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Microwave spectrum and molecular structure parameters for the 1,2-cyclohexanedione (monoenolic)–formic acid dimer

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A R T I C L E   I N F O

A B S T R A C T

The microwave spectrum for the 1,2-cyclohexanedione (monoenolic)–formic acid dimer was measured for four isotopologues in the 4.5–9 GHz range using a Flygare–Balle type spectrometer. Rotational and distortion constants (A, B, C, D_J, D_{JK}) were obtained. Measured rotational constants were used in a least squares fit to determine some of the gas phase structural parameters of the dimer. Rotational constants and distortion constants of the parent isotopologue are $A = 2415.044(18)$ MHz, $B = 543.6907(2)$ MHz, $C = 451.6663(2)$ MHz, $D_J = 0.0220(13)$ kHz, and $D_{JK} = 0.119(31)$ kHz. The experimental hydrogen bond lengths are 1.97 Å, somewhat longer than the values calculated using GAUSSIAN 09 with MP2/6-311++G**.

1. Introduction

There has been substantial interest in doubly and triply hydrogen-bonded complexes since they provide simple models for the hydrogen bonding that exists between the complementary base pairs in DNA. These hydrogen-bonded dimers are not static structures. They have been shown to exhibit proton tunneling dynamics. There have been several doubly hydrogen-bonded dimers in which the structure and proton tunneling have been studied. These dimers include complexes such as propiolic acid–formic acid [1–3] and acetic acid–formic acid [4]. 1,2-cyclohexanedione (1,2-CDO) exhibits tautomerization [5] and the favorable tautomer for forming a dimer with formic acid is monoenolic form. This results in a dimer structure capable of forming two hydrogen bonds similar the above dimers. Since 1,2-CDO is nonplanar, the complex with formic acid is a bit more complex than the above hydrogen-bonded dimers.

2. Microwave measurements

The microwave spectrum was measured in the 4.5–9 GHz range for the hydrogen bonded dimer between 1,2-cyclohexanedione (1,2-CDO) and formic acid (FA). Measurements were made using a transverse beam, pulsed-beam Fourier transform (PBFT) microwave spectrometer [6,7]. Four isotopologues were measured,

including the parent, a single deuterium substitution at H12 on FA, a single deuterium substitution at H14 on 1,2-CDO, and a double deuterium substitution at H12 and H14 on FA and 1,2-CDO respectively. The atom numbering scheme is shown in Figure 1. There were 49 transitions measured in total; 19 for the parent isotopologue, 10 for the single deuterium substitution at H12 on FA, 10 for the single deuterium substitution at H14 on 1,2-CDO, and 10 for the double deuterium substitution at H12 on FA and H14 on 1,2-CDO.

The 1,2-CDO (97%) and FA (98%) samples were purchased from Sigma–Aldrich and were used without further purification. The deuterated FA used was purchased from CDN isotopes (99.2% D) and was also used without further purification. The deuterated 1,2-CDO sample was prepared by mixing equimolar quantities of 1,2-CDO (Sigma–Aldrich, 97%) and MeOD (Cambridge Isotope Lab, Inc., 99%) and letting them exchange overnight. The MeOH was removed from the mixture under vacuum and the deuterated 1,2-CDO crystallized in the flask and was removed and transferred to a small vial to be used to measure the spectra.

The samples of 1,2-CDO and FA were transferred into separate glass sample cells. The cell containing 1,2-CDO was attached to the pulsed-valve (General Valve series 9) and was heated to ∼35 °C. The cell containing FA was placed in the neon gas line leading to the cell containing 1,2-CDO. The FA sample was maintained at −10 °C using a Peltier cooling system. The pressure inside the spectrometer was maintained at 10^{-6}–10^{-7} Torr prior to the pulsed injection of the samples and the Ne carrier gas, which was maintained at ∼1 atm. The valve was set to pulse at ∼2 Hz. A similar set up was used to measure the transitions of all other isotopologues, using the respective isotopic samples of either the deuterated 1,2-CDO or FA. All

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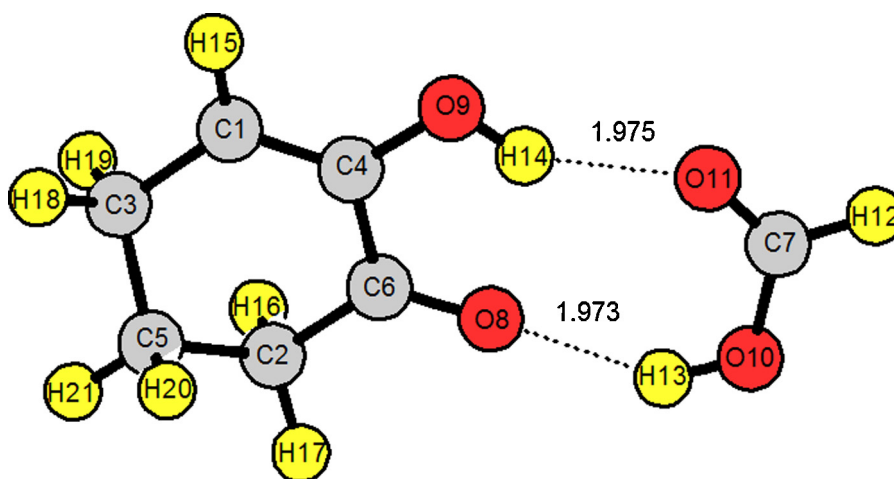 *E-mail address:* kukolich@u.arizona.edu (S.G. Kukolich).

Figure 1. Best fit structure of the 1,2-CDO and FA hydrogen-bonded dimer.
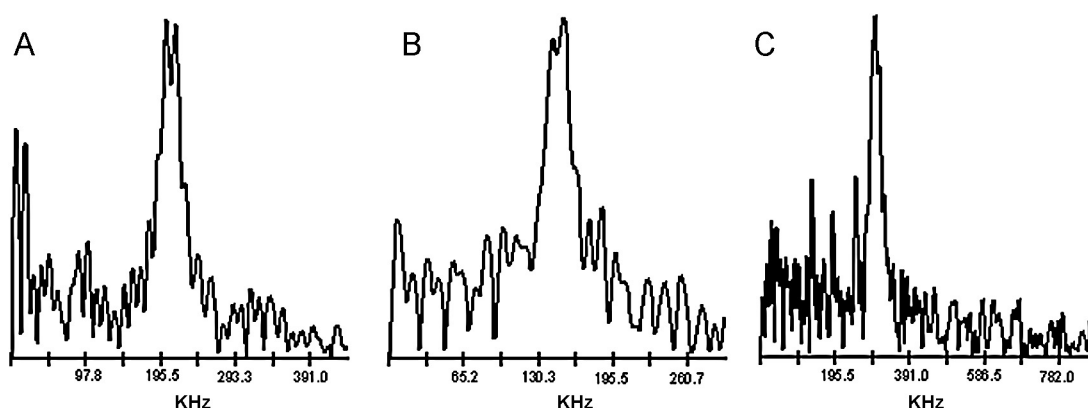

Figure 2. Examples of observed transitions for (A) CDO–FA parent (5_{05}–6_{06}, 245 pulsed-beam cycles) at stimulating frequency 5860.900 MHz, (B) DCDO–FA isotopologue (5_{05}–6_{06}, 354 pulsed-beam cycles) at stimulating frequency 5848.760 MHz, and (C) DCDO–DFA isotopologue (5_{15}–6_{16}, 346 pulsed-beam cycles) at stimulating frequency 5544.750 MHz. The horizontal axis represents the difference of the observed transition from the stimulating frequency, shown in KHz.

Table 1
Results of the measurements and least squares fit calculations for 1,2-CDO/FA parent dimer isotopologue transitions. The standard deviation of the fit is 0.002 MHz. Frequencies are given in MHz.

$J'_{Ka'Kc'}$	$J''_{Ka''Kc''}$	ν_{obs}	ν_{o-c}
5_{15}	4_{14}	4732.9860	−0.002
5_{05}	4_{04}	4911.8100	−0.002
5_{24}	4_{23}	4969.4110	−0.001
5_{23}	4_{23}	5034.3650	0.001
5_{14}	4_{13}	5191.5510	0.002
6_{16}	5_{15}	5671.5780	−0.001
6_{06}	5_{05}	5860.6920	0.000
6_{25}	5_{24}	5957.2310	−0.000
6_{24}	5_{23}	6068.6140	0.001
6_{15}	5_{14}	6219.5780	0.002
7_{17}	6_{16}	6606.4180	0.002
7_{07}	6_{06}	6794.6320	−0.001
7_{26}	6_{25}	6941.7680	0.001
7_{25}	6_{24}	7114.4330	−0.003
7_{16}	6_{15}	7241.2990	−0.001
8_{18}	7_{17}	7537.3440	0.002
8_{08}	7_{07}	7714.6800	0.001
8_{27}	7_{26}	7922.5080	0.000
9_{09}	8_{08}	8623.3360	−0.001

Table 2
Results of the measurements and least squares fit calculations for 1,2-CDO/DFA parent dimer isotopologue transitions. The standard deviation of the fit is 0.003 MHz. Frequencies are given in MHz.

$J'_{Ka'Kc'}$	$J''_{Ka''Kc''}$	ν_{obs}	ν_{o-c}
4_{13}	3_{12}	4064.9410	0.002
5_{15}	4_{14}	4635.9410	0.001
5_{05}	4_{04}	4809.4060	−0.000
5_{24}	4_{23}	4862.0070	−0.000
5_{14}	4_{13}	5075.0680	0.001
6_{16}	5_{15}	5555.7840	−0.000
6_{06}	5_{05}	5740.5340	−0.001
6_{15}	5_{14}	6080.7580	−0.002
7_{07}	6_{06}	6657.6900	−0.001
8_{08}	7_{07}	7561.5940	0.001

axis, so we would expect an asymmetric tunneling potential making it unlikely that concerted proton tunneling splittings would be observed.

3. Calculations

Ab initio calculations were performed using GAUSSIAN 09 suite [8] using a MP2/6-311++G** basis set in order to obtain initial values of rotational constants. The rotational constants from the calculated Gaussian structure were used to predict the a-dipole transitions for the rotational spectrum of the dimer. The calculated values of the rotational constants were $A = 2413.722$ MHz, $B = 544.074$ MHz,

measured transitions are given in Tables 1–3. An example of an observed transition is shown in Figure 2. Some small splittings of lines were observed but none are assigned to possible proton tunneling [3]. The present complex does not possess a C$_2$ symmetry

Table 3

Results of the measurements and least squares fit calculations for 1,2-DCDO/FA and 1,2-DCDO/DFA dimer isotopologue transitions. Frequencies are in MHz. The standard deviation of the fits is 0.003 MHz and 0.002 MHz respectively.

$J'_{Ka'Kc'}$	$J''_{Ka''Kc''}$	1,2-DCDO/FA		1,2-DCDO/DFA	
		ν_{obs}	ν_{o-c}	ν_{obs}	ν_{o-c}
5_{15}	4_{14}	4723.0850	−0.002	4626.7041	−0.001
5_{05}	4_{04}	4901.9722	0.004	4800.2813	0.002
6_{16}	5_{15}	5659.5898	−0.004	5544.6025	−0.001
6_{06}	5_{05}	5848.4570	−0.001	5729.1812	0.000
7_{17}	6_{16}	6592.3052	−0.001	6458.9888	−0.003
7_{07}	6_{06}	6779.8853	−0.001	6643.9844	−0.001
8_{18}	7_{17}	7521.0698	0.002	7369.7031	−0.001
8_{08}	7_{07}	7697.3687	0.000	7545.4683	−0.002
9_{19}	8_{18}	8445.8906	0.004	8276.7246	0.004
9_{09}	8_{08}	8603.4980	−0.000	8435.7979	0.001

and $C = 454.138$ MHz. These calculated rotational constants were all within 0.6% of the experimental values making the task of searching for and assigning the rotational transitions considerably easier. A comparison of the hydrogen bond distances and the center of mass separations of the calculated Gaussian and experimental structure are shown in Table 6.

4. Rotational constants

Experimental rotational and centrifugal distortion constants for the parent isotopologue of the dimer were determined using a least-squares fitting program and are given in Table 5. A similar analysis was carried out for the remaining 3 isotopologues of the dimer, but the centrifugal distortion constants were held fixed to the values obtained from the parent isotopologue. The observed (o) and calculated (c) rotational transition frequencies from the microwave fit for each of the isotopologues are given in Tables 1–3.

5. Molecular structure

The rotational constants acquired from each of the microwave fits of the isotopologues were used in a nonlinear least squares fitting program to determine the experimental hydrogen bond lengths and the center of mass separation of the 1,2-CDO and FA monomers. In the fit, 1,2-CDO coordinates were held fixed to those obtained previously [9]. Structural parameters for formic acid

Table 4

Measured rotational constants and the 'best fit' calculated values for rotational constants obtained from the structure fit. The standard deviation for the fit is 1.12 MHz. Also shown are the distortion constants (kHz) of the parent isotopologue, held fixed for all other isotopic substitutions.

Isotopologue	Measured	Calculated	(M.–C.)
Parent			
A	2415.0439(179)	2417.1848	−2.1410
B	543.6907(2)	543.7113	−0.0206
C	451.6663(2)	450.8779	0.7884
D_J	0.0220(13)		
D_{JK}	0.119(31)		
CDO-DFA			
A	2414.7543(379)	2413.7931	0.9613
B	530.9216(2)	531.4466	−0.5250
C	442.8253(3)	442.2975	0.5278
DCDO-FA			
A	2399.6875(257)	2400.6990	−1.0115
B	542.9527(9)	543.2486	−0.2959
C	450.6175(3)	449.9907	0.6267
DCDO-DFA			
A	2399.4147(226)	2397.5249	1.8897
B	530.2502(7)	531.0291	−0.7789
C	441.8415(2)	441.4666	0.3749

were obtained from the work of Gerry et al. [10] and were also held fixed. The coordinates of both monomers were initially set up in such a way that the sp^2 hybridized carbon atoms of 1,2-CDO (C1, C4, and C6) and FA (C7), as well as all oxygen atoms and the hydrogen atoms H12-15, were in the same plane (the x–y plane). There were two variable parameters assigned during the structure fit representing the x–y coordinates of the center of mass of FA, with respect to the coordinate system of 1,2-CDO. A third fixed parameter, ϕ, represented the rotation of the formic acid moiety in the x–y plane. The rotation of the FA moiety was held fixed to $\phi = -0.1047$ radians, as this angle produced the best structure fit with the smallest fit standard deviation. The center of mass separation of the monomers was calculated using the equation $I_{CC} = I_{CC}(\text{1,2-CDO}) + I_{CC}(\text{FA}) + \mu R^2_{CM}$. The calculated and experimental values for the hydrogen bond lengths and the center of mass separations are shown in Table 6.

The experimental A, B, and C rotational constants and the deviations from the best fit calculated values are listed in Table 4. Values of the atomic coordinates obtained from the structure fit are shown in Table 5. Coordinates for the substituted atoms were also obtained

Table 5

Atom Cartesian coordinates in a, b, c system for the best fit structure of 1,2-CDO/FA hydrogen bonded dimer, and the Kraitchman determined values (Krait.) for the isotopic substitutions.

Atom	a	b	c	$|a|$-Krait.	$|b|$-Krait.	$|c|$-Krait.
C1	2.236	0.100	1.290			
C2	1.676	0.257	−1.554			
C3	3.383	0.124	0.308			
C4	0.946	0.037	0.887			
C5	2.981	−0.394	−1.074			
C6	0.582	0.031	−0.543			
C7	−3.616	0.001	0.165			
O8	−0.608	−0.031	−0.846			
O9	−0.089	−0.103	1.753			
O10	−3.374	−0.001	−1.240			
O11	−2.840	0.000	0.943			
H12	−4.631	0.006	0.550	4.7(8)	0.06(1)	0.15(3)
H13	−2.459	0.014	−1.527			
H14	−0.884	−0.094	1.195	1(1)	0.03(2)	1(1)
H15	2.448	0.075	2.357			
H16	1.832	1.344	−1.616			
H17	1.341	−0.088	−2.536			
H18	4.245	−0.436	0.687			
H19	3.707	1.173	0.227			
H20	2.817	−1.477	−1.013			
H21	3.782	−0.221	−1.800			

Table 6
Interatomic distances obtained by fitting the experimental rotational constants for four isotopologues. hydrogen bond lengths and COM separations are in Å.

Interatomic distance	Microwave fit value (Å)	Calculated value (Å)
$r(H_{13}-O_8)$	1.973(30)	1.771
$r(H_{14}-O_{11})$	1.975(30)	1.886
COM separation	4.591(2)	4.571

by performing a Kraitchman analysis. We do not believe that all of the magnitudes of coordinates from the Kraitchman analysis are very accurate nor reliable, but they are all included in Table 5 for reference.

6. Discussion

The pure rotational spectrum of the doubly hydrogen bonded dimer of 1,2-cyclohexanedione and formic acid has been measured using a PBFT microwave spectrometer and all measured rotational transitions were assigned. The experimental rotational transitions are shown in Tables 1–3 and the best fit structural coordinates of the dimer and the hydrogen bond lengths and center of mass separations are given in Tables 5 and 6 respectively. The best fit structure shown in Figure 1 produced more symmetric and slightly longer hydrogen bond lengths when compared with the Gaussian calculation. The experimental hydrogen bond lengths of 1.97 Å are a bit longer than the calculated (Gaussian) values of 1.77 Å and 1.89 Å. This difference is a bit larger than expected, but in the correct direction since the experimental values are r_0 and calculated values are

for r_e. We believe that the average of the hydrogen-bond lengths is quite accurate ($r_{OH} = 1.97(1)$) but the uncertainty is perhaps a factor of 2 or 3 higher for the individual hydrogen-bond lengths ($r_{OH} = 1.97(3)$) because the fit was not very sensitive to the angle ϕ. More isotopologue transitions need to be measured to determine a more complete and accurate gas phase structure.

Acknowledgements

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