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Microwave measurements and structure calculations for a glyoxylic acid – Water complex

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ABSTRACT

The microwave spectra for a hydrogen-bonded *trans*-2 glyoxylic acid–water complex were measured in the 6–16 GHz frequency range using two Flygare-Balle type pulsed beam Fourier transform microwave (FTMW) spectrometers. The rotational constants for the dimer were determined to have the following values: A = 9384.2354(31), B = 1707.63973(73), and C = 1447.44879(56) MHz. The hydrogen bonded structures and rotational constants were calculated for the lowest energy dimglyoxylic acid - water using DFT, MP2 and CCSD calculations with various basis sets. The B3LYP/aug-cc-PVQZ-DG3 calculations yielded rotational constants of A = 9393.59, B = 1713.76, and C = 1453.23 MHz, in very good agreement with experimental values. The calculations show two feasible tunneling motions involving hydrogen atoms in this complex.

1. Introduction

Glyoxylic acid is important in many reactions in biochemistry. It is involved in key reactions in both plants and animals [1]. There has been interest in glyoxylic acid and the dimers with water to better understand the properties of the water complexes and their roles in the important reactions atmospheric chemistry [2,3]. Two of the trans conformers for the glyoxylic acid monomer, labeled, *trans*-1-glyoxylic acid and *trans*-2-glyoxylic acid are shown in Fig. 1. The lowest energy, trans- 1 monomer microwave spectrum was reported by Mollendal et al. [4–6]. Rotational transitions and properties of the *trans*-2 conformer were reported by Van Eijk [7].

Microwave spectra, calculations and analysis for two distinct structural isomers of glyoxylic acid–formic acid complexes were recently reported by our group [8,9].

Following the previous work on the glyoxylic acid–formic acid complexes, calculations of structures and rotational complexes were made for low-energy complexes between glyoxylic acid and water. Two low energy complexes were obtained from the calculations and are shown in Fig. 2. The first complex (a) is identified as the end- trans2 configuration (ET2), and the second (b) is the side-trans1 configuration (ST1). Calculations and matrix-IR measurements on similar complexes were reported by Lundell and Olbert-Majkut. [10] We have now obtained microwave spectra which can be assigned to the ET2 glyoxylic acid–water complex. This assignment is supported by the very good agreement between the measured and the calculated rotational constants.

Both of these structures are planar exceptt for the H atom on left side. The O4-H3 bond is about 60° out of the plane of the heavy atoms. The experimental inertial defect is $\Delta = 0.654$ amu Å^2, and this is consistent with the structure shown. Another type of complex between glyoxylic acid and water is a more compact, germinal diol structure described by Vaida, et al [3]. The calculated low-energy structures for this diol complex are discussed briefly below.

2. Experimental

Two Flygare-Balle type pulsed-beam Fourier transform microwave spectrometers were used to measure rotational transitions of the glyoxylic water dimer in the region of 6–16 GHz. One has the molecular beam perpendicular to the cavity axis, the second has the beam at a 45° angle to the cavity axis. These instruments, at the University of Arizona, have been previously described [11–13]. Measurements of rotational transitions were saved at multiple frequencies using a Labview program that analyzes the results of a fast Fourier transform of a free-induction decay (FID) signal. An example of the recorded spectrum with the stimulating microwave frequency of 12555.600 MHz is given in Fig. 3. Typical linewidths are 15–20 kHz, so there is likely some unresolved structure in this line.

Glyoxylic acid monohydrate (98 %) was purchased from Sigma-Aldrich, and it was used without further purification. The glyoxylic acid monohydrate was placed in a glass sample cell, and it was heated to 50 ℃ to produce sufficient vapor pressure. For some runs small amounts of water were added to the sample system. Argon was passed through

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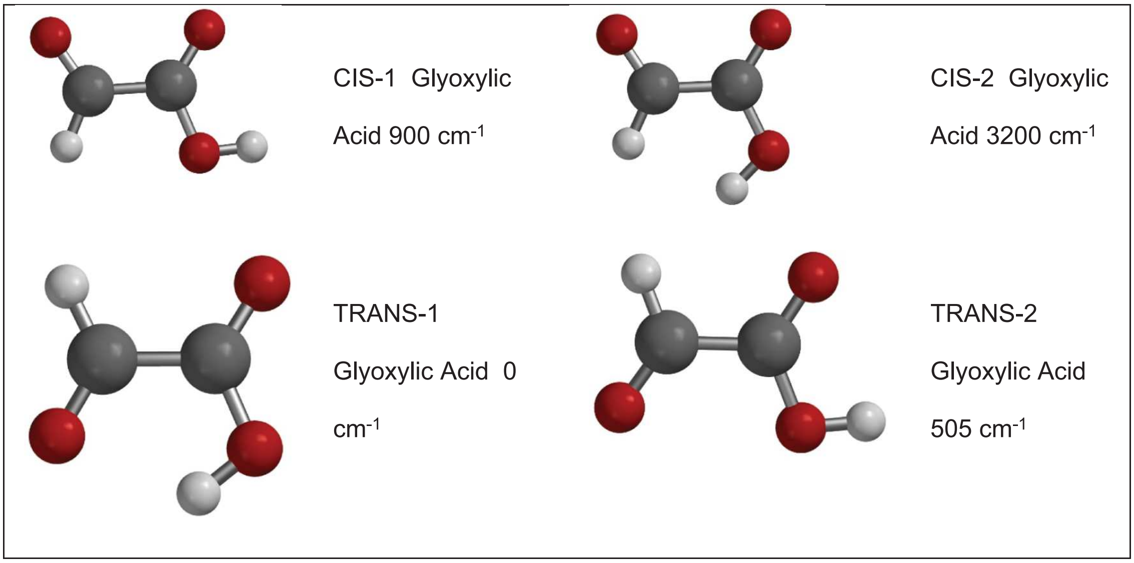


Fig. 1. Structures and relative energies for four possible isomers of the glyoxylic acid monomer.

the cell containing glyoxylic acid and pulsed into the cavity of the spectrometer. The system was maintained at a backing pressure of 1 atm. The pressure inside the cavity of the instrument was maintained in the range of 10^{-6}–10^{-7} torr using a Varian VHS-10 diffusion pump. The dimer of glyoxylic acid–water was pulsed into the chamber at a frequency of 2 Hz using a General Valve Series 9 pulsed valve.

3. Computational

Calculations were performed on the University of Arizona HPC puma system using Gaussian G-16 [14,15] with 94 cores and using 470 Gb of memory. Calculations focused on methods that have been shown to predict good gas phase structures for hydrogen bonded complexes and include M11 [16], MP2 [17] and B3LYP [18]. Various basis sets were used to explore the range of structures and possible differences in energy ordering. MP2 calculations used the cc-pVQZ [19] basis set. B3LYP and M11 calculations were done with aug-cc-pVQZ [20], cc-pVQZ [19], cc-pVDZ [20] and def2-QZVPP [21] basis sets. Slightly better results were obtained using the GD3(EmpiricalDispersion = GD3) keyword. A summary of the predicted rotational constants and experimentally determined constants is given in Table 1. Two CCSD calculations (columns 6 and 8) were tried, but results were not the best, because only smaller basis sets could be used. Basis sets with dispersion terms included were more successful.

Calculations of the rotational constants for the v = 0 vibrationally averaged structures, using freq = anharm were also done with results shown in Table 2. These did not agree quite as well with the measured values.

The B3LYP-cc-pVQZ calculation yielded a binding energy of 3630 cm^{-1} for the ET2 complex and 3372 cm^{-1} for the ST1 complex. These calculations were made using the option counterpoise = 2, starting with an optimized structure.

4. Feasible tunneling motions for the ET2 complex

One feasible proton tunneling motion for the ET2 complex involves motion of H3 from the top of the plane of the heavy atoms in the complex around the end to the bottom of the complex. This motion represents an increase in the dihedral angle C1-H4-O4-H3, shown in Fig. 4. This angle changes from 140° to 230° equilibrium values during the tunneling process. The calculated value of C = 1453.2 is in excellent agreement with the experimental value of C = 1447.4 so we believe that his is an accurate representation of the structure. The hydrogen bond lengths of 1.75 and 2.13 Å are reasonable for a fairly strongly bonded complex.

This is similar to the inversion tunneling for cyanamide [22]. The calculated barrier for this tunneling inversion is 304 cm^{-1}, so the tunneling frequency is expected to be very high. Therefore, if the O^- state had an estimated energy near 100 GHz (3.3 cm^{-1}), allowed a and b-dipole transitions within this state would be very weak (Boltzmann factor 0.02). This tunneling energy would also cause very large (order of 100 MHz) splittings (splittings were estimated using FINDIF program [23]) of potential c-dipole transitions. No c-dipole transitions were observed in this work. The potential for this tunneling motion, calculated using the G-16 scan function is shown in Fig. 5.

The second feasible tunneling motion is the concerted proton tunneling of H2 and H4, similar to that observed in the formic acid-propiolic acid dimer [24–26]. The calculated barrier for this tunneling motion is much higher, 4622 cm^{-1}. This makes it unlikely that splittings from this motion would be observed in the spectra. This tunneling would also make it unlikely to observe c-dipole transitions.

5. Analysis of the spectra

The predicted spectrum of the lowest energy complex of *trans*-2-glyoxylic acid and water was computed using the SPCAT program [27] available from JPL. The values of the rotational constants obtained from the calculations performed are given in Table 1. The predicted a-dipole

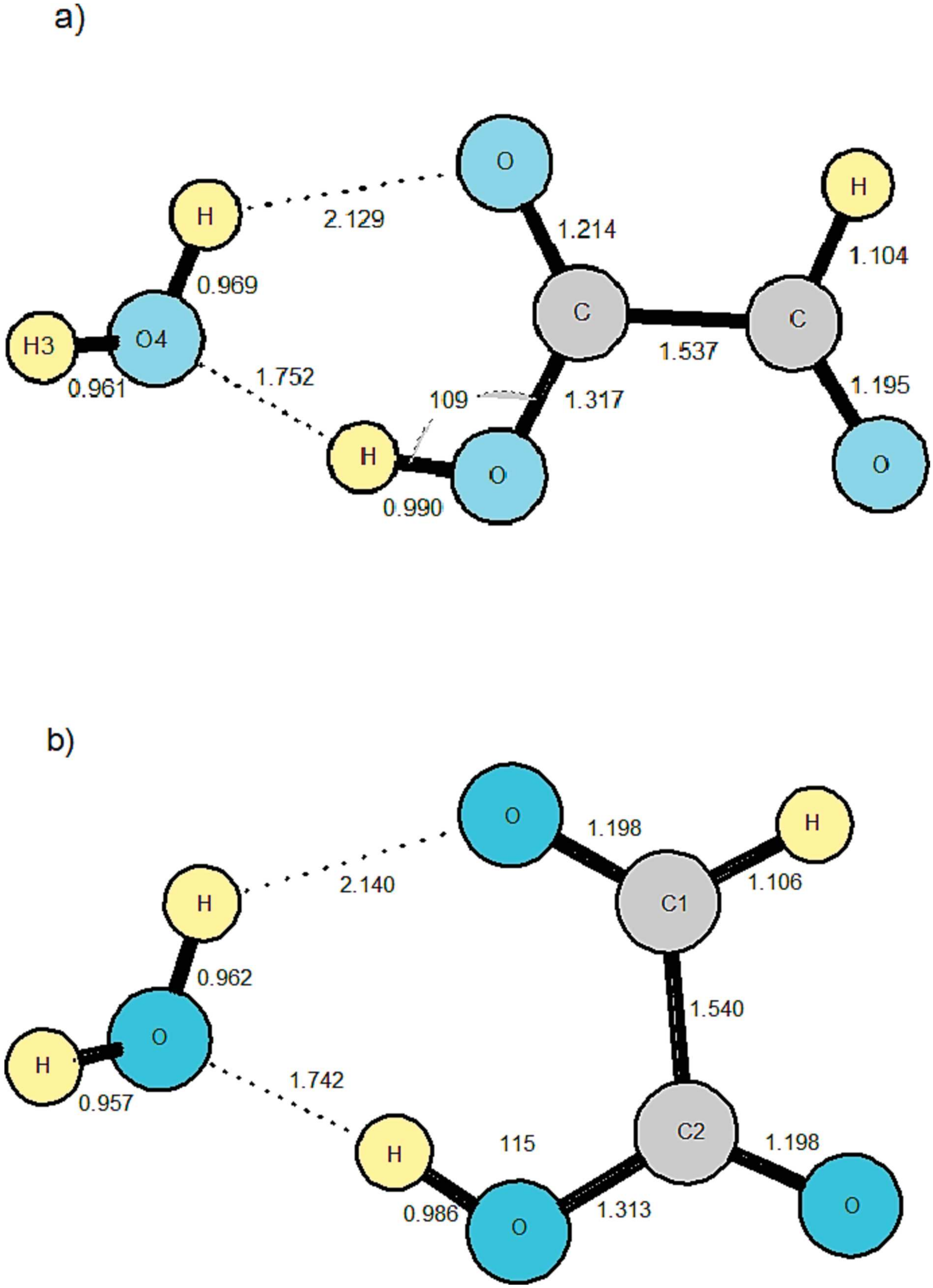


Fig. 2. The two lowest energy calculated structures for glyoxylic acid–water dimer. (a) Is identified as the end- trans2 configuration (ET2) (Bond lengths from 1. B3LYP-augQZ-GD3 calculation), (b) is the side-trans1 configuration (ST1).

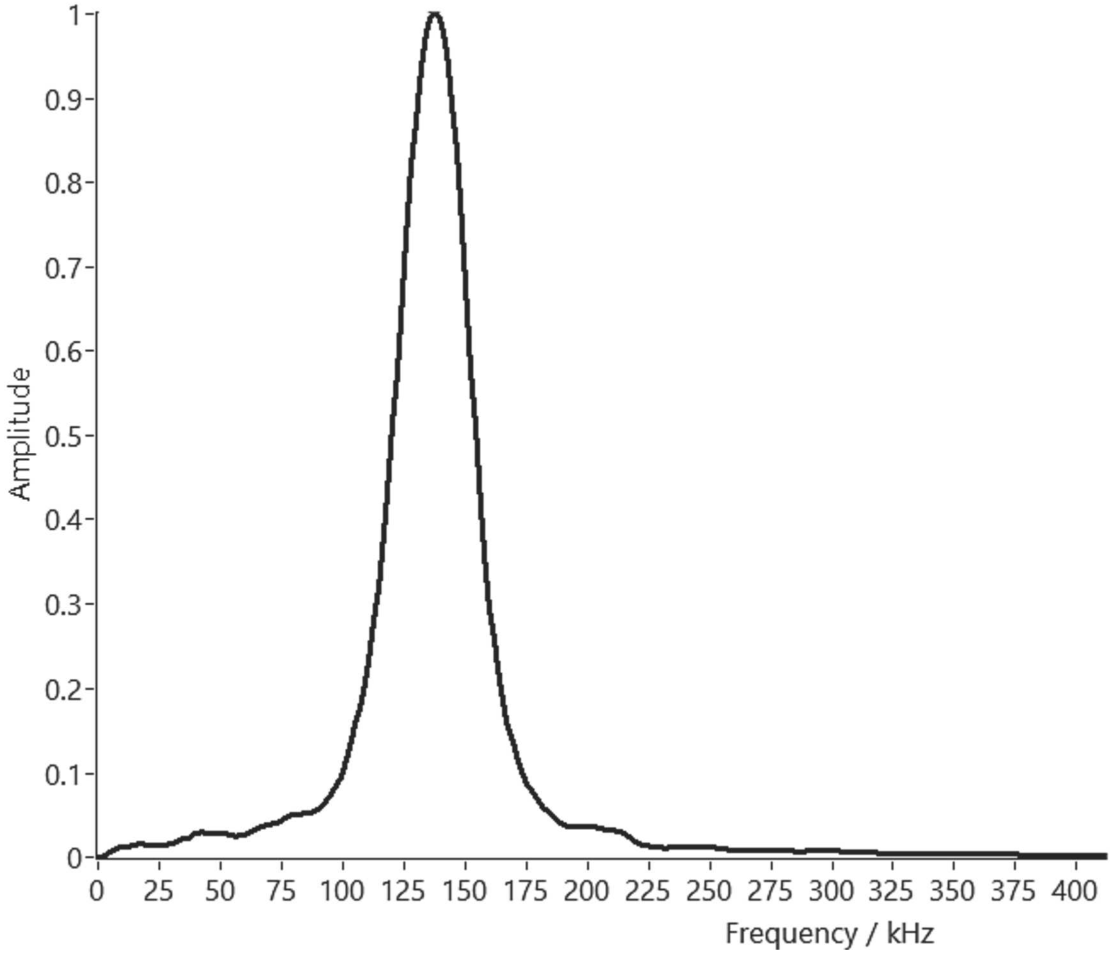


Fig. 3. Direct measurement of the $4_{04} \rightarrow 3_{03}$ transition. The microwave stimulating frequency was 12555.600 MHz. The molecular signal was recorded at 12555.466 MHz. There were 200 beam pulses with a sample frequency of 3.125 MHz. The frequency scale (kHz) is the amount below the stimulating signal.

Table 1
Experimental parameters compared to calculated equilibrium parameters for the dimer structure ET2. E_B is the binding energy.

Parameter	1. Exp.	2. B3-augQZ-DG3	3. B3 aug QZ	4. B3 QZ	5. B3 DG3 QZ	6. CCSD/cc-pVDZ	7. M11	8. CCa	9. MP2
A(MHz)	9384.2354 (31)	9393.58	9436.64	9414.75	9387.12	9197.71	9567.54	9413.38	9390.14
B(MHz)	1707.63973 (73)	1713.76	1715.82	1719.70	1718.51	1721.08	1741.24	1725.60	1744.30
C(MHz)	1447.44879 (56)	1453.23	1455.51	1458.33	1456.95	1455.78	1476.18	1462.59	1474.66
μ_a(D)		2.42	2.41	2.35	2.35	1.99	2.43	2.18	2.39
μ_b(D)		1.10	1.11	1.10	1.09	1.23	1.28	1.22	1.19
μ_c(D)		1.18	1.16	1.27	1.24	1.35	1.12	1.25	1.16
E(H)		−379.715	−379.709	−379.706	−379.712	−378.584	−379.596	−378.947	−379.078
E_B(cm^{-1})				3630.46 cm^{-1}					3602.5 cm^{-1}
Method		B3LYP/aug-cc-pVQZ /GD3	B3LYP/aug-cc-pVQZ	B3LYP/cc-pVQZ	B3LYP/cc-pVQZ /GD3	CCSD/cc-pVDZ	M11/ def2qzvpp	CCSD/cc-pVTZ	MP2/aug-cc-pVQZ

Table 2
Rotational constants from anharmonic calculations to obtain vibrationally averaged parameters (A_0, B_0, C_0) for v = 0. Method - B3LYP/aug-cc-pVQZ EmpiricalDispersion = GD3, freq = anharm.

Parameter	1. Exp.	2. B3-augQZ-DG3	3. MP2/aug-cc-pVQZ
A_e(MHz)		9393.58	9390.143
B_e(MHz)		1713.76	1744.293
C_e(MHz)		1453.23	1474.663
A_0(MHz)	9384.2354(31)	9291.496	9214.435
B_0(MHz)	1707.63973(73)	1686.513	1701.418
C_0(MHz)	1447.44879(56)	1431.382	1439.027

values ranged from 2.2 to 2.5 D in our calculations and the predicted b-dipole values ranged from 1.1 to 1.2 D. The *trans*-1 monomer transition of $1_{01} \rightarrow 0_{00}$ was predicted at 7848.15 MHz [4]. The water dimer transition 1_0 B2+ → 0_0 B2- at 7354.96 MHz [28] was monitored throughout the experiment. Based on the predicted value of the $3_{03} \rightarrow 2_{02}$ transition near 9400 MHz, a scan covering this region was performed. A signal at 9439.237 MHz was observed. Based on this detection, a scaling was made of the predicted spectrum and a scaled prediction of $2_{02} \rightarrow 1_{01}$ near 6300 was obtained. A signal at 6303.663 was measured in experiments with glyoxylic acid containing water and

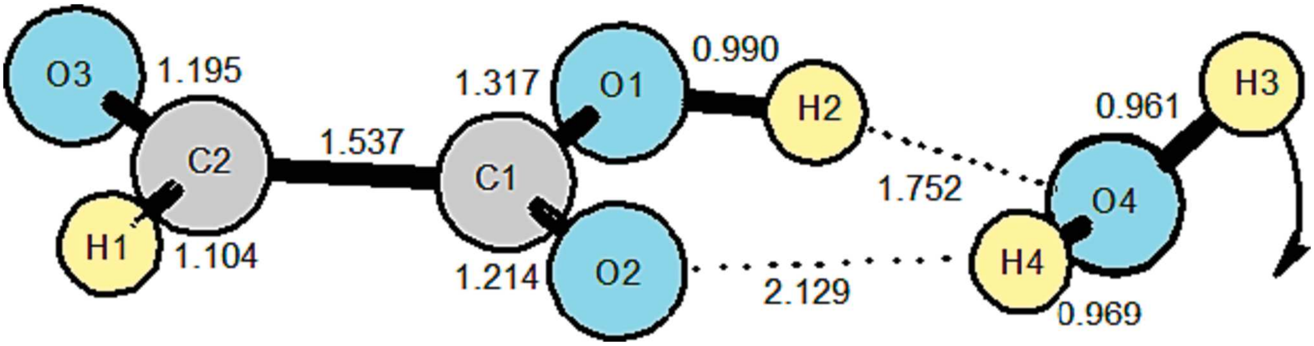


Fig. 4. Structure of the complex showing the proposed feasible tunneling motion. (Bond lengths in this figure are from a lower level B3LYP calculation).

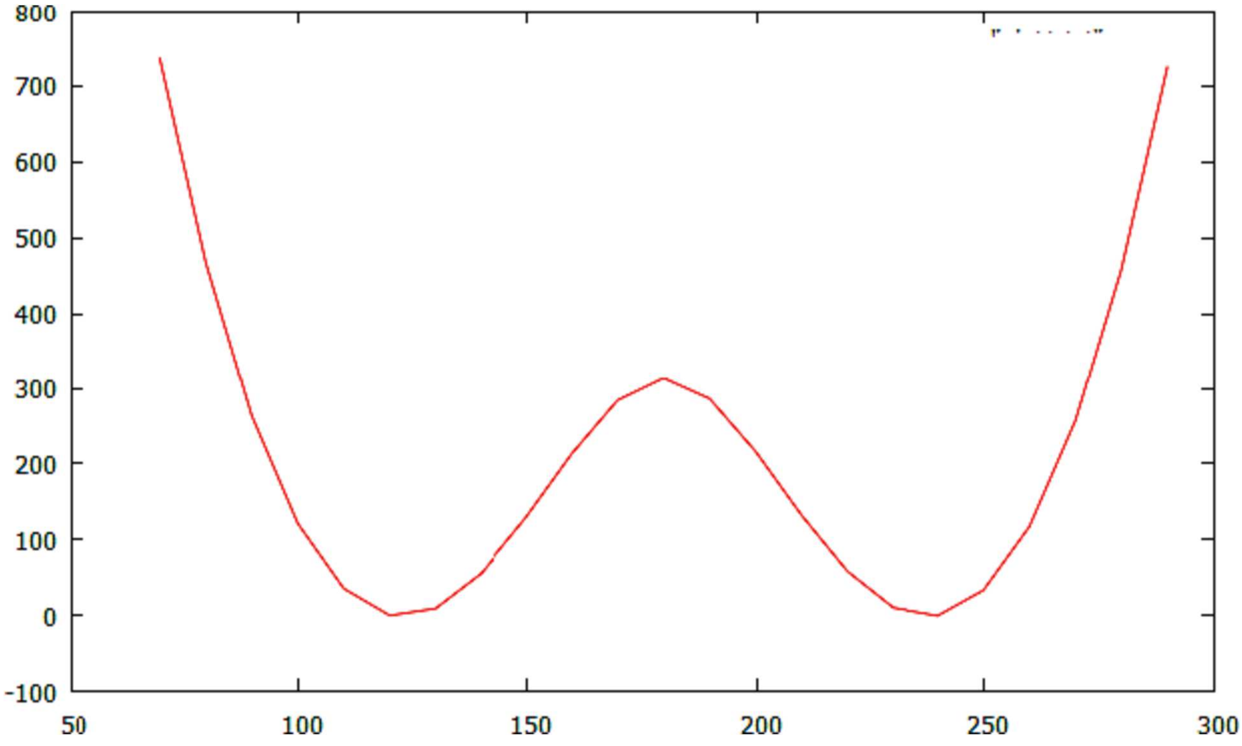


Fig. 5. Potential energy plot for the concerted proton tunneling motion. Energy in cm^{-1} vs bending angle in degrees. This was obtained by scanning the dihedral angle C1-H4-O4-H3 using the G-16 scan function. The barrier for this motion is 304 cm^{-1}.

Table 3
Results of the SPFIT least squares fit to 18 measured transitions. The resulting parameters are given in Table 4.

$J_{KaKc}{}'$	$J_{KaKc}{}''$	Measured (MHz)	Obs-calc (kHz)	dipole
2 1 2	1 1 1	6049.96390	0.04	a
2 0 2	1 0 1	6303.66310	2.78	a
2 1 1	1 1 0	6570.35240	6.66	a
3 1 3	2 1 2	9070.90430	0.55	a
4 1 3	4 0 4	9187.45840	15.62	b
3 0 3	2 0 2	9439.23780	3.30	a
3 2 2	2 2 1	9465.16970	0.54	a
3 2 1	2 2 0	9491.14870	−4.00	a
3 1 2	2 1 1	9851.37780	1.75	a
1 1 1	0 0 0	10831.67000	−8.38	b
4 1 4	3 1 3	12087.15030	12.70	a
4 0 4	3 0 3	12555.46560	6.89	a
4 2 3	3 2 2	12615.11660	−1.29	a
4 2 2	3 2 1	12679.89440	−4.91	a
4 1 3	3 1 2	13127.28010	−11.85	a
2 1 2	1 0 1	13726.54830	−7.19	b
5 1 5	4 1 4	15097.33480	10.83	a
5 1 4	4 1 3	16396.13560	−11.92	a

Table 4
The molecular parameters for glyoxylic water ET2 dimer from the least squares fit to data in Table 3, 18 transitions were in the fit. The standard deviation for the fit, σ = 7.8 kHz.

A (MHz)	9384.2354(31)
B (MHz)	1707.63973(73)
C (MHz)	1447.44879(56)
D_J (kHz)	−0.440(14)
D_{JK}(kHz)	−2.04(12)
σ (kHz)	7.8
N_{lines}	18

is included in Table 2. A scan near the scaled value for the $3_{13} \rightarrow 2_{12}$ transition near 9180 MHz was made and signal at 9187.458 was observed. A preliminary fit of the rotational constants B and C using the three lines was made while fixing A to the average predicted A rotational constant of 9400 MHz. The $2_{11} \rightarrow 1_{10}$ transition was predicted at 6570 MHz and readily found at 6570.372 MHz. With four transitions in the fit, the rotational constant A was fit. The remaining 15 transitions were measured and included in the fit along with 4 $K_a = 2$ a-dipole transitions with a maximum J = 5, and the $5_{14} \rightarrow 4_{13}$ transition at 16396.13 MHz. Careful experiments were necessary at optimal conditions to measure the 4b-dipole transitions reported in Table 3. The first b-dipole transition measured was 10831.67 MHz. This led to a modified value of the rotational constant A, and facilitated finding three more b-dipole transitions. Inclusion of the distortion constant D_J and D_{JK} was found to be necessary to fit the data to experimental accuracy. The fit parameters are listed in Table 4.

6. Discussion

The microwave spectrum for the lowest energy structure of the complex made from glyoxylic acid and water has been measured. Based on the fit of assigned rotational transitions to within experimental accuracy, we believe that the complex is composed of *trans*-2-gyloxylic acid and water in the ET2 configuration. The doubly hydrogen bonded complex was predicted to be the lowest energy structure in the study of glyoxylic acid and water in the matrix isolation study using infrared spectroscopy [10]. We do not find evidence for the ST1 structure, or other higher energy structures discussed in this work. Significant effort was expended to find the next lowest energy structure, *trans*-1-glyoxylic acid and water but no adequate fit to signals can be reported at this time.

A non-zero c-dipole was predicted for the complex originating from the out-of-plane hydrogen atom in water. As described in the complex between formic acid and water [29], the low energy barrier (304 cm^{-1}) to tunneling through the a-b plane leads to difficulty in observing c-dipole transitions, and none were found in the spectra.

7. Glyoxylic acid–Water diol calculations

The glyoxylic acid–water geminal diol may be another gas-phase complex present in the expansion. This complex was recently discussed by Vaida, et al. [3] four low energy structures were found using G-16 calculations. The results are summarized in Table 5. Some of the transitions predicted from these calculations were searched for, but no good assignments were found.

8. Conclusions

A doubly hydrogen-bonded glyoxylic acid–water hydrogen-bonded complex has been investigated using microwave spectroscopy. The structure most consistent with the microwave measurements is the end-trans2 configuration (ET2) shown in Fig. 2. These results should help to understand glyoxylic acid binding with other molecules.

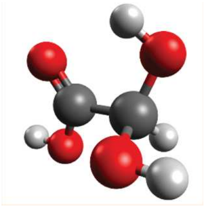
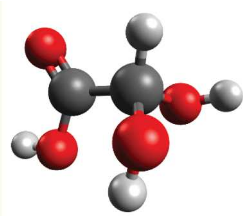
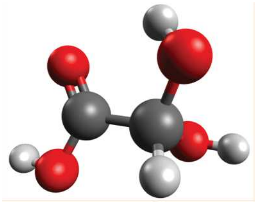
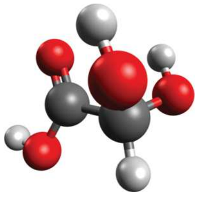
CRediT authorship contribution statement

Adam M. Daly: Conceptualization, Methodology, Project administration, Writing – original draft, Writing – review & editing, Investigation, Methodology, Supervision. **Rhett P. Hill:** Data curation, Writing – review & editing, Investigation. **Myla G. Gonzalez:** Data curation, Investigation. **Stephen G. Kukolich:** Conceptualization, Methodology, Project administration, Writing – original draft, Writing – review & editing, Funding acquisition, Software, Supervision, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 5
Calculated structures for four possible diol structures. Method - B3LYP/cc-pvqz.

				
Complex	Diol1	Diol2	Diol3	Diol4
Energy(H)	−379.7091	−379.7068	−379.7092	−379.7080

Data availability

Data will be made available on request.

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