Terahertz Vibration-Rotation-Tunneling Spectroscopy of the Propane-Water Dimer: the *ortho*- state of a 20 cm⁻¹ Torsion

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Abstract

We report the detailed characterization of a torsional vibration-rotation-tunneling band of the *ortho*- state of the propane-water dimer in the spectral region near 20 cm^{-1} (0.6 THz). This work extends the previously reported studies with more than one hundred new transitions included in a combined fit with the 155 previously reported transitions in both the microwave and terahertz regions for this torsional band. More than six hundred transitions have now been recorded in the interval 500 and 810 GHz.

Introduction

Terrestrial clathrate hydrates are envisioned as a potentially major energy source of the future¹, and may be an important factor in both past and future climate change². The detailed composition of natural-gas clathrates is quite variable; methane is always the dominant hydrocarbon component, but ethane, propane, and butane are also abundant (in the 1-10% range). The presence of these higher hydrocarbons engenders greater stability for natural gas clathrate hydrates relative to pure methane clathrates³, clearly an important consideration for designing schemes to extract clathrates from their extreme geological environments¹. Computer simulations of clathrate stability and decomposition pathways are an essential component of this scenario, and these require accurate potential-surface models for describing the interactions among water and hydrocarbon molecules. Precise spectroscopic measurements of the intermolecular vibration-rotation-tunneling (VRT) states of gaseous water-hydrocarbon clusters, particularly the dimers, provide an important route to developing and calibrating such potential models, as has been demonstrated for the case of pure-water models^{4,5,6}.

Water-hydrocarbon interactions are important in another context, viz. elucidating the details of "hydrophobic effects"⁷. In the case of water-methane interactions, we have shown⁸ that the repulsive wall of the pairwise interaction potential directs the OH bond of water into the threefold hollow of the methyl group, thereby facilitating closest approach of the molecules. Other studies support this conclusion^{9,10,11,12}.

Extending this picture to higher hydrocarbons is a goal of our ongoing work, and this paper continues that effort.

We have published the results of previous studies of the propane-water dimer by microwave and terahertz VRT spectroscopy^{13,14}. In the latter work, we described the observation and partial characterization of a low-frequency torsional vibration. Here we extend this study to include 144 additional transitions near 20 cm⁻¹ involving this same torsional state. From analysis of the spectra, we deduce that the excited state of this torsional band is fairly rigid. There is no significant perturbation for the excited state, contrary to what we suggested earlier¹⁸.

For the propane-water dimer, there are two low-lying states corresponding to the two nuclear spin states of water: the two spin ½ hydrogen nuclei can form two orientations (*ortho*- and *para*-) having a statistical weight ratio of 3:1, respectively. These two states can be interpreted as the result of water proton interchange tunneling. The direct measurement of the splitting between the two states is, however, hindered by electric-dipole selection rules forbidding nuclear spin flips. The previous microwave spectroscopy study of the propane-water dimer¹³ unambiguously determined the rotational constants for both states from the intensities of the pure rotational transitions. Based on those results, we can assign the present band to propane-water dimer states correlating to the *ortho*- state of water. In the current analysis, we included both the microwave and the VRT datasets in the same fit, with the proper statistical weights for the two types of measurements.

Experiment

Terahertz VRT spectra of the propane-water dimer were observed in a continuous supersonic planar jet expansion probed by a tunable far infrared (terahertz) laser spectrometer. The spectrometer has been described in detail elsewhere^{15,16}, so only a brief description is given here. The tunable terahertz radiation is generated by mixing the output from an optically pumped line-tunable far infrared gas laser with continuously tunable frequency-modulated microwaves using a Schottky barrier diode. Light is generated at the sum and difference frequencies ($\nu = \nu_{\text{FIR}} \pm \nu_{\text{MW}}$). A Michelson polarizing interferometer is used to separate the tunable sideband radiation from the much stronger residual THz center frequency radiation. The sidebands are then directed to multipass optics that encompass the supersonic expansion of the target molecular system. This supersonic expansion, formed by expanding 1-2 atm of a 3% mixture of propane (instrument purity, 99.5%, flow rate 0.02 SSCFM, Matheson) in argon (99.995% pure, Liquid Air Corporation) bubbled through distilled water under a backing pressure of 1120 torr through a 4" x 0.005" slit nozzle, creates a population of propane-water dimers with a temperature of about 4K. After passing ~10 times through the expansion, the radiation is detected by a liquid helium-cooled detector (either a Rollins-mode indium antimonide detector or a Putley-mode indium antimonide detector). The far infrared laser lines used for this scan were 527.9260 GHz (DCOOD), 584.3882 GHz (HCOOH), 639.1846 GHz (CH₃OH), 692.9513 GHz (HCOOH), 716.1574 GHz (HCOOH), 761.6083 GHz (HCOOH), 768.8820 GHz (DCOOD), 787.7555 GHz (DCOOD). The microwave frequency ranges were chosen

so that the complete frequency range from 498 GHz to 810 GHz was covered. The Stark effect was used to help assign the complicated spectra¹⁴. The spectra carrier of each absorption line was checked by first turning off the propane flow while leaving the argon-water flow on and then vice versa. This check eliminated many transitions from the scan that do not depend on the propane (and are presumably due to argon-water clusters). Only the transitions that require both the propane flow and argon-water flow were kept in the dataset.

Observed spectra and analysis

A total of more than 600 transitions was recorded with ca. 2 MHz precision. 146 transitions were assigned to a *c*-type band involving the *ortho*- state of the propane-water dimer¹⁴. The initial assignment method was described previously in terms of using the Stark effect measurements and the lower/higher state combination-differences¹⁴. Clearly, many unassigned transitions remain in this region. In particular, there is a stack of $K_a = 2$ -3 transitions wherein the measured frequencies are consistently lower by about 20 MHz than predicted. After reassigning the 512616.5 MHz transition, rather than that at 512635.8 MHz in Ref. 14, to the $7_{26} \leftarrow 8_{36}$ transition, we were able to add many transitions to the fit and refine the prediction for the $K_a = 3$ -4 stack. After several iterations, we added more than one hundred transitions to the fit, while keeping rms error lower than the experimental error of several MHz. Figure 1 shows a stick spectrum of the previously 146 assigned transitions and of the 290 assigned transitions after this work. The added new transitions are listed in Table 1. These transitions have been least-squares fit together with the previous 146 THz-regime transitions and 9 microwave transitions in a weighted fit to the standard semi-rigid rotor Hamiltonian using SPFIT¹⁷.

Table 2 lists the spectroscopic constants resulting from the fit, in comparison to the previous results. The transitions were fitted to an asymmetric top semi-rigid Hamiltonian with three rotational constants, five quartic centrifugal distortion constants, a few sextic centrifugal distortion constants for both the ground state and

the excited state and the band origin of the excited state. As shown in Table 2, after adding the additional transitions to the fit, most of the rotational constants for the ground state and upper state remain near their previous values. These transitions, however, made it possible to precisely determine the important D_K value for the ground state for the first time. Some of the centrifugal distortion constants have also been significantly revised. It also clarified the origin of the > 100 lines remaining in the same frequency region assigned for the torsional band. It is clear after the analysis presented here that the excited state of this torsional band is free from any large perturbation, unlike what had been suggested previously¹⁸.

For most weakly bound dimers, the a inertial axis is aligned very closely with the line connecting the centers of mass of the two subunits. The A rotational constant of the *ortho*- propane-water dimer ground state was determined to be 8442.152(62) MHz, whereas the B rotational constant of free propane was reported as 8446.07 MHz¹⁹. The fact that these two constants are so close indicates that the a inertial axis of the dimer is approximately aligned with the b inertial axis of the free propane molecule. This would be true if propane were forming a dimer with a rare gas atom like argon or neon²⁰. However, in the case of the propane-water dimer, water is of a structure that will contribute at least somewhat to I_a . If we assume a rigid structure for the dimer such that the center of mass of water lies on the b inertial axis of the free propane molecule, we can rationalize a value for the A rotational constant of 8330 MHz. Reference 13 considered a scenario wherein the center of mass of water is slightly displaced from the b inertial axis of the propane molecule, but concluded that

it would rapidly decrease A , while increasing the C rotational constant. A possible explanation for this is the large amplitude motions of the water molecule. As observed for the ammonia dimer^{21,22,23} and argon-water dimer²⁴, a large amplitude motion of similar timescale can exhibit significant mixing with A axis rotation and other internal motions. The proposed structure for the propane-water dimer is shown in Figure 2.

We assigned this torsional band of the propane-water dimer comprising all of the P -, Q -, and R -branches using a semi-rigid rotor Hamiltonian and obtained the new information given in Table 2, including refined values for the rotational constants and band origin, but this single VRT band does not allow a definite vibrational assignment. After the assignment of the additional transitions described above, there remain about three hundred unassigned transitions between 680 GHz and 810 GHz, as shown in Figure 1. It is possible that these transitions belong to either the *para*-state of the propane-water dimer or larger propane water clusters, or perhaps to a VRT state of the argon-propane dimer. Extensive continuous spectral coverage at higher frequency is needed in order to make further progress on assigning these transitions, and alternative technology is currently being explored to effect such additional study²⁵.

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Table 1. Measured new frequencies for the *ortho*- state of the propane water dimer.

$J'_{Ka'}, Kc' \leftarrow J''_{Ka'', Kc''}$	Freq./MHz	Residual	$J'_{Ka'}, Kc' \leftarrow J''_{Ka'', Kc''}$	Freq./MHz	Residual
$7_{0,7} \leftarrow 7_{1,7}$	579112.7	0.9	$7_{3,5} \leftarrow 8_{4,5}$	501685.3	0.3
$5_{0,5} \leftarrow 4_{1,3}$	592614.8	0.8	$7_{3,4} \leftarrow 8_{4,4}$	501897.1	-0.3
$6_{0,6} \leftarrow 5_{1,4}$	595098.0	2.2	$6_{3,4} \leftarrow 7_{4,4}$	505992.3	0.1
$7_{0,7} \leftarrow 6_{1,5}$	597016.9	1.7	$6_{3,3} \leftarrow 7_{4,3}$	505079.0	-0.8
$7_{1,6} \leftarrow 8_{0,8}$	562961.5	1.2	$5_{3,3} \leftarrow 6_{4,3}$	510308.7	-3.1
$5_{1,4} \leftarrow 6_{0,6}$	565286.0	1.9	$4_{3,2} \leftarrow 5_{4,2}$	514652.2	-0.5
$4_{1,3} \leftarrow 5_{0,5}$	567431.3	-0.9	$4_{3,1} \leftarrow 5_{4,1}$	514659.4	-0.9
$3_{1,2} \leftarrow 4_{0,4}$	570203.8	-1.4	$3_{3,1} \leftarrow 4_{4,1}$	519021.4	2.1
$2_{1,1} \leftarrow 3_{0,3}$	573527.9	-0.3	$3_{3,0} \leftarrow 4_{4,0}$	519021.4	1.0
$1_{1,0} \leftarrow 2_{0,2}$	577310.2	-0.9	$4_{3,2} \leftarrow 4_{4,0}$	537074.5	0.6
$2_{1,2} \leftarrow 2_{2,0}$	560421.3	1.7	$4_{3,1} \leftarrow 4_{4,1}$	537082.4	0.4
$3_{1,3} \leftarrow 3_{2,1}$	559584.3	1.9	$5_{3,3} \leftarrow 5_{4,1}$	537237.2	-2.3
$4_{1,4} \leftarrow 4_{2,2}$	558305.3	0.6	$6_{3,4} \leftarrow 6_{4,2}$	537437.7	1.2
$6_{1,6} \leftarrow 6_{2,4}$	553968.9	0.5	$6_{3,3} \leftarrow 6_{4,3}$	537534.4	0.4
$6_{1,5} \leftarrow 5_{2,3}$	592253.4	1.8	$7_{3,5} \leftarrow 7_{4,3}$	537655.9	1.8
$7_{1,6} \leftarrow 6_{2,4}$	597267.1	2.2	$7_{3,4} \leftarrow 7_{4,4}$	537898.3	0.9
$8_{1,7} \leftarrow 7_{2,5}$	601874.2	1.5	$8_{3,6} \leftarrow 8_{4,4}$	537874.6	2.3
$9_{1,8} \leftarrow 8_{2,6}$	605967.7	1.9	$8_{3,5} \leftarrow 8_{4,5}$	538404.8	0.5
$10_{1,9} \leftarrow 9_{2,7}$	609462.8	-0.3	$9_{3,6} \leftarrow 9_{4,6}$	539110.0	0.1
$11_{2,9} \leftarrow 12_{1,11}$	547926.1	1.5	$10_{3,7} \leftarrow 10_{4,7}$	540078.8	-0.5
$9_{2,7} \leftarrow 10_{1,9}$	551806.8	-0.1	$11_{3,9} \leftarrow 11_{4,7}$	538133.9	-1.4
$7_{2,5} \leftarrow 8_{1,7}$	558710.9	0.8	$11_{3,8} \leftarrow 11_{4,8}$	541377.2	-0.9
$6_{2,4} \leftarrow 7_{1,6}$	563092.2	0.6	$13_{3,11} \leftarrow 13_{4,9}$	537293.3	0.4
$2_{2,0} \leftarrow 2_{1,2}$	599443.1	-0.9	$4_{4,0} \leftarrow 4_{3,2}$	624189.1	1.1
$3_{2,1} \leftarrow 3_{1,3}$	600467.7	1.2	$5_{4,1} \leftarrow 5_{3,3}$	624277.8	0.1
$4_{2,2} \leftarrow 4_{1,4}$	601980.6	0.8	$8_{4,4} \leftarrow 8_{3,6}$	624664.6	1.6
$5_{2,3} \leftarrow 5_{1,5}$	604091.2	-3.0	$9_{4,5} \leftarrow 9_{3,7}$	624893.7	1.9
$6_{2,4} \leftarrow 6_{1,6}$	606918.1	1.2	$14_{4,10} \leftarrow 14_{3,12}$	629170.1	-1.3
$7_{2,5} \leftarrow 7_{1,7}$	610530.1	-1.2	$14_{4,11} \leftarrow 13_{3,11}$	690420.9	1.2
$5_{2,4} \leftarrow 4_{1,4}$	623956.1	-4.1	$4_{4,0} \leftarrow 5_{5,0}$	502619.8	1.9
$9_{2,8} \leftarrow 10_{3,8}$	502617.9	-0.5	$4_{4,1} \leftarrow 5_{5,1}$	502619.8	1.9
$9_{2,7} \leftarrow 10_{3,7}$	508300.7	-1.6	$5_{4,2} \leftarrow 6_{5,2}$	498303.9	1.0
$8_{2,7} \leftarrow 9_{3,7}$	507700.0	-0.7	$5_{4,1} \leftarrow 6_{5,1}$	498303.9	0.7

$8_{2,6} \leftarrow 9_{3,6}$	511850.9	-1.3	$5_{5,1} \leftarrow 4_{4,1}$	659585.7	0.9
$7_{2,6} \leftarrow 8_{3,6}$	512616.5	-0.5	$6_{5,2} \leftarrow 5_{4,2}$	664212.5	0.5
$7_{2,5} \leftarrow 8_{3,5}$	515410.1	-1.4	$12_{5,7} \leftarrow 11_{4,7}$	691895.2	0.9
$6_{2,5} \leftarrow 7_{3,5}$	517385.6	-1.1	$12_{5,8} \leftarrow 11_{4,8}$	692164.1	0.7
$6_{2,4} \leftarrow 7_{3,4}$	519086.8	-1.4	$13_{5,8} \leftarrow 12_{4,8}$	696324.2	4.1
$5_{2,4} \leftarrow 6_{3,4}$	522030.5	-3.8	$13_{5,9} \leftarrow 12_{4,9}$	696846.7	6.5
$3_{2,2} \leftarrow 4_{3,2}$	531077.1	0.1	$14_{5,9} \leftarrow 13_{4,10}$	700594.7	-3.3
$3_{2,1} \leftarrow 4_{3,1}$	531219.2	0.2	$14_{5,10} \leftarrow 13_{4,10}$	701537.8	-1.3
$2_{2,1} \leftarrow 3_{3,1}$	535531.7	0.8	$6_{5,2} \leftarrow 6_{6,0}$	513372.0	-1.0
$2_{2,0} \leftarrow 3_{3,0}$	535560.5	0.5	$6_{5,1} \leftarrow 6_{6,1}$	513372.0	-1.0
$7_{2,6} \leftarrow 7_{3,4}$	548352.7	0.1	$7_{5,3} \leftarrow 7_{6,1}$	513645.4	1.3
$6_{2,5} \leftarrow 6_{3,3}$	548775.5	-0.1	$7_{5,2} \leftarrow 7_{6,2}$	513645.4	1.3
$5_{2,4} \leftarrow 5_{3,2}$	548975.9	-3.4	$8_{5,4} \leftarrow 8_{6,2}$	513956.3	-0.9
$4_{2,3} \leftarrow 4_{3,1}$	549045.1	1.2	$8_{5,3} \leftarrow 8_{6,3}$	513956.3	-1.2
$3_{2,2} \leftarrow 3_{3,0}$	549031.2	0.3	$8_{6,2} \leftarrow 9_{5,4}$	610186.4	6.2
$3_{2,1} \leftarrow 3_{3,1}$	549184.7	0.5	$8_{6,3} \leftarrow 9_{5,5}$	610186.4	4.8
$4_{2,2} \leftarrow 4_{3,2}$	549505.2	0.9	$11_{6,5} \leftarrow 11_{5,7}$	651104.2	-2.3
$5_{2,3} \leftarrow 5_{3,3}$	550045.1	-2.7	$10_{6,4} \leftarrow 10_{5,6}$	650930.2	-2.6
$6_{2,4} \leftarrow 6_{3,4}$	550882.3	-0.7	$9_{6,4} \leftarrow 9_{5,4}$	650748.8	-1.8
$7_{2,5} \leftarrow 7_{3,5}$	552057.4	-0.8	$8_{6,2} \leftarrow 8_{5,4}$	650574.2	3.9
$8_{2,6} \leftarrow 8_{3,6}$	553590.6	-0.6	$8_{6,3} \leftarrow 8_{5,3}$	650574.2	4.3
$10_{2,8} \leftarrow 10_{3,8}$	557662.6	0.4	$7_{6,1} \leftarrow 7_{5,3}$	600387.8	-5.5
$9_{2,7} \leftarrow 8_{3,5}$	595380.3	0.4	$7_{6,2} \leftarrow 7_{5,2}$	600387.8	-5.4
$11_{2,9} \leftarrow 10_{3,7}$	607453.7	4.8	$7_{6,1} \leftarrow 6_{5,1}$	681756.1	-4.7
$12_{2,10} \leftarrow 11_{3,8}$	613135.7	0.9	$7_{6,2} \leftarrow 6_{5,2}$	681756.1	-4.8
$6_{3,4} \leftarrow 7_{2,6}$	581258.1	0.3	$8_{6,2} \leftarrow 7_{5,2}$	686447.8	4.4
$13_{3,10} \leftarrow 13_{2,12}$	629180.0	-1.0	$8_{6,3} \leftarrow 7_{5,3}$	686447.8	4.3
$11_{3,8} \leftarrow 11_{2,10}$	620927.6	0.0	$9_{6,4} \leftarrow 8_{5,4}$	691139.7	-1.1
$9_{3,6} \leftarrow 9_{2,8}$	615872.7	2.6	$10_{7,3} \leftarrow 10_{6,5}$	664067.7	1.6
$8_{3,5} \leftarrow 8_{2,7}$	614284.9	1.0	$7_{7,0} \leftarrow 6_{6,0}$	694657.3	5.5
$8_{3,6} \leftarrow 8_{2,6}$	607772.7	2.6	$7_{7,1} \leftarrow 6_{6,1}$	694657.3	5.5
$7_{3,4} \leftarrow 7_{2,6}$	613163.7	0.6	$8_{7,1} \leftarrow 7_{6,1}$	699361.7	-1.2
$6_{3,3} \leftarrow 6_{2,5}$	612395.9	-1.3	$10_{7,3} \leftarrow 9_{6,3}$	708850.3	3.0
$5_{3,3} \leftarrow 5_{2,3}$	610687.6	-3.8	$10_{7,4} \leftarrow 9_{6,4}$	708850.3	3.0
$4_{3,1} \leftarrow 4_{2,3}$	611578.8	1.2	$11_{7,5} \leftarrow 10_{6,5}$	713613.4	0.4
$3_{3,0} \leftarrow 3_{2,2}$	611387.1	-0.4	$12_{7,5} \leftarrow 11_{6,5}$	718388.8	0.9

$5_{3,3} \leftarrow 4_{2,3}$	634152.0	-4.8	$12_{7,6} \leftarrow 11_{6,6}$	718388.8	0.7
$13_{3,10} \leftarrow 12_{2,10}$	665510.5	-0.5	$8_{8,0} \leftarrow 7_{7,0}$	712218.9	-1.0

Table 2. Spectroscopic constants for the combined fit of the *ortho*- state of the propane water dimer.

State		Steyert <i>et al</i> ¹⁴	New fit
Ground state	<i>A</i> /MHz	8443.24 (12)	8442.160 (57)
	<i>B</i> /MHz	2507.6611 (22)	2507.6622 (14)
	<i>C</i> /MHz	1969.3165 (22)	1969.3159 (17)
	<i>D_J</i> /kHz	10.203 (78)	10.173 (30)
	<i>D_{JK}</i> /kHz	211.44 (50)	212.14 (24)
	<i>D_K</i> /kHz	0.0 ^a	-212.3 (38)
	<i>d₁</i> /kHz	4.166 (46)	-4.188 (25)
	<i>d₂</i> /kHz	8.68 (49)	-0.933 (20)
	<i>H_J</i> /kHz	0.00023 (18)	0.00035 (35)
	<i>H_{JK}</i> /kHz	0.0095 (23)	0.0389 (50)
	<i>H_{KJ}</i> /kHz	-1.26 (12)	-0.976 (24)
	<i>H_K</i> /kHz	-15.1 (22)	0.488 (58)
Excited state	<i>E</i> /MHz	579691.20 (24)	579690.38 (32)
	cm ⁻¹	19.336417 (8)	19.336390 (11)
	<i>A</i> /MHz	8512.765 (61)	8513.112 (49)
	<i>B</i> /MHz	2503.631 (18)	2503.614 (20)
	<i>C</i> /MHz	1997.940 (18)	1997.983 (24)
	<i>D_J</i> /kHz	12.009 (61)	12.02 (19)
	<i>D_{JK}</i> /kHz	87.0 (12)	89.12 (94)
	<i>D_K</i> /kHz	51.0 (28)	164.09 (89)
	<i>d₁</i> /kHz	3.348 (94)	-3.118 (86)
	<i>d₂</i> /kHz	-0.875 (29)	-0.923 (32)
	<i>H_J</i> /kHz	0.0 ^a	-1.90 (70)
	<i>H_{JK}</i> /kHz	-0.0216 (74)	-0.0204 (46)
	<i>H_{KJ}</i> /kHz	-0.027 (25)	0.0 ^a
	<i>H_K</i> /kHz	10.539 (25)	0.0 ^a
	N	155	299
	σ/MHz	1.1	1.6

^aValue within one standard deviation of zero, fixed at zero for this fit.

Figure 1. a) Stick spectrum of the 146 assigned transitions from reference 14. b) Stick spectrum of the 290 assigned transitions including the ones from reference 14 and the new transitions from this work. It should be noted that this is a composite spectrum, including transitions from five laser lines. Only the intensities of transitions recorded using a given laser line can be sensibly compared.

a)

b)

Figure 2. One of the proposed equilibrium structures for the propane-water dimer¹³ based on the projection of dipole moment of water, wherein the oxygen atom sits on the C_2 axis of propane monomer and all three atoms of water remain in the plane of the carbon atoms of propane.

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