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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.

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1. Introduction

Terrestrial clathrate hydrates are envisioned as a potentially major energy source of the future [1], and may be an important factor in both past and future climate change [2]. 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 clathrates [3], clearly an important consideration for designing schemes to extract clathrates from their extreme geological environments [1]. 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 shown [8] 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 letter 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 earlier [18].

For the propane–water dimer, there are two low-lying states corresponding to the two nuclear spin states of water: the two spin $\frac{1}{2}$ 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 dimer [13] 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

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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.

2. 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 $4'' \times 0.005''$ slit nozzle, creates a population of propane–water dimers with a temperature of about 4 K. 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 (CH_3OH), 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 spectra [14]. 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.

3. 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 dimer [14]. The initial assignment method was described previously in terms of using the Stark effect measurements and the lower/higher state combination-differences [14]. 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 512 616.5 MHz transition, rather than that at 512 635.8 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

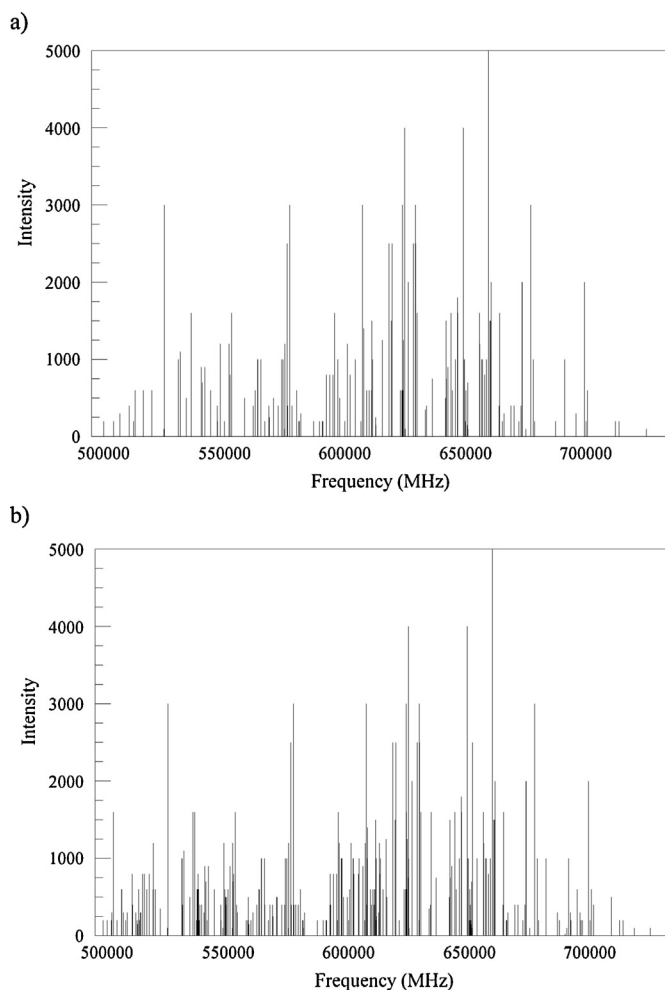


Figure 1. (a) Stick spectrum of the 146 assigned transitions from reference 14. (b) Stick spectrum of the 290 assigned transitions including the ones from Ref. [14] and the new transitions from this work. It should be noted that this is a composite spectrum, including transitions from five laser lines.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

weighted fit to the standard semi-rigid rotor Hamiltonian using SPFIT [17].

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 previously [18].

For most weakly bound dimers, the *a* inertial axis is aligned very closely with the line connecting the centers of mass of the two sub-units. 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 MHz [19]. The fact that these two constants are so close indicates that

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} ← 7 _{1,7}	579 112.7	0.9	7 _{3,5} ← 8 _{4,5}	501 685.3	0.3
5 _{0,5} ← 4 _{1,3}	592 614.8	0.8	7 _{3,4} ← 8 _{4,4}	501 897.1	−0.3
6 _{0,6} ← 5 _{1,4}	595 098.0	2.2	6 _{3,4} ← 7 _{4,4}	505 992.3	0.1
7 _{0,7} ← 6 _{1,5}	597 016.9	1.7	6 _{3,3} ← 7 _{4,3}	505 079.0	−0.8
7 _{1,6} ← 8 _{0,8}	562 961.5	1.2	5 _{3,3} ← 6 _{4,3}	510 308.7	−3.1
5 _{1,4} ← 6 _{0,6}	565 286.0	1.9	4 _{3,2} ← 5 _{4,2}	514 652.2	−0.5
4 _{1,3} ← 5 _{0,5}	567 431.3	−0.9	4 _{3,1} ← 5 _{4,1}	514 659.4	−0.9
3 _{1,2} ← 4 _{0,4}	570 203.8	−1.4	3 _{3,1} ← 4 _{4,1}	519 021.4	2.1
2 _{1,1} ← 3 _{0,3}	573 527.9	−0.3	3 _{3,0} ← 4 _{4,0}	519 021.4	1.0
1 _{1,0} ← 2 _{0,2}	577 310.2	−0.9	4 _{3,2} ← 4 _{4,0}	537 074.5	0.6
2 _{1,2} ← 2 _{2,0}	560 421.3	1.7	4 _{3,1} ← 4 _{4,1}	537 082.4	0.4
3 _{1,3} ← 3 _{2,1}	559 584.3	1.9	5 _{3,3} ← 5 _{4,1}	537 237.2	−2.3
4 _{1,4} ← 4 _{2,2}	558 305.3	0.6	6 _{3,4} ← 6 _{4,2}	537 437.7	1.2
6 _{1,6} ← 6 _{2,4}	553 968.9	0.5	6 _{3,3} ← 6 _{4,3}	537 534.4	0.4
6 _{1,5} ← 5 _{2,3}	592 253.4	1.8	7 _{3,5} ← 7 _{4,3}	537 655.9	1.8
7 _{1,6} ← 6 _{2,4}	597 267.1	2.2	7 _{3,4} ← 7 _{4,4}	537 898.3	0.9
8 _{1,7} ← 7 _{2,5}	601 874.2	1.5	8 _{3,6} ← 8 _{4,4}	537 874.6	2.3
9 _{1,8} ← 8 _{2,6}	605 967.7	1.9	8 _{3,5} ← 8 _{4,5}	538 404.8	0.5
10 _{1,9} ← 9 _{2,7}	609 462.8	−0.3	9 _{3,6} ← 9 _{4,6}	539 110.0	0.1
11 _{2,9} ← 12 _{1,11}	547 926.1	1.5	10 _{3,7} ← 10 _{4,7}	540 078.8	−0.5
9 _{2,7} ← 10 _{1,9}	551 806.8	−0.1	11 _{3,9} ← 11 _{4,7}	538 133.9	−1.4
7 _{2,5} ← 8 _{1,7}	558 710.9	0.8	11 _{3,8} ← 11 _{4,8}	541 377.2	−0.9
6 _{2,4} ← 7 _{1,6}	563 092.2	0.6	13 _{3,11} ← 13 _{4,9}	537 293.3	0.4
2 _{2,0} ← 2 _{1,2}	599 443.1	−0.9	4 _{4,0} ← 4 _{3,2}	624 189.1	1.1
3 _{2,1} ← 3 _{1,3}	600 467.7	1.2	5 _{4,1} ← 5 _{3,3}	624 277.8	0.1
4 _{2,2} ← 4 _{1,4}	601 980.6	0.8	8 _{4,4} ← 8 _{3,6}	624 664.6	1.6
5 _{2,3} ← 5 _{1,5}	604 091.2	−3.0	9 _{4,5} ← 9 _{3,7}	624 893.7	1.9
6 _{2,4} ← 6 _{1,6}	606 918.1	1.2	14 _{4,10} ← 14 _{3,12}	629 170.1	−1.3
7 _{2,5} ← 7 _{1,7}	610 530.1	−1.2	14 _{4,11} ← 13 _{3,11}	690 420.9	1.2
5 _{2,4} ← 4 _{1,4}	623 956.1	−4.1	4 _{4,0} ← 5 _{5,0}	502 619.8	1.9
9 _{2,8} ← 10 _{3,8}	502 617.9	−0.5	4 _{4,1} ← 5 _{5,1}	502 619.8	1.9
9 _{2,7} ← 10 _{3,7}	508 300.7	−1.6	5 _{4,2} ← 6 _{5,2}	498 303.9	1.0
8 _{2,7} ← 9 _{3,7}	507 700.0	−0.7	5 _{4,1} ← 6 _{5,1}	498 303.9	0.7
8 _{2,6} ← 9 _{3,6}	511 850.9	−1.3	5 _{5,1} ← 4 _{4,1}	659 585.7	0.9
7 _{2,6} ← 8 _{3,6}	512 616.5	−0.5	6 _{5,2} ← 5 _{4,2}	664 212.5	0.5
7 _{2,5} ← 8 _{3,5}	515 410.1	−1.4	12 _{5,7} ← 11 _{4,7}	691 895.2	0.9
6 _{2,5} ← 7 _{3,5}	517 385.6	−1.1	12 _{5,8} ← 11 _{4,8}	692 164.1	0.7
6 _{2,4} ← 7 _{3,4}	519 086.8	−1.4	13 _{5,8} ← 12 _{4,8}	696 324.2	4.1
5 _{2,4} ← 6 _{3,4}	522 030.5	−3.8	13 _{5,9} ← 12 _{4,9}	696 846.7	6.5
3 _{2,2} ← 4 _{3,2}	531 077.1	0.1	14 _{5,9} ← 13 _{4,10}	700 594.7	−3.3
3 _{2,1} ← 4 _{3,1}	531 219.2	0.2	14 _{5,10} ← 13 _{4,10}	701 537.8	−1.3
2 _{2,1} ← 3 _{3,1}	535 531.7	0.8	6 _{5,2} ← 6 _{6,0}	513 372.0	−1.0
2 _{2,0} ← 3 _{3,0}	535 560.5	0.5	6 _{5,1} ← 6 _{6,1}	513 372.0	−1.0
7 _{2,6} ← 7 _{3,4}	548 352.7	0.1	7 _{5,3} ← 7 _{6,1}	513 645.4	1.3
6 _{2,5} ← 6 _{3,3}	548 775.5	−0.1	7 _{5,2} ← 7 _{6,2}	513 645.4	1.3
5 _{2,4} ← 5 _{3,2}	548 975.9	−3.4	8 _{5,4} ← 8 _{6,2}	513 956.3	−0.9
4 _{2,3} ← 4 _{3,1}	549 045.1	1.2	8 _{5,3} ← 8 _{6,3}	513 956.3	−1.2
3 _{2,2} ← 3 _{3,0}	549 031.2	0.3	8 _{6,2} ← 9 _{5,4}	610 186.4	6.2
3 _{2,1} ← 3 _{3,1}	549 184.7	0.5	8 _{6,3} ← 9 _{5,5}	610 186.4	4.8
4 _{2,2} ← 4 _{3,2}	549 505.2	0.9	11 _{6,5} ← 11 _{5,7}	651 104.2	−2.3
5 _{2,3} ← 5 _{3,3}	550 045.1	−2.7	10 _{6,4} ← 10 _{5,6}	650 930.2	−2.6
6 _{2,4} ← 6 _{3,4}	550 882.3	−0.7	9 _{6,4} ← 9 _{5,4}	650 748.8	−1.8
7 _{2,5} ← 7 _{3,5}	552 057.4	−0.8	8 _{6,2} ← 8 _{5,4}	650 574.2	3.9
8 _{2,6} ← 8 _{3,6}	553 590.6	−0.6	8 _{6,3} ← 8 _{5,3}	650 574.2	4.3
10 _{2,8} ← 10 _{3,8}	557 662.6	0.4	7 _{6,1} ← 7 _{5,3}	600 387.8	−5.5
9 _{2,7} ← 8 _{3,5}	595 380.3	0.4	7 _{6,2} ← 7 _{5,2}	600 387.8	−5.4
11 _{2,9} ← 10 _{3,7}	607 453.7	4.8	7 _{6,1} ← 6 _{5,1}	681 756.1	−4.7
12 _{2,10} ← 11 _{3,8}	613 135.7	0.9	7 _{6,2} ← 6 _{5,2}	681 756.1	−4.8
6 _{3,4} ← 7 _{2,6}	581 258.1	0.3	8 _{6,2} ← 7 _{5,2}	686 447.8	4.4
13 _{3,10} ← 13 _{2,12}	629 180.0	−1.0	8 _{6,3} ← 7 _{5,3}	686 447.8	4.3
11 _{3,8} ← 11 _{2,10}	620 927.6	0.0	9 _{6,4} ← 8 _{5,4}	691 139.7	−1.1
9 _{3,6} ← 9 _{2,8}	615 872.7	2.6	10 _{7,3} ← 10 _{6,5}	664 067.7	1.6
8 _{3,5} ← 8 _{2,7}	614 284.9	1.0	7 _{7,0} ← 6 _{6,0}	694 657.3	5.5
8 _{3,6} ← 8 _{2,6}	607 772.7	2.6	7 _{7,1} ← 6 _{6,1}	694 657.3	5.5
7 _{3,4} ← 7 _{2,6}	613 163.7	0.6	8 _{7,1} ← 7 _{6,1}	699 361.7	−1.2
6 _{3,3} ← 6 _{2,5}	612 395.9	−1.3	10 _{7,3} ← 9 _{6,3}	708 850.3	3.0
5 _{3,3} ← 5 _{2,3}	610 687.6	−3.8	10 _{7,4} ← 9 _{6,4}	708 850.3	3.0
4 _{3,1} ← 4 _{2,3}	611 578.8	1.2	11 _{7,5} ← 10 _{6,5}	713 613.4	0.4
3 _{3,0} ← 3 _{2,2}	611 387.1	−0.4	12 _{7,5} ← 11 _{6,5}	718 388.8	0.9
5 _{3,3} ← 4 _{2,3}	634 152.0	−4.8	12 _{7,6} ← 11 _{6,6}	718 388.8	0.7
13 _{3,10} ← 12 _{2,10}	665 510.5	−0.5	8 _{8,0} ← 7 _{7,0}	712 218.9	−1.0

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

State		Steyert et al. [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	579,691.20 (24)
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
<i>N</i>		155	299
<i>σ</i> /MHz		1.1	1.6

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

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 neon [20]. 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. Ref. [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 [21–23] and argon–water dimer [24], 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. 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 study [25].

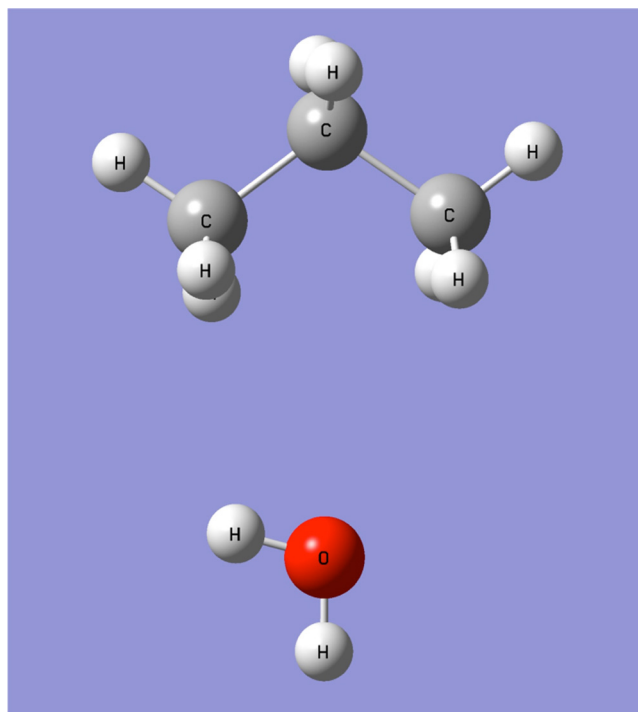


Figure 2. One of the proposed equilibrium structures for the propane–water dimer [13] based on the projection of dipole moment of water, wherein the oxygen atom sits on the *C₂* axis of propane monomer and all three atoms of water remain in the plane of the carbon atoms of propane.

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