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Gas phase measurements of mono-fluoro-benzoic acids and the dimer of 3-fluoro-benzoic acid

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The microwave spectrum of the mono-fluoro-benzoic acids, 2-fluoro-, 3-fluoro-, and 4-fluoro-benzoic acid have been measured in the frequency range of 4-14 GHz using a pulsed beam Fourier transform microwave spectrometer. Measured rotational transition lines were assigned and fit using a rigid rotor Hamiltonian. Assignments were made for 3 conformers of 2-fluorobenzoic acid, 2 conformers of 3-fluorobenzoic acid, and 1 conformer of 4-fluorobenzoic acid. Additionally, the gas phase homodimer of 3-fluorobenzoic acid was detected, and the spectra showed evidence of proton tunneling. Experimental rotational constants are $A(0^+) = 1151.8(5)$, $B(0^+) = 100.3(5)$, $C(0^+) = 87.64(3)$ MHz and $A(0^-) = 1152.2(5)$, $B(0^-) = 100.7(5)$, $C(0^-) = 88.85(3)$ MHz for the two ground vibrational states split by the proton tunneling motion. The tunneling splitting (ΔE) is approximately 560 MHz. This homodimer appears to be the largest carboxylic acid dimer observed with F-T microwave spectroscopy. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4917031>]

I. INTRODUCTION

The spectroscopy of carboxylic acids in the gas phase has been studied to characterize the structure and dynamics of hydrogen bonding. Hydrogen bonds are not simply static structural features, but can exhibit concerted proton tunneling which produces splittings of the energy levels. Since the publication of results for the formic acid homodimer measurements in the infrared by Havenith *et al.*,¹ there have been studies made on heterodimers in the microwave region and one study on a homodimer. A permanent dipole moment allows the study by rotational spectroscopy and the following systems have been reported: propionic acid-formic acid,²⁻⁴ acetic acid-formic acid,⁵ formic acid-fluoroacetic acid,⁶ formic acid-trifluoroacetic acid, and acetic acid-trifluoroacetic acid,⁷ formic acid-benzoic acid,⁸ and more recently the dimers of acrylic acid with fluoroacetic acid.⁹ The analysis of the homodimer of acrylic acid¹⁰ demonstrated proton tunneling amongst identical molecules. The results provided by the analysis of gas phase dimers by microwave spectroscopy are twofold: (1) accurate gas phase structures of the dimer can be determined and (2) provide a description of the dynamics regarding concerted proton tunneling. This provides information on the tunneling potential energy surface and barrier height. The concerted proton exchange can be modeled using a double well potential¹ in which the first two vibrational states are very close in energy and are usually denoted as 0^+ and 0^- as a split ground state. The rotational constants of the states are usually very close but not identical, creating closely spaced doublets. The resolution of rotational spectroscopy is usually sufficient to fully resolve the doublets to allow fitting

of each state's rotational constants and, if enough transitions or if different dipole allowed transitions are measured, the $\Delta E(0^- - 0^+)$ (tunneling splitting) and F_{ab} (axis-switching) term¹¹ can be determined. Pulsed beam microwave spectroscopy with a Fabry-Perot cavity offers excellent resolution and this allows resolved measurements for different conformers,¹² multiple isotopologues,¹³ and various excited vibrational states.¹⁴ Small changes in the geometries for the lowest two tunneling states cause subtle changes in the rotational constants that lead to distinct spectra. It has been suggested that the concerted exchange of protons may also occur in the base pairs of DNA¹⁵ and this may have consequences for genetic mutations.¹⁶

Often, the monomers have well characterized microwave spectra that help in identifying the monomer signals, facilitating the correct assignment of the weaker dimer lines. In an effort to aid assigning lines for dimers of the singly fluorinated benzoic acids, we first studied the gas phase spectra of the monomers. We report the gas phase measurements of new rotational transition frequencies for the monomers of 2-F-benzoic acid (or *o*-fluorobenzoic acid), 3-F-benzoic acid (or *m*-fluorobenzoic acid), and 4-F-benzoic acid (or *p*-fluorobenzoic acid). The laser-induced fluorescence (LIF) spectra of homodimers of *o*-fluorobenzoic acid and heterodimer of *o*-fluorobenzoic acid and benzoic acid have been reported by Nandi *et al.*¹⁷ The monomers were not clearly characterized in the LIF study, and we now provide definitive measurements and identification of three distinct monomers present in the gas phase for 2-fluoro-benzoic acid. The only previous reports of experimental work on 3-fluoro-benzoic and 4-fluoro-benzoic acids are the crystal structures reported by Pattison *et al.*¹⁸ and Colapietro.¹⁹ Although the heavy atom structures of the monomers were reported for *m*-fluorobenzoic acid, the two configurations which depend on the relative

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FIG. 1. The three fluorine positions for mono-substituted positions on benzoic acid as observed in this study: I (2-fluorobenzoic acid), II (3-fluorobenzoic acid), and III (4-fluorobenzoic acid).

position of OH and F could not be distinguished. Both of our new studies revealed planar molecules, very similar to the solid state structures and to the other substituted benzoic acid molecular structures. The gas phase homodimer of 3F-benzoic acid was measured and exhibited strong evidence for concerted proton tunneling. Two distinct sets of rotational transitions and an approximate tunneling frequency were obtained.

II. METHODS

A. Experimental

Measurements in the 4–14 GHz range were performed using a Fourier transform microwave spectrometer, with several modifications that will be described. This spectrometer was described previously.^{20,21} The microwave pulses, for microwave transmit, tune the cavity and trigger the acquisition, and valve pulses are produced by custom boards that use transistor-transistor logic (TTL) off-the-shelf chips. The control of the spectrometer and these pulses is made in either manual or computer controlled mode. An automated scanning algorithm was utilized to automatically perform long scans. This was accomplished by creating a mode following procedure that provides reliable tracking of the microwave stimulating frequency with the cavity mode frequency. This is done by sweeping the microwave generator frequency and finding the mode minimum, which was detected by the reflection of microwave radiation through a circulator and detected with a diode detector and digitized using a measurement computing DAC. The initial microwave test signal for cavity tuning is a 50 ms pulse, and the cavity reflection is integrated (with an op-amp) to provide a “cavity

response” reflected signal. The software, written in C++, searches for the minimum reflected signal and sets the frequency for data acquisition. The data are recorded in the time domain, along with all the important information such as stimulation frequency, number of acquisitions, and sampling rate. A pulse-width modulated control circuit is used to move the motor. Optimized pulses are sent to the motor give about 250 kHz steps of the cavity frequency. This usually gives about 3–5 free induction decay (FID) molecular responses for different steps, from the molecular resonance at a given frequency. For stronger signals, more responses from the same line are obtained from different frequency steps in the scan. The individual data files are imported to a laboratory written LabVIEW program and processed using a FFT fitting function. An example output is given in Figure 2, which displays “probability of line detection” maps from the dataset. The intensity and phase of the FFT signals are used in the fitting procedure to construct the probability of detection chart (shown in Figure 2), with level controls adjusted by the user. This program is connected to a viewer that allows the user to step through the individual files and analyze individual signals. A general list of frequencies can be obtained, and confirmations of the signals are subsequently performed on the spectrometer (in non-scanning mode). An average frequency and standard deviation are determined for each set and used in the fits. This program (scan data viewer) has been extremely helpful in finding weak lines in the spectra that might have been missed.

Samples of 2-fluorobenzoic acid, 3-fluorobenzoic acid, and 4-fluorobenzoic acid were purchased from Sigma-Aldrich and used as received. Approximately 200 mg was placed into a special glass cell that can be evacuated and maintained under an atmosphere of neon and secured to a pulsed valve. The temperature was maintained at 100 °C by placing the sample cell in a vacuum insulated can with a heating coil. The sample in neon (0.8 atm) was introduced into the spectrometer cavity transverse to the microwave cavity axis at 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. Following the molecular pulse (about 1 ms delay), a $\pi/2$ microwave excitation pulse (1 μ s duration) was sent into the cavity resonator to coherently excite the molecules, using a Herley SPDT microwave switch. The molecular FID signal was transmitted via the same SPDT switch and passed to a Miteq 6–18 GHz low noise amplifier. The deuterated species of each monomer were prepared by mixing equimolar amounts of the monomer with deuterated methanol and letting them exchange overnight. The methanol was removed from the

TABLE I. Experimental and calculated rotational constants for the of 3-fluoro-benzoic acid dimer (Calc—calculated values and QZ—quadruple zeta basis).

MHz	Experimental	Calc-M06HF	Calc-B97D-QZ	Calc-B97D-TZ	Calc-MP2-TZ
A	1151.8(5)	1167.5	1150.2	1148.9	1159.2
B	100.3(5)	98.6	94.5	94.6	96.0
C	87.64(3)	90.9	87.3	87.4	88.6

FIG. 2. Program used to analyze automatic scanning data. Each column is a frequency bin with entries from multiple files (albeit at different frequencies away from the stimulation signal). The color is a probability map based on phase and intensity fitting of the FID to the data. The white lines have high probability of being fit to the FID signal, whereas the blue lines represent low probability of a fit to the FID signal. Three transitions are shown corresponding to the three different conformers of 2-fluorobenzoic acid (I). All three were predicted to arise from a-dipole allowed transitions, 404-303.

sample by pumping with a vacuum. The measurements from these deuterated species were performed using the same techniques as described above.

B. Theoretical methods

Predictions were made using the Gaussian 09 suite²² to optimize the gas phase structure to obtain rotational constants and the total energy. Conformers of each species were calculated, and all bond lengths and angles were optimized without constraints. The basis set 6-311++g(d,p)²³ with the B3LYP²⁴ hybrid functional was used for all the monomer calculations. Rigid potential energy scans were performed for each conformer to scan the energy space for conformer identification, specifically with rotation labeled α in Figure 1. It was also anticipated that hydrogen bonding could cause rotation of the O-H group about the C-O bond depicted as the β -rotation in Figure 1, and so energy scans using this angle were also performed. At each minimum, a full optimization was performed and rotational constants were

FIG. 3. Rigid scan performed along the α -rotation where two minima were found. A rotation of the angle β about the C-O bond revealed another minimum which involves hydrogen bonding.

FIG. 4. The 3 observed conformers for 2-fluorobenzoic acid, (a) conformer 1, (b) conformer 2, and (c) conformer 3.

TABLE II. Experimental and calculated rotational constants and predicted dipole moments for the parent 2-fluorobenzoic acid as well as the-OD deuterated species.

	Conformer 1 (a)		Conformer 2 (b)		Conformer 3 (c)	
	2FBzAc—15 lines—C 1		2FBzAc-R—17 lines—C2		2FBzAc-F—16 lines—C3	
	Expt.	Calc	Expt.	Calc	Expt.	Calc
$A_{\text{expt.}}/A_{\text{calc}}$ (MHz)	2294.226 2(133)	2287.4	2271.730 30(490)	2264.4	2284.825 50(220)	2281.1
$B_{\text{expt.}}/B_{\text{calc}}$ (MHz)	1210.356 090(620)	1208.8	1212.615 350(600)	1211.4	1210.926 020(336)	1207.6
$C_{\text{expt.}}/C_{\text{calc}}$ (MHz)	793.576 430(580)	790.8	792.268 032(309)	789.2	792.040 188(158)	789.6
N	15	...	17	...	16	...
σ/kHz	2.5		3.7		5.2	
Dipole moments (calculated)	$\mu_a = 2.1$ D		$\mu_a = 2.2$ D		$\mu_a = 5.0$ D	
	$\mu_b = 2.1$ D		$\mu_b = 2.6$ D		$\mu_b = 1.4$ D	
	$\mu_c = 0.0$ D		$\mu_c = 0.0$ D		$\mu_c = 0.0$ D	
ΔE	0 cm^{-1}		235 cm^{-1}		643 cm^{-1}	
	D-2FBzAc—11 lines		D-2FBzAc-R—11 lines		D-2FBzAc-F—15 lines	
$A_{\text{expt.}}/A_{\text{calc}}$ (MHz)	2291.573 30(930)	2284.4	2255.398 11(105)	2247.9	2262.870 95(168)	2258.7
$B_{\text{expt.}}/B_{\text{calc}}$ (MHz)	1180.373 620(550)	1178.7	1183.565 29(159)	1182.2	1201.271 070(590)	1197.7
$C_{\text{expt.}}/C_{\text{calc}}$ (MHz)	780.274 340(390)	777.5	777.910 679(237)	774.7	785.258 163(285)	782.7
N	11	...	11	...	15	...
σ	4.0		32.3		32.3	

predicted. Density functional theory (DFT) methods using the M06HF and B97D functionals available in Gaussian 09 were used for all dimer calculations. The results are shown in Table I. TZ refers to the “triple zeta” basis and QZ to the “quadruple zeta” basis.

III. RESULTS OF CALCULATIONS AND MEASUREMENTS

A. 2-fluoro-benzoic acid (I)

Potential energy scans were performed and two minima were found upon the α -rotation corresponding to two configurations of the planar structure (see Figure 3). Additionally,

the β -rotation where a hydrogen bond ($\text{O}-\text{H} \cdots \text{F}$) is formed also has a minimum in the plane of the heavy atoms of the molecule.

Large frequency scans were performed around the predicted common a-dipole transitions. The $4_{04}-3_{03}$ transitions were predicted using the calculated rotational constants and the SPCAT²⁵ program to be near 7400 MHz. Within the 100 MHz scan, three transitions were observed within 15 MHz of each other. These signals are too close to be the $4_{14}-3_{13}$ transition, which is predicted to about 300 MHz lower in frequency. Similar scans at predicted transitions for $5_{05}-4_{04}$ and $4_{14}-3_{13}$ (as shown in Figure 2) were successfully used in the detection of this triad of signals. A fit was performed using the SPFIT and more transitions were obtained. Transitions were

TABLE III. Experimental and predicted 3F-benzoic acid parent, conformers 1 (left) and 2 (right), and d₁-3F-benzoic acid (lower set) rotational constants and dipole moments.

	Conformer 1 (a)		Conformer 2 (b)	
	Expt.	Calc	Expt.	Calc
$A_{\text{expt.}}/A(\text{predicted})^*$	2636.514 0(320)	2635	2685.085 90(600)	2684
$B_{\text{expt.}}/B(\text{predicted})^*$	937.229 950(670)	934	926.774 41(160)	923
$C_{\text{expt.}}/C(\text{predicted})^*$	691.792 880(560)	689	689.324 84(177)	687
N	7		16	
σ/kHz	1.9		10	
Dipole moment	$\mu_a = 0.5$ D		$\mu_a = 0.2$ D	
	$\mu_b = 0.3$ D		$\mu_b = 2.9$ D	
ΔE	0 cm^{-1}		9 cm^{-1}	
DOOC-3F-Bz	Expt.	Calc	Expt.	Calc
$A_{\text{expt.}}/A(\text{predicted})^*$	2602.243 3(273)	2600	2684.520 20(98)	2684
$B_{\text{expt.}}/B(\text{predicted})^*$	919.647 80(60)	916	903.527 421(300)	900
$C_{\text{expt.}}/C(\text{predicted})^*$	679.854 06(66)	678	676.354 502(274)	674
N	7		7	
σ/kHz	4		11

FIG. 5. 3-fluoro-benzoic acid showing conformer 1 (a) and conformer 2 (b).

measured and assigned for the 3 conformers shown in Figure 4. The measured lines and deviations of lines calculated with the “best fit” parameters are listed in Tables S1, S2, and S3 in the supplementary material.²⁶ The molecular parameters are given in Table II.

The three conformers have been identified as the hydrogen bonded ($\text{O}-\text{H}\cdots\text{F}$) species (2-F conformer 1) and the two hydrogen bonded ($\text{O}-\text{H}\cdots\text{O}$) conformers (2-F conformers 2 and 3) have been predicted to be planar, with the angles α of 0° and 180° . The lowest energy conformer has the hydroxyl group nearest the fluorine atom hydrogen bonded to

the ketone oxygen. The a-dipole moment is largest for the lowest energy conformer. Intensities of the transitions cannot be directly compared due to the differences in populations and dipole moments. The singly deuterated 2-fluorobenzoic acid was analyzed to confirm the assignments of the conformers. Distinct and signature changes in the rotational constants were predicted for the three conformers using the calculated gas phase structures. Three species were observed in the experiment and the fits yielded experimental constants given in Table III. The results for the three species support the assignment of the conformers to the predicted gas phase structures.

B. 3-fluoro-benzoic acid (II)

1. Monomer

Unlike 2-fluorobenzoic acid, 3-fluorobenzoic acid has a change in the dipole moment projection upon change in conformation. The two lowest energy conformers of the ($\text{O}-\text{H}\cdots\text{O}$) hydrogen bonded species are almost equal in energy, separated by 9 cm^{-1} . Most likely, the fluorine is effectively shielded from the carboxylic group and this is supported by a lack of a minimum in the β -rotation angle energy scans. Due to the very different predicted spectra, very long scans were needed to optimally search for and assign spectra for the two conformers. Large scans in the regions 6400-6800 and 7000-7600 MHz were performed covering the predicted frequencies for a-dipole transitions $5_{05}-4_{04}$ and $5_{15}-4_{14}$ and the b-dipole transition $4_{14}-3_{03}$. Using the signal identification software described in Sec. II, signals were observed and fit using the SPFIT software. The preliminary fit allowed rapid detection of many transitions and ultimately seven a-dipole transitions were detected for one conformer, and 16 a-dipole and b-dipole allowed transitions were measured, which could be assigned to the lowest energy structures predicted. The 2 observed conformers are shown in Figure 5. The measured lines and fit deviations for conformers 1 and 2 are given in Tables S4 and S5 (supplementary material).²⁶ The experimental, best fit, and calculated rotational constants and calculated dipole moment components are shown in Table III.

2. 3-fluorobenzoic acid dimer

During the analysis of the long scans for the monomers, weak doublets were observed. These frequencies were not

TABLE IV. Best fit molecular constants obtained from a least squares fit to 52 transitions. 0^+ refers to the lower tunneling state and 0^- to the upper tunneling state. ΔE is the tunneling splitting and F_{ab} the axis-switching term.

State	0^+ Expt.	Calc	0^- Expt.	Calc
A (expt.)/A (predicted)*	1151.75(48)	1167.5	1152.19(50)	1167.5
B (expt.)/B (predicted)*	100.30(45)	98.6	100.68(52)	98.6
C (expt.)/C (predicted)*	87.638(34)	90.9	88.850(34)	90.9
$\Delta E(0^--0^+)$ (MHz)		563.(10)		
F_{ab} (MHz)		73.1(35)		
μ_b		5 D (calculated)		
Number of transitions		52		
σ/kHz		7

FIG. 6. Structure of the 3-fluorobenzoic acid dimer.

present in the predicted spectra for the monomers and could not be assigned to known transitions of either monomer. Guided by calculations of structures and rotational constants for the possible dimers, the weak b-dipole spectrum of the homodimer of 3-fluorobenzoic acid was assigned in the region of 6200–6400 MHz, to the $7_{35}-6_{24}$ transition. Inspection of other regions in the scan led to the identification of three other transitions and a preliminary fit was obtained. Predictions based on the assignments led to measurements of 52 b-dipole transitions which could be assigned to transitions for this homodimer. The two sets of rotational constants are $A(0^+) = 1151.8(5)$, $B(0^+) = 100.3(5)$, $C(0^+) = 87.64(3)$ MHz and $A(0^-) = 1152.2(5)$, $B(0^-) = 199.7(5)$, $C(0^-) = 88.85(3)$ MHz for the two ground vibrational states split by the proton tunneling motion. The tunneling splitting is approximately 560 MHz, and best fit parameters are listed in Table IV. The two states arise from the ground state and first excited tunneling states for the concerted proton tunneling with a double well potential. Similar to the analysis for acrylic acid, the b-dipole allowed transitions between the same vibrational symmetries ($0^+ \rightarrow 0^+$ and $0^+ \rightarrow 0^+$) were measured. These are the stronger allowed transitions. There are potentially much weaker “allowed” vibration-rotation combination lines ($0^- \rightarrow 0^+$ and $0^+ \rightarrow 0^-$) with a-dipole selection rules as were measured for the propiolic-

acid-formic acid dimer.^{2,3} These transitions would provide a more direct measure of ΔE , the tunneling frequency, but are likely too weak to obtain in this large complex. Both acrylic acid-homodimer and 3F-benzoic homodimer have the symmetry axis as the b-axis which is the component of the non-zero permanent dipole. This results in only even pairing of transitions between the same vibrational states for the stronger transitions. Similar to the acrylic acid analysis, if enough transitions are measured, enough information can be gleaned from the rotational spectrum that a fit of the energy separation can be made. This was determined to be 563(10) MHz. The real uncertainty is likely much larger than the listed 10 MHz statistical uncertainty owing to the difficulty of making accurate assignments in a weak, highly congested spectrum. The measured transitions and fit deviations are given in Table S6.²⁶ The dimer is shown in Figure 6. The experimental and calculated rotational constants and calculated dipole moment components are shown in Table IV.

C. 4-fluoro-benzoic acid (III)

Only one conformer was obtained from the scans of 4F-benzoic acid. Full optimization calculations for this molecule showed equivalent rotational constants and energies for the two planar configurations with respect to the β -rotation. The predicted b-dipole spectrum led to scans that targeted the $J_{1,0^-}-(J-1)_{0,1}$ type transitions, with $J = 3, 4$, and 5. Signals were obtained at each J value, and a fit of the rotational constants A and C was made while fixing B . A new prediction was made

FIG. 7. Structure of 4-fluoro-benzoic acid.

TABLE V. Experimental and predicted 4F-benzoic acid parent rotational constants and dipole moments.

$A_{\text{expt.}}/A(\text{predicted})^*$	3856.587 9(53)	3866
$B_{\text{expt.}}/B(\text{predicted})^*$	775.286 71(58)	772
$C_{\text{expt.}}/C(\text{predicted})^*$	645.843 63(33)	644
Dipole moments (calculated)	$\mu_a = 0.1$ D $\mu_b = 1.4$ D	
ΔE	0	
N	7	
σ/kHz	1.3	

and four more transitions were measured. Using the fit results, the $J_{1,0^-} (J-1)_{0,1}$ transitions were predicted within a few megahertz. The $J_{1,0^-} (J-1)_{1,0}$, however, were much farther away from the predictions (e.g., 50 MHz). The predicted rotational constants were very close to those measured values obtained from the fits. The structure is shown in Figure 7. The measured transitions and fit deviations are given in Table S7.²⁶ The experimental and calculated rotational constants and calculated dipole moment components are shown in Table V.

IV. DISCUSSION AND CONCLUSIONS

We report the first high resolution gas phase measurements of three mono-fluorinated benzoic acid isomers with single fluorine substitutions on the aromatic ring. The multiple low energy conformers for 2F-benzoic acid and 3F-benzoic acids were predicted using quantum mechanical models and were detected using the pulse beam microwave spectrometer. The changes in rotational constants with single deuterium substitution provide definitive identification of each conformer. The hyperfine splittings of the lines of the deuterated species, caused by the nuclear spin of deuterium, were not resolved in this study. Only one conformer was predicted for 4F-benzoic acid which is consistent with our measurements and this was assigned and analysed. The rotational constants of the gas phase structures are consistent with the lower energy hydrogen bonded species predicted using the DFT method B3LYP/6-311G⁺⁺. This suggests that hydrogen bonding is the main driving force that lowers the energy for favored configurations.

In the course of scanning for lines for the two conformers of 3F-benzoic acid, lines for the homo-dimer of 3F-benzoic acid were detected. The non-zero b-dipole transitions consist mostly of doublets. The doublet splittings arise primarily for the small differences in rotational constants for two tunneling states, 0^+ and 0^- . The predicted and experimental spectra for this dimer are very congested as might be expected for a near-prolate top with such small rotational constants. Some of the assignments are uncertain but a reasonable fit to the 52 measured transitions was obtained. The approximate tunneling splitting is near 560 MHz with estimated uncertainty (larger than the fit uncertainty) of 100 MHz.

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