotational wave function is symmetric or anti-symmetric with respect to the 180° rotation about the symmetry axis.²⁸ The b-dipole combination transitions connect different tunneling level states 0⁺ \rightarrow 0⁻ or 0⁻ \rightarrow 0⁺ and these transitions provide direct information on the tunneling splitting.

TABLE V. Measured transitions of ProOD-FAOD. Units are Obs. (MHz), Obs. – calc. (kHz).

J _{KaKc}	$\mathbf{v}^{\prime\prime}$	J _{KaKc}	\mathbf{v}'	Obs.	Obs. – calc.
414	0	3 ₁₃	0	6614.545	-0.4
404	0	303	0	6846.504	1.7
413	0	312	0	7116.369	1.8
515	0	414	0	8263.894	-0.6
5 ₀₅	0	404	0	8540.464	-2.4
514	0	413	0	8890.790	-1.5
616	0	5 ₁₅	0	9910.536	0.7
606	0	5 ₀₅	0	10 222.995	0.9
7 ₁₇	0	606	1	15 329.450	85.3
717	1	606	0	15336.074	< 0.1
616	0	505	1	13998.200	-84.8
616	1	505	0	14 005.000	6.2

The C-13 formic substituted isotopologue spectrum also consisted of pairs of lines which indicated tunneling similar to the parent but only the a-type transitions were observed. The ¹³C data is listed in Table IV and the centrifugal distortion constants were fixed to the parent values of the lowest vibrational state.

The deuterated isotopologue data has provided a valuable contribution for the analysis for the concerted proton exchange in the propiolic–formic complex. The ProOD-FAOD a-type dipole spectrum was measured first at the University of Arizona. To measure the tunneling splitting in the doubly deuterated complex, microwave-microwave double resonance in a cavity FTMW spectrometer was used at the University of Virginia, as described above. The transitions are given in Table V. Using this method four b-type transitions (7₁₇⁻- 6_{06}^{+} , 7₁₇⁺- 6_{06}^{-} , 6_{16}^{-} - 5_{05}^{+} , and 6_{16}^{+} - 5_{05}^{-}) were measured, which yielded a tunneling splitting of 3.35(2) MHz. Representative spectra are shown in Fig. 7.



FIG. 6. The alternating 3:1 intensity pattern is observed for the different Ka and vibrational states.

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FIG. 7. Detection of b-type transitions in the OD/OD isotopologue of formic acid–propiolic acid complex. (a) Microwave-microwave double resonance measurement. The 6_{06} - 5_{05} transition of the complex was monitored in the FTMW cavity. The double resonance frequency was moved in steps of 50 kHz, and 100 signal averages were acquired at each frequency. The two transitions are each offset by ~3.4 MHz from the calculated b-type transition frequency without tunneling included. (b) A b-type transition measured in single resonance on the FTMW cavity. For this spectrum, 10 000 signal averages were acquired. The transition is doubled due to the coaxial arrangement of the microwave source and the molecular beam. The transition at slightly lower frequency than the b-type transition is due to a different species in the sample.

Only one set of rotational constants was observed for the isotopologues that contain single deuterium substitution for either hydrogen-bonding proton 1 or 2, Pro-FAOD, and ProOD-FA. A search for another set of possible splitting transitions was performed and none were observed. The btype transitions for these singly deuterated isotopologues were measured and found to fit a ground state only spectrum with two b-type transitions observed by double resonance and are given in Table VI for each. The transitions were fit with the "center of gravity" of the unresolved deuterium splitting assigned to the transition frequency and spectroscopic constants are reported in Table VII. Weak signals were obtained with the isotopologue DCOOH \cdots HOOCCCH and no tunneling doublets were observed. We may speculate that the upper tunneling state transitions were not observed for this isotopologue because of

		Pro-1	FAOD	AOD ProOD-FA		Pro-	FACD	Pro-FAODCD	
J' _{KaKc}	J" _{KaKc}	Obs	Obs. – calc.	Obs	Obs. – calc.	Obs	Obs. – calc.	Obs	Obs. – calc.
31.3	21.2	4990.429	-1	4979.931	-8			4873.273	0
30,3	20,2					5059.377	0		
31,2	21,1	5365.113	6	5352.602	6				
41,4	31,3	6651.259	0	6637.306	3	6518.853	-3		
40,4	30,3	6882.509	0	6867.432	0	6736.415	_9	6716.320	-4
42,3	32,2			6888.464	0				
42,2	32,1	6926.922	1	6911.304	2				
41,3	31,2	7150.724	5	7134.075	4			6970.767	0
51,5	41,4	8309.898	1	8292.506	3	8144.944	-6	8115.342	0
5 _{0,5}	40,4	8585.927	1	8567.293	3	8405.498	6	8379.865	-5
5 _{2,4}	42,3	8626.840	0						
5 _{2,3}	42,2	8672.939	-1	8653.242	-1				
5 _{1,4}	41,3	8933.861	2	8913.106	0				
61,6	5 _{1,5}	9965.893	0	9945.092	-1	9768.731	20		
60,6	50,5	10278.184	-3	10256.124	1	10064.792	14	10033.314	-2
61,5	51,4	10713.820	-2	10 689.005	-1				
71,7	61,6	11618.860	0	11 594.690	0				
70,7	60,6	11957.579	1	11 932.232	-1	11712.715	-11		
5 ₁₅	404	12763.78 ^a	-2						
616	5 ₀₅	14 143.75 ^a	2	14 134.85 ^a	16				
717	606	15 473.45 ^a	-16						

TABLE VI. Summary of measured transition frequencies (MHz) and fit deviations [Obs. - calc. (kHz)] for the deuterium-substituted isotopologues.

^aAccuracy good to ± 50 kHz.

TABLE VII. Rotational and distortion constants for measured isotopologues of the propiolic-formic dimer. The square brackets indicate parameters that were fixed to values obtained for the normal isotopologue fit of 0^+ .^a

	$Pro-FA^{13}C(+)$	Pro-FA ¹³ C (-)	Pro-FAOD	ProOD-FA	Pro-FAODCD	Pro-FACD
A (MHz)	5987.5(4)	5987.4(3)	5912.92(1)	5918.65(1)	5920(5)	5898.2(8)
B (MHz)	915.2551(4)	915.2604(3)	925.658(1)	923.4004(7)	901.600(2)	903.130(3)
C (MHz)	794.3132(4)	794.6304(3)	800.753(1)	799.1699(9)	782.699(2)	786.026(1)
$\Delta_{\rm J}$ (kHz)	[0.12(3)]	[0.12(3)]	0.07(1)	0.054(8)	0.12(7)	[0.12(3)]
$\Delta_{\rm JK}$ (kHz)	[-5.0(5)]	[-5.0(5)]	0.8(2)	0.6(1)	-6(3)	[-5.0(5)]
$\delta_{\rm J}$ (kHz)	[0.05(1)]	[0.05(1)]				[0.05(1)]
$\delta_{\rm K}$ (kHz)	[52(5)]	[52(5)]				[52(5)]
ϕ_{ik} (kHz)	[-0.15(2)]	[-0.15(2)]				[-0.15(2)]
N	11	11	18	18	7	8
σ (kHz)	4	3	3	7	5	13

^aUncertainties refer to the last digit and are type b coverage factor k = 2.

poorer signal-to-noise due to lower sample quality and quantity.

B. Fitting the microwave spectra

The Hamiltonian used for fitting the spectra contains the rotational and distortion constants, $H_{rot} + H_{cd}$, plus two additional terms, $H_{tun} + H_{int}$, the tunneling splitting energy splitting for the ground vibrational state (ΔE_{01}) plus the vibration-rotation interaction (sometimes called "axisswitching") term (F_{ab}). The fitting program was Herb Pickett's SPFIT (Ref. 13) with Watson's A representation, including the vibration-rotation term, $F_{ab}(P_a P_b + P_b P_a)$, (Pickett code 610001), where F_{ab} and ΔE_{01} were adjustable parameters in this fit. The F_{ab} term was not fit for the doubly deuterated ProOD-FAOD because only one set of a-type transitions were observed. The values for the adjustable parameters determined from the global fit to the normal-isotopomer Pro-FA data are given in Table VIII.

TABLE VIII. Molecular parameters obtained from the global fit of 166 transitions (138 a-type and 28 b-type) proton-proton exchange and 12 transitions (8 a-dipole and 4 b-type) deuterium-deuterium exchange. H–H refers to the normal isotopologue and D–D refers to the isotopomer with D substitution at both hydrogen-bonding sites.^a

Constant	H–H	D–D
A ⁰⁺ (MHz)	6005.289(8)	5824.53(2)
A^{0-} (MHz)	6005.275(8)	
B^{0+} (MHz)	930.553(8)	921.5311(2)
B ⁰⁻ (MHz)	930.546(8)	
C ⁰⁺ (MHz)	803.9948(6)	796.0334(3)
C ⁰⁻ (MHz)	803.9907(5)	
ΔJ^{0+} (kHz)	0.075(1)	0.086(4)
ΔJ^{0-} (kHz)	0.076(1)	
$\Delta_{\rm JK}{}^{\rm 0+}$ (kHz)	0.70(2)	2.7(1)
Δ_{JK}^{0-} (kHz)	0.69(2)	
δ_J^{0+} (kHz)	0.011(1)	
δ_J^{0-} (kHz)	0.008(1)	
$\Delta E (MHz)$	291.428(5)	3.35(2)
F _{ab} (MHz)	-120.7(2)	
σ (kHz)	4.0	27.0
N	166	12

^aUncertainties refer to the last digit and are type b coverage factor k = 2

C. Structure determination

The B and C rotational constants for the 6 isotopologues (using only the 0⁺ state) are listed in Tables I and VII and were used in a structural fit to determine the three structural parameters shown in Fig. 8. The parameters used in the leastsquares regression analysis were the monomers' centers of mass separation, R_{c.m.}, rotation angle for the formic monomer about its centers of mass, θ , and the formic acid angle, ε , <(C–O4–H2). Attempts to include other parameters such as rotation of propiolic about its center of mass or the propiolic <(C–O1–H1) angle were unsuccessful due to correlation effects and lack of more propiolic acid isotopologues.

Several different fits were performed using different fixed angles of propiolic acid <(C-O1-H1) to compare with Fit 1, where <(C-O1-H1) was fixed at the monomer value of 106° ,²⁹ and ε , R_{c.m.}, and θ were fit. The starting point for the structural analysis was to calculate initial dimer coordinates using the experimental gas phase structures for the propiolic and formic acid monomers and arranging the relative orientations to form two typical hydrogen bonds.

Results from the structural fits indicate that the <(C-O4-H2) of formic acid may open up from the gas phase determined monomer angles of 107° .³⁰ The propiolic acid angle, <(C-O1-H1), was fixed at different values to explore combinations that may result in a better fit because the two angles could not be fit simultaneously. A summary of the results is in Table IX. When the propiolic acid angle is held at the monomer value of 106° , the angle in formic acid, <(C-O4-H2), was fit to 118° , much different than the reported monomer value of 107° . Using 109° for the <(C-O1-H1)



FIG. 8. Structural fit parameters include the distance between the centers of mass of the monomers ($R_{c.m.}$), the angle ε , <(C–O4–H2) of formic acid, and the rotation of formic acid about its center of mass, θ .

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Propiolic acid<(C–O1–H1) ^b	Formic acid <(C–O4–H2) ^{a,c}	Fit standard deviation (MHz)
106	118(16)	1.88
109	116(16)	1.85
109	109 ^b	1.88
106	106 ^b	1.97

TABLE IX. Summary of results from the structure fits with the propiolic acid C–O–H angle fixed and formic acid C–O–H angle, ε , varied. R_{c.m.} is 3.878(2) Å and θ is +5.0°(2) from the MP2 calculated starting structure (counterclockwise).

^aUncertainties refer to the last digit and are type b coverage factor k = 2.

^bValue fixed in the fit.

°Result from fit allowed to vary.

angle, result is 116° for the $\langle (C-O4-H2) \rangle$ angle and gives the lowest obtained standard deviation of $\sigma = 1.85$ MHz. Using 109° for both angles results in a standard deviation of $\sigma = 1.88$ MHz and is more consistent with the 109.4(2) reported by Martinache et al.³¹ with the gas phase dimer of CF₃COOH–HCOOH. The fit standard deviation reported for the various fits in Table IX is essentially the same, indicating that the structural fit is not very sensitive to these angles and some correlation is present. In Fit I, using the monomer <(C-O1–H1) angle, the coordinates obtained in the structure fit are very different than those obtained with the Kraitchman analysis for the a coordinate of the H1 atom. The results of the Kraitchman analysis to obtain atomic coordinates are given in Table X. The structure that results from Fit I gives an asymmetric (O1-H1...O3) and (O2...H2-O4) distances of 1.57 Å and 1.77 Å, respectively.

D. One-dimensional potential well tunneling calculation

The double well potential is a well-known problem and if modeled using a potential of the form $V = a^*X^4 + b^*X^2$, solutions for the energy levels can be obtained using Kisiel's ANHARM program that is based on the work of Laane.³² The dimensions for the double well are obtained from the structure fit. The O–O distance was determined to be 2.7 Å and the O–H distance is taken to be 1 Å. Using this information the protons are 0.35 Å from the barrier maximum. Calculated values for the barrier height ranged from 2000 cm⁻¹ using DFT to 3800 cm⁻¹ using MP2 with the basis set 6-311++G**. There are three independent parameters in this double well problem: the reduced mass, the barrier height, and the position of the two minima. To obtain a barrier height of 3800 cm⁻¹, as predicted using MP2 with 0.35 Å as the

TABLE X. Key atomic coordinates from the Kraitchman analysis and Structure Fit I. Fit I is a three parameter fit, $R_{c.m.}$ using θ and ε with the propiolic angle < (C–O1–H1) fixed at 106°.^a

	K	St	Structure Fit I				
Atom	а	b	с	а	b	с	
C1	2.7(3)	0.054(7)	0.12(2)	2.74	-0.10	0.0	
H1	1.6(1)	1.00(9)	0.063(6)	0.41	-1.05	0.0	
H2	1.1(2)	1.0(2)	.07(1)	1.32	1.08	0.0	
H3	3.72(2)	0.544(3)	1.019(6)	3.84	-0.11	0.0	

^aUncertainties refer to the last digit and are type b coverage factor k = 2.

spacing from the barrier maximum to the minimum, the equation for the potential has the form $265,000*X^4-65115*X^2$. The reduced mass was estimated to be 2 amu. This information was transformed in the reduced coordinates as described by Laane giving, $V(Z) = 141.5^{*}(-10.1^{*}Z^{2} + Z^{4})$. The results of the ANHARM calculation give the difference between the first two energy levels as 0.0034 cm⁻¹, or 243 MHz. Using these parameters with a reduced mass of 4 amu gives 0.00002 cm⁻¹, 0.3 MHz. The measured splitting for the Pro-FA isotopologue with hydrogen-bonding sites doubly deuterated is 3.35(2) MHz and is an order of magnitude higher than that predicted with this model. Other calculations using a WKB approximation model also did not yield accurate quantitative results. So it is apparent that these simple onedimensional models are not adequate to accurately describe the concerted proton tunneling. This is likely due to the large amplitude of the tunneling motion, coupled with significant motion of the heavy atoms during the tunneling motion.

E. Dipole moment

The a-type dipole moment of the formic acid-propiolic acid complex was measured by observing Stark effect shifts, using a Stark cage of the design of Emilsson *et al.*,²⁷ in which the electrodes consist of aluminum wires. The electrodes are connected by a series of 20 M Ω resistors which serve as a three-dimensional voltage divider to provide good field homogeneity. Two high-voltage power supplies were connected to the two electrodes with voltages of +6 kV and -6 kV. The field was calibrated using the J = 1-0 transition of OCS, which has a known dipole moment of 2.3851×10^{-30} C m (0.71519 D).³³ A total of 300 000 FIDs were acquired with the external electric field applied, using the 7.0-18.5 GHz CP-FTMW spectrometer design that has been described in Ref. 26. The field strength was determined by the Stark shift of OCS, which was observed in the same spectrum as the formic acid-propiolic acid dimer, guaranteeing that the two species were influenced by the same electric field.

Panel (a) of Fig. 9 shows the zero-field and Stark-shifted spectra of OCS. The Stark cage is oriented so that the transitions obey $\Delta M = 0$ selection rules, but a small $\Delta M = 1$ component is observed. In panel (b), the 5₁₅-4₁₄ transition of the formic acid–propiolic acid dimer is shown with and without the applied Stark field, compared to simulations of the spectra of the two states with the fit dipole moment. A total of 9 transitions of the 0⁺ species, and 10 transitions of the 0⁻ species,

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FIG. 9. Dipole moment determination of the formic acid–propiolic acid complex. (a) Calibration of the electric field using OCS. (b) The 5_{15} - 4_{14} transition of formic acid–propiolic acid, showing the spectrum with and without an applied electric field, compared to simulations of the two states using the fit dipole moments.

all a-type, were fit using EXCEL with second order Stark coefficients from SPCAT (SZK).¹³ The dipole moments of the two states were fit separately, and their values agree within experimental uncertainty, $\mu_a = 0.584(8)$ D, $1.95(3) \times 10^{-30}$ C m (2σ error limits) for the 0⁺ species, and $\mu_a = 0.576(14)$ D, $1.92(5) \times 10^{-30}$ C m (2σ error limits) for the 0⁻ species. The measured shifts and results of the analysis are shown in Table III. This value is substantially lower than that calculated by the electronic structure theory, 2.67×10^{-30} C m (0.80 D) at a MP2/6-311++G(d,p) level of theory.

The relative intensities of the b-type tunneling-rotation transitions and the stronger a-type transitions were measured in order to estimate the dipole moment component along the b principal axis. Broadband CP-FTMW spectroscopy was used for this measurement because of the accurate relative intensities of this spectrometer.²⁶ A total of 350 000 FIDs were acquired, using three pulsed nozzles. The relative intensities of a-type to b-type transitions were observed to be \sim 65:1, accounting for the transition dipole matrix elements of the observed transitions. The transition moment of the b-type transitions is doubled from the permanent b-type dipole moment due to the inversion of μ_b between the initial and final states. If one makes the simplifying assumption that the b-dipole intensities only depend on the rotational transition matrix element, then the ratio μ_a : μ_b is estimated to be 16:1 (giving, μ_b $\sim 0.035 \text{ D}, 0.12 \times 10^{-30} \text{ C m}$). This determination depends on assuming the additional term

$$(1/2)[\langle 0^+ | \mu_b | 0^- \rangle + \langle 0^- | \mu_b | 0^+ \rangle]$$

(Eqs. (14–85) of Ref. 34) does not make a significant contribution to the transition dipole matrix element. The relative intensities of a- and b-type transitions are shown in Fig. 10.

V. DISCUSSION

The first evidence of a concerted proton exchange between two carboxylic acids measured in the microwave region between propiolic acid and formic acid was reported earlier⁸ and we have now extended the work with isotopic studies to obtain a partial gas phase structure. In addition, many more transitions were measured for the parent isotopologue using three different spectrometers spanning 1–21 GHz. Microwave double resonance measurements were useful in confirming some common levels involved in both a-dipole and b-type transitions. The intensities of the a-type transitions follow the spin statistics that result from having an equivalent pair of hydrogen nuclei which are exchanged by a 180° rotation about the a-axis. This also supports the $C_{2v}(m)$ symmetry designation for this complex. This predicted ratio of intensities was observed for different K_a states.

The lack of observed tunneling splittings upon deuteration of either the H1 or H2 atoms gives strong evidence for assigning observed splittings to the concerted proton tunneling. This lack of observed tunneling splittings for these isotopologues support the concerted proton exchange since the $C_{2v}(m)$ symmetry is not preserved as in Pro-FA and ProOD-FAOD. Additionally, microwave double resonance was used to measure two b-dipole transitions for two isotopolgues.

The structural information obtained in this work reveals a tightly bound heterodimer that has slightly asymmetric hydrogen bond distances. Calculations using MP2/aug-cc-pVDZ



FIG. 10. CP-FTMW spectrum of Pro-FA. The strongest transitions are the atype pure rotational transitions. The inset shows a b-type tunneling-rotation transition. The relative intensities between the a- and b-type transitions were used to estimate the ratio of the dipole moment components $\mu_a : \mu_b$.

and CCSD/6-311++G^{**} give a structure similar to that obtained from the structural fit with both <(C–O–H) angles at 109°. Substitution with ¹⁸O at O1 or O2 and ²H at H3 would help refine parameters defining the orientation of propiolic acid in the dimer. In this study there is only one substitution on propiolic acid and three on formic acid. This is thought to be the reason that the structural fit results were fairly independent of the rotation of propiolic acid about its center of mass. Fit I improves slightly with an increase of <(C–O1–H1) from the monomer value of 106° and more isotopic substitutions may make this angle more reliably determined.

The one-coordinate double well potential model for the concerted proton tunneling has been tested for this system. The reduced mass and the potential barrier height are the most significant variables to be determined. Both the structure fit and calculations give the distance of 0.70 Å as the distance between well minima. The energy difference between the ground state and the first vibrational state was experimentally determined to be 291.428(5) MHz. Using this information and a reduced mass of 1 amu, the barrier height is computed to be close to 8000 cm⁻¹. Calculations with MP2/6-311++G** and B3PW91/6-311++G** give barrier heights between 2000 and 4000 cm⁻¹. A reduced mass of 2 amu more accurately reproduces the energy difference of 240 cm⁻¹ with a barrier height of 3800 cm⁻¹ using this simplified model.

The double proton transfer time for the ground state has been determined to be 1.71567(2) ns using the following relationship,³⁵ $\tau = 1/2\Delta_0$. The unambiguous determination of the double proton transfer time should aid theory in accurately predicting the proton transfer time. The proton transfer time in formic acid dimer has been previously determined by Madeja *et al.*⁴ to be either 5.8 ns or 1.3 ns for the ground state. The calculations by Smedarchina *et al.*⁹ indicate that a 1.3 ns transfer time is proper assignment for the ground state which would result in very similar proton transfer times for the Pro-FA and (HCOOH)₂ systems.

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