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Microwave measurements of the tropolone–formic acid doubly hydrogen bonded dimer

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The microwave spectrum was measured for the doubly hydrogen bonded dimer formed between tropolone and formic acid. The predicted symmetry of this dimer was $C_{2v}(M)$, and it was expected that the concerted proton tunneling motion would be observed. After measuring 25 a- and b-type rotational transitions, no splittings which could be associated with a concerted double proton tunneling motion were observed. The calculated barrier to the proton tunneling motion is near 15 000 cm^{-1}, which would likely make the tunneling frequencies too small to observe in the microwave spectra. The rotational and centrifugal distortion constants determined from the measured transitions were $A = 2180.7186(98)$ MHz, $B = 470.873\,90(25)$ MHz, $C = 387.689\,84(22)$ MHz, $D_J = 0.0100(14)$ kHz, $D_{JK} = 0.102(28)$ kHz, and $D_K = 13.2(81)$ kHz. The B3LYP/aug-cc-pVTZ calculated rotational constants were within 1% of the experimentally determined values. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4940775]

I. INTRODUCTION

Proton tunneling is a large-amplitude vibrational motion which has been observed and could be present in a wide range of molecules and complexes involved in important chemical reactions and biological systems such as DNA. The tropolone monomer exhibits proton tunneling, and this work was initiated to look for possible proton tunneling in the tropolone–formic acid doubly hydrogen bonded dimer.

Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), a seven-membered ring pseudoaromatic molecule, is considered as a prototypical molecule for proton transfer. The carbonyl group is located on one of the carbon atoms within the ring, and the OH group is attached to the carbon atom at the α position with respect to the carbonyl group. The neighboring C=O and OH groups interact and form an intramolecular hydrogen bond. The non-symmetric hydrogen atom tunnels between the two carbonyl oxygen atoms during the tautomerization of the carbon ring. The resulting structure after the tunneling motion is identical to the structure beforehand. This tunneling effect results in a double minimum well in the potential energy surface and a transition state of $C_{2v}(M)$ symmetry along the proton-transfer coordinates. The tunneling motion is described by a vibrational motion which results in two vibrational states that represent each of the tunneling states observed. This proton tunneling effect has been extensively studied using microwave spectroscopy,[1,2] rotationally resolved degenerate four-wave mixing,[3–7] matrix-isolated infrared spectroscopy,[8,9] laser-induced fluorescence (LIF) techniques,[10,11] and gaseous infrared spectroscopy.[12–15]

The magnitude of the tunneling splitting of tropolone can be affected by a number of factors. Among them are the motion of the tunneling proton, the displacement of heavy nuclei, redistribution of electronic charge density among various atoms, energy and mode of vibrational excitation,

and introduced asymmetric isotopic substitutions. The barrier height can also be influenced by intermolecular interactions, such as forming van der Waals complexes with rare gases or hydrogen bonded systems with other carboxylic acids. These intermolecular interactions can both perturb the molecule's vibrational coupling and change the barrier height and shape of the potential energy surface. The rare gases Ar, Kr, and Xe were the simplest complexing agents studied to form the tropolone van der Waals complexes. Sekiya et al.[16] studied the fluorescence excitation spectra of jet-cooled tropolone-Rg (Rg = Ar, Kr, Xe). They found that the tunneling doublet separation $|\Delta'_v - \Delta''_0|$ for the tunneling states of Ar-tropolone to be close to that of the tropolone monomer. Δ'_v is the tunneling splitting of the v level in $\tilde{A}^1B_2$ state, and Δ''_0 is that of the zero-point level in X^1A_1. Lin et al.[17] reported the microwave spectrum of Ar-tropolone and found that even the weak interaction between argon and tropolone quenches the proton tunneling. Keske and Plusquellic[18] reported the microwave spectrum of tropolone-H$_2$O and found that the tropolone monomer tunneling splitting vanishes upon addition of a water molecule.

Formic acid (FA) is known to form doubly hydrogen bonded dimers with several carboxylic acids[19–25] that exhibit a concerted double proton tunneling. Some other doubly hydrogen bonded dimers do not exhibit the concerted proton tunneling.[26,27] We recently reported the microwave spectrum of cyclopropanecarboxylic acid–formic acid (CPCA-FA) dimer[28] and no tunneling was observed for this doubly hydrogen bonded dimer. The doubly hydrogen bonded tropolone–formic acid dimer introduces a new interesting question about whether or not the tunneling splitting can be observed in this larger more symmetric complex. We expect the concerted double proton tunneling motion to be present in the dimer since it possesses the required $C_{2v}(M)$ symmetry, but the tunneling splittings would not be observed if the potential

barrier is too high. In this paper, we report the microwave spectrum and *ab initio* calculations of the tropolone–formic acid doubly hydrogen bonded dimer.

II. MICROWAVE MEASUREMENTS

The microwave spectrum was measured for the tropolone–formic acid doubly hydrogen bonded dimer in the 4.7–9 GHz range, and all the assigned transitions are shown in Table I. These measurements were taken using a Flygare-Balle type pulsed-beam Fourier transform microwave spectrometer that has been previously described.[29,30] The tropolone (98%) and formic acid (98%) samples were both purchased from Sigma Aldrich and used without further purification. The samples were transferred to separate glass sample cells. The cell containing tropolone was placed in the Ne gas line just before the pulsed valve (General Valve, Series 9) and was set to pulse at room temperature. The Ne backing pressure was maintained at about 1 atm. The tropolone sample was pulsed until there was a strong parent test signal recorded. Once the tropolone signal was sufficiently strong, the sample cell containing the formic acid was placed in the Ne gas line, before the tropolone sample, and the formic acid vapor was passed over the tropolone sample with each molecular beam pulse. The sample of formic acid was brought to −8 °C before attaching to the Ne gas line and this temperature was maintained using a Peltier cooling device. The formic acid vapor was pulsed over the solid tropolone sample for about

TABLE I. Measured a- and b-type rotational transitions of the tropolone–formic acid doubly hydrogen bonded dimer. Values are shown in MHz.

$J'_{Ka' Kc'}$	$J''_{Ka'' Kc''}$	ν_{obs}	ν_{o-c}
$4_{1\,4}$	$3_{0\,3}$	4776.994	0.006
$6_{1\,6}$	$5_{1\,5}$	4879.911	−0.001
$6_{0\,6}$	$5_{0\,5}$	5051.614	−0.002
$6_{3\,3}$	$5_{3\,2}$	5169.534	0.000
$6_{2\,4}$	$5_{2\,3}$	5237.764	0.000
$5_{1\,5}$	$4_{0\,4}$	5444.692	−0.007
$7_{1\,7}$	$6_{1\,6}$	5683.893	0.004
$7_{0\,7}$	$6_{0\,6}$	5855.119	0.004
$7_{3\,5}$	$6_{3\,4}$	6030.552	0.001
$7_{3\,4}$	$6_{3\,3}$	6038.775	0.002
$6_{1\,6}$	$5_{0\,5}$	6089.936	0.003
$7_{2\,5}$	$6_{2\,4}$	6141.604	−0.005
$7_{1\,6}$	$6_{1\,5}$	6257.955	0.001
$8_{1\,8}$	$7_{1\,7}$	6484.354	0.001
$8_{0\,8}$	$7_{0\,7}$	6646.059	−0.001
$7_{1\,7}$	$6_{0\,6}$	6722.206	0.000
$8_{1\,7}$	$7_{1\,6}$	7133.512	0.003
$9_{1\,9}$	$8_{1\,8}$	7281.295	−0.003
$8_{1\,8}$	$7_{0\,7}$	7351.443	−0.001
$9_{0\,9}$	$8_{0\,8}$	7426.650	−0.002
$9_{1\,9}$	$8_{0\,8}$	7986.682	−0.001
$10_{0\,10}$	$9_{0\,9}$	8199.868	−0.003
$10_{1\,9}$	$9_{1\,8}$	8856.853	−0.003
$11_{1\,11}$	$10_{1\,10}$	8865.250	0.005
$11_{0\,11}$	$10_{0\,10}$	8968.743	0.000

TABLE II. Experimental and calculated rotational constants of the tropolone–formic acid doubly hydrogen bonded dimer.

	Parent(experimental)	B3LYP/aug-cc-pVTZ
A/MHz	2180.718 6(98)	2191.393 1
B/MHz	470.873 90(25)	474.395 67
C/MHz	387.689 84(22)	389.974 57
D_J/kHz	0.010 0(14)	
D_{JK}/kHz	0.102(28)	
D_K/kHz	13.2(81)	
Δ/amu Å^2	−1.46	−0.003
N	25	
σ/kHz	3	

15 min and then was removed from the Ne gas line as this provided a sufficient concentration of formic acid to measure the dimer transitions in a single pulsed beam cycle.

III. CALCULATIONS AND ROTATIONAL CONSTANTS

Ab initio calculations were performed on the HPC (High Performance Computing) system at the University of Arizona using the Gaussian 09[31] using the B3LYP method with the aug-cc-pVTZ basis. The results from this calculation are shown in Table II, and the calculated structure showing the hydrogen bond lengths is shown in Figure 1. The calculated rotational constants were used in the Pickett SPCAT[32] program to predict the rotational transitions expected to be observed. The calculated dipole moment components were 3.8 D along the a-axis and 0.6 D along the b-axis, so it was expected that the a-type transitions would be the strongest and these were the transitions that were initially searched for. The rotational and centrifugal distortion constants were determined from the measured 25 a- and b-type rotational transitions using the Pickett SPFIT program, and the experimentally determined parameters are also shown in Table II.

IV. DISCUSSION

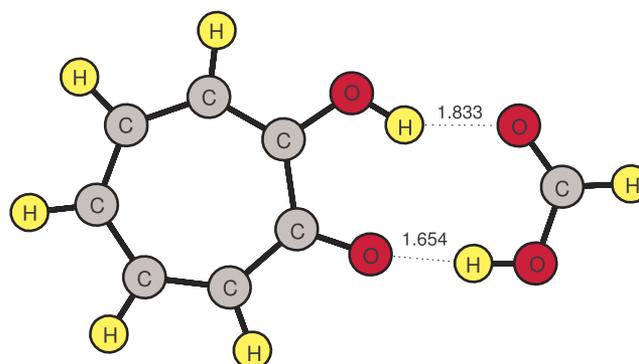The rotational spectrum was measured for the tropolone–formic acid doubly hydrogen bonded dimer in

FIG. 1. Calculated B3LYP/aug-cc-pVTZ structure of the tropolone–formic acid doubly hydrogen bonded dimer. Hydrogen bond lengths are shown in Å.

the 4.7-9 GHz range using a pulsed-beam Fourier transform microwave spectrometer. It was expected that this doubly hydrogen bonded dimer would exhibit a concerted double proton tunneling motion as the dimer has a $C_{2v}(M)$ symmetry. This symmetry has been proposed as a requirement to observe the proton tunneling motion, and this symmetry has been present in numerous other hydrogen bonded dimers exhibiting observable tunneling splittings. When the doubly hydrogen bonded dimer exhibits proton tunneling, each rotational transition measured is split; the magnitude of this splitting ranges up to a few MHz for a-type transitions and it can be hundreds of MHz for b-type transitions and is dependent on the barrier height and separation of the minima for the potential energy surface. When the splittings due to tunneling are observed, a vibration-rotation coupling analysis needs to be performed to fit the spectra from the two tunneling states which are treated as two vibrational states. After measuring both a- and b-type transitions for this dimer, no splittings for any transition were observed indicating that this doubly hydrogen bonded dimer did not exhibit the concerted double proton tunneling motion.

To get an estimate of the barrier height in the potential energy surface for the tunneling motion, the two tunneling protons were held fixed between the tropolone and formic acid molecules such that the distance of the proton between the two oxygen atoms in each molecule was equivalent, and the energy of this transition-state structure was calculated using B3LYP/aug-cc-pVTZ. The difference in energy of the calculated equilibrium structure and this transition state structure was about 15 000 cm^{-1}. The distance that each proton was estimated to move during the tunneling process is about 0.8 Å, which is similar to what was found for the propiolic–formic acid dimer.[20] The distance each proton moves was found by taking the transition state O—H bond lengths and subtracting the B3LYP optimized bond lengths and multiplying by 2 to get to the next tunneling state. The large barrier height between the two tunneling states is, very likely, why the concerted double proton tunneling motion was not observed for this doubly hydrogen bonded dimer. The estimated distance between the potential minima was similar to that for propiolic acid–formic acid complex for which the proton tunneling process was observed in the microwave spectra.

While measuring the rotational transitions from this dimer, the spectrum was congested with numerous other transitions that were significantly strong. From the *ab initio* calculations, it was predicted that there are many low energy out of plane vibrational modes. The inertial defect calculated from the experimentally determined rotational constants is $\Delta = -1.46$ amu Å^2. This is indicative of a planar structure with the magnitude not being significantly large, but because of the nonzero negative value, this is a confirmation that there are significant out of plane vibrations for this dimer.[33] After measuring many transitions and attempting to make sense and assign the congested spectra, none of the additional transitions measured were able to be fit to an excited vibrational state. The additional transitions are most likely from other complexes formed with formic acid or water or due to the excited vibrational states.

[1]K. Tanaka, H. Honjo, T. Tanaka, H. Kohguchi, Y. Ohshima, and Y. Endo, J. Chem. Phys. **110**, 1969 (1999).

[2]J. C. Keske, W. Lin, W. C. Pringle, S. E. Novick, T. A. Blake, and D. F. Plusquellic, J. Chem. Phys. **124**, 074309 (2006).

[3]A. E. Bracamonte and P. H. Vaccaro, J. Chem. Phys. **120**, 4638 (2003).

[4]L. A. Burns, D. Murdock, and P. H. Vaccaro, J. Chem. Phys. **124**, 204307 (2006).

[5]D. Murdock, L. A. Burns, and P. H. Vaccaro, J. Chem. Phys. **127**, 081101 (2007).

[6]L. A. Burns, D. Murdock, and P. H. Vaccaro, J. Chem. Phys. **130**, 144304 (2009).

[7]D. Murdock, L. A. Burns, and P. H. Vaccaro, Phys. Chem. Chem. Phys. **12**, 8285 (2010).

[8]R. L. Redington and T. E. Redington, J. Mol. Spectrosc. **78**, 229 (1979).

[9]R. L. Redington and T. E. Redington, J. Chem. Phys. **122**, 124304 (2005).

[10]R. Rossetti and L. E. Brus, J. Chem. Phys. **73**, 1546 (1980).

[11]Y. Tomioka, M. Ito, and N. Mikami, J. Phys. Chem. **87**, 4401 (1983).

[12]R. L. Redington, J. Chem. Phys. **113**, 2319 (2000).

[13]R. L. Redington and R. L. Sams, J. Phys. Chem. A **106**, 7494 (2002).

[14]R. L. Redington, T. E. Redington, and R. L. Sams, J. Phys. Chem. A **110**, 9633 (2006).

[15]R. L. Redington, T. E. Redington, and R. L. Sams, J. Phys. Chem. A **112**, 1480 (2008).

[16]H. Sekiya, T. Nakajima, H. Ujita, T. Tsuji, S. Ito, and Y. Nishimura, Chem. Phys. Lett. **215**, 499 (1993).

[17]W. Lin, W. C. Pringle, S. E. Novick, and T. A. Blake, J. Phys. Chem. A **113**, 13076 (2009).

[18]J. C. Keske and D. F. Plusquellic, in International Symposium of Molecular Spectroscopy, TD10, Columbus, OH, 2003.

[19]O. Birer and M. Havenith, Annu. Rev. Phys. Chem. **60**, 263–275 (2009), and references therein.

[20]A. M. Daly, P. R. Bunker, and S. G. Kukolich, J. Chem. Phys. **132**(20), 201101 (2010).

[21]A. M. Daly, P. R. Bunker, and S. G. Kukolich, J. Chem. Phys. **133**(7), 079903 (2010).

[22]A. M. Daly, K. O. Douglass, L. C. Sarkozy, J. L. Neill, M. T. Muckle, D. P. Zaleski, B. H. Pate, and S. G. Kukolich, J. Chem. Phys. **135**, 154304-1–154304-12 (2011).

[23]G. Feng, L. B. Favero, A. Maris, A. Vigorito, W. Caminati, and R. Meyer, J. Am. Chem. Soc. **134**, 19281–19286 (2012).

[24]L. Evangelisti, P. Ecija, E. J. Cocinero, F. Castano, A. Lessarri, W. Caminati, and R. Meyer, J. Phys. Chem. Lett. **3**, 3770–3775 (2012).

[25]M. C. D. Tayler, B. Ouyang, and B. J. Howard, J. Chem. Phys. **134**, 054316-1–054316-9 (2011).

[26]A. M. Pejlovas, M. Barfield, and S. G. Kukolich, Chem. Phys. Lett. **613**, 86–89 (2014).

[27]A. M. Pejlovas and S. G. Kukolich, "Rotational spectra and gas phase structure of the maleimide - Formic acid doubly hydrogen bonded dimer," J. Mol. Spectrosc. (to be published).

[28]A. M. Pejlovas, W. Lin, and S. G. Kukolich, J. Chem. Phys. **143**, 124311 (2015).

[29]R. E. Bumgarner and S. G. Kukolich, J. Chem. Phys. **86**, 1083 (1987).

[30]S. T. Brandon, C. Karunatilaka, A. M. Daly, and S. G. Kukolich, Organometallics **26**(8), 2070 (2007).

[31]M. J. Frisch *et al.*, GAUSSIAN 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.

[32]H. M. Pickett, J. Mol. Spectrosc. **148**, 371 (1991).

[33]T. Oka, J. Mol. Struct. **352-353**, 225–233 (1995).