

# Terahertz vibration-rotation-tunneling spectroscopy of the water tetramer-d8: Combined analysis of vibrational bands at 4.1 and 2.0 THz

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We report the measurement of terahertz vibration-rotation-tunneling spectra of  $(D_2O)_4$  in the spectral region near 4.13 THz. The characterization of this perpendicular band extends a previously reported study [J. Chem. Phys. **111**, 7801 (1999)]. We observed 239 new transitions, each being split into a doublet of constant (approximately 192 MHz) spacing. These are included in a combined fit with the 113 previously measured transitions of the 2.03 THz parallel band using an effective Hamiltonian similar to that used in the global fit of the water trimer. The detailed understanding of the water tetramer evolving from this work underlies our efforts to quantify the contribution of many-body forces to the hydrogen bonding interactions in condensed phase water.

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## INTRODUCTION

Significant advances in the characterization of water clusters by terahertz vibration-rotation-tunneling (VRT) spectroscopy were achieved in a concerted effort to quantitatively describe the bulk phases of water at the molecular level. Water clusters up to the hexamer<sup>1-3</sup> have been studied in detail with this technique, and this work has been accompanied by important recent progress in theoretical calculations. Notably, Leforestier *et al.*<sup>4</sup> have developed a full dimensional (12D) potential surface for the water dimer via direct inversion of spectroscopic data and subsequently used it to evaluate the equilibrium constant for dimer formation in the atmosphere and the absorption of radiation by atmospheric dimers.<sup>5</sup> Bukowski *et al.*<sup>6,7</sup> have developed a force field for water entirely from first principles, which predicts energy levels in excellent agreement with VRT experiments of the water dimer and provides a good description of bulk liquid properties. The extensive VRT spectroscopic studies of the water dimer have facilitated the determination of such accurate potential surface by providing rigorous benchmarks.<sup>8-13</sup> The potential role of the water clusters in atmospheric chemistry is also generating much interest.<sup>5</sup> Pfeilsticker *et al.*<sup>14</sup> recently reported near-IR absorption of atmospheric dimers and suggested that the concentration of dimers was about  $6 \times 10^{14} \text{ cm}^{-3}$  at room temperature. This figure agrees with the calculated value of  $4 \times 10^{14} \text{ cm}^{-3}$  ob-

tained by Dunn *et al.*,<sup>15</sup> who also calculated concentrations of water trimers, tetramers, and pentamers of  $10^{12}$ ,  $10^{11}$ , and  $10^{10} \text{ cm}^{-3}$ , respectively.

The water trimer [both  $(H_2O)_3$  and  $(D_2O)_3$ ] is the most highly studied water cluster beyond the dimer.<sup>16,17</sup> The trimer has an almost planar equilibrium structure, wherein each of the water molecules acts as both a hydrogen bond donor and acceptor. The three nonhydrogen bonded hydrogen (deuteron) atoms can undergo large amplitude motions, flipping from one side of the plane formed by the three oxygen atoms to the other side, resulting in six equivalent structures. The sequential flipping of these “free” hydrogen (deuteron) atoms can be thought of as a “pseudorotation,” and the energy barrier for these torsional motions is very low. Fowler and Schaefer<sup>18</sup> calculated this barrier to be equal to 0.26 kcal/mol using their TZ2P\_diff//DZP\_diff CCSD potential energy surface of the water trimer. Terahertz vibration-rotation-tunneling spectroscopy provides a direct probe of these torsional potentials. The torsional levels below  $100 \text{ cm}^{-1}$  for both  $(H_2O)_3$  and  $(D_2O)_3$  have been precisely characterized and included in the global fits.<sup>16,17</sup> The other feasible rearrangement of the structures involves the exchange of two hydrogen (deuteron) atoms of the same water molecule. This “bifurcation” tunneling<sup>19</sup> has a higher potential barrier [2.04 kcal/mol for  $(H_2O)_3$  from Ref. 18] than pseudorotation, and results in a characteristic small quartet splitting for each experimentally observed VRT torsional band transition of the water trimer (with the exception of the 583 GHz hot band Keutsch *et al.*<sup>20</sup> reported and some transitions involving  $K=0$  of degenerated torsional levels). Keutsch *et al.*<sup>21</sup> subsequently characterized a perpendicular band of  $(D_2O)_3$  at  $142.8 \text{ cm}^{-1}$  in the “translational band” region of the liquid. This band was assigned to a hydrogen bond stretching vibration and was fitted using the torsional Hamiltonian developed by Viant *et al.*<sup>22</sup> No bifurcation tunneling splittings were observed in this band either.

The existing data sets for the water tetramer [both

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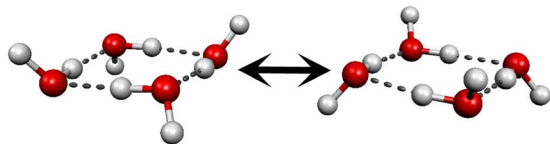


FIG. 1. (Color online) The degenerate torsional structures of the water tetramer.

$(\text{H}_2\text{O})_4$  and  $(\text{D}_2\text{O})_4$ ] are relatively sparse compared to those for the trimer. Only one parallel band at 2.04 THz for  $(\text{H}_2\text{O})_4$  (Ref. 23) has been characterized. For  $(\text{D}_2\text{O})_4$ , two bands have been measured, including one parallel band at 2.03 THz (Refs. 24 and 25) and one perpendicular band at 4.13 THz.<sup>26</sup> The equilibrium structure of the water tetramer is calculated to have  $S_4$  symmetry.<sup>27–31</sup> It is a cyclic homodromic structure, with each water subunit acting as both a hydrogen bond donor and an acceptor. The frame of the ring is almost planar and the four nearly linear O–H···O bonds make the four oxygen atoms lay near the four corners of a square. The nonhydrogen bonded hydrogen (deuteron) atoms alternatively point up and down (abbreviated *u* and *d*) relative to the quasiplane of the oxygen atoms. As shown in Fig. 1, there are two equivalent global minima (*udud* and *dudu*). These two equilibrium structures are interconvertible through torsional flipping of all free hydrogen (deuteron) atoms, though the exact tunneling path involved is not yet clear.<sup>32–34</sup> The higher symmetry of the water tetramer, relative to the water trimer and pentamer, has marked effects on its tunneling dynamics. For the trimer, because of the odd number of the free hydrogen (deuteron) atoms, there will always be a pair of neighboring free hydrogen atoms on the same side of the oxygen ring. This results in a “frustrated” equilibrium structure for the water trimer and thus lowers the barrier of the torsional motions that move the hydrogens from one side of the ring to the other. This is also the case for the water pentamer.<sup>35</sup> This motion generates the manifolds of torsional levels in the terahertz frequency region for the water trimer and pentamer that have been characterized by VRT spectroscopy. In contrast, for the water tetramer, flipping of a single free hydrogen atom is not favored as it yields a higher energy structure. Sabo *et al.*<sup>34</sup> and Graf and Leutwyler<sup>36</sup> calculated the four-dimensional torsional energy surface of the tetramer and found that the torsional levels are much higher in energy than those of the trimer and pentamer. Their calculated potential surface for the interconversion of the two equilibrium structures is similar to that for the inversion of the ammonia molecule.

Here we report further progress toward the complete characterization of the VRT dynamics and potential surface of the water tetramer. In particular, 239 new transitions were measured near 4.13 THz and fitted along with the previously measured data. We present the details of this study below.

## EXPERIMENT AND RESULTS

In this work, we used the Berkeley terahertz spectrometer that has been described in detail previously.<sup>37–39</sup> Briefly, a line-tunable  $\text{CO}_2$  laser is used to optically pump a molecular gas terahertz laser. The radiation generated from the tera-

hertz laser is then directed to an antenna, which is in contact with a Schottky barrier diode. Tunable microwave radiation is coupled to the diode via the same antenna. The nonlinear response of the diode mixes the terahertz and microwave radiation and generates sidebands of frequency  $\nu(\text{laser}) \pm \nu(\text{microwave})$ . These tunable sidebands are multipassed in the throat of a pulsed planar supersonic expansion of  $\text{D}_2\text{O}$  seeded in argon carrier gas. The absorption is detected by a liquid helium cooled Ge/Ga photoconductive detector. The region scanned in this work is  $\pm 118$  GHz around the  $70 \mu\text{m}$  (4251.6736 GHz,  $\text{CH}_3\text{OH}$ ) and  $72 \mu\text{m}$  (4158.9158 GHz,  $^{13}\text{CH}_3\text{OH}$ ) laser lines. 2 mm wave synthesizers (53–78 and 78–118 GHz, Kvarz, Russia) were used in addition to an HP8367B microwave synthesizer (2–26 GHz), extending the previous scanning regions in both directions.

More than 250 pairs of transitions have been identified for this 4.13 THz band from the characteristic 192 MHz doublet splitting of each transition. 239 of them are included in a combined fit with 118 transitions from the previously reported 2.03 THz band.<sup>24,25</sup> For the 4.13 THz band, only the frequencies of the upper band were included in the fit. These transitions and their assignments are listed in Table I. Cruzan *et al.*<sup>23–25</sup> reported unusual additional splittings of  $K=2$  transitions for the parallel bands of  $(\text{H}_2\text{O})_4$  and  $(\text{D}_2\text{O})_4$ , wherein the splittings increase with  $J^2$ . This is probably due to the coupling between internal motion and overall rotation. In that analysis, the average frequencies of the additional splittings were used. The analysis in our previous report of this band<sup>26</sup> was hindered by severe Coriolis interactions, particularly for low  $K$  transitions, such that only the high- $K$  transitions were included in a fit to the standard symmetric top rotational energy level expression. Similar problems were reported for the earlier works of the VRT spectroscopy of the water trimer. Viant *et al.*<sup>22</sup> proposed the torsional model analysis for the water trimer and predicted that both first- and second-order Coriolis effects exist and they arise from second order Coriolis coupling. The effective Hamiltonian developed from their model was successfully applied to the analysis of the water trimer and resulted in the satisfactory global fits of both  $(\text{H}_2\text{O})_3$  and  $(\text{D}_2\text{O})_3$ .<sup>16</sup> However, the VRT spectra of the water pentamer were analyzed without the second order Coriolis terms in the Hamiltonian. In the present study, we attempted to fit the new transitions to an effective Hamiltonian similar to that developed for the water trimer. These transitions have been least squares fit to the following energy level expressions using the SPFIT (Ref. 40) program,

$$E = v + BJ(J+1) + (C-B)K^2 - D_J(J(J+1))^2 - D_{JK}(J(J+1)K^2) - D_K K^4, \quad (1)$$

$$E = v + BJ(J+1) + (C-B)K^2 - D_J(J(J+1))^2 - D_{JK}(J(J+1)K^2) - D_K K^4 \pm q_B \delta_{K,1} K \mp 2\xi CK. \quad (2)$$

Here,  $B(=A)$  and  $C$  are the rotational constants,  $D_J$ ,  $D_{JK}$ , and  $D_K$  are the centrifugal distortion constants,  $2\xi C$  corresponds to the first order Coriolis coupling term, and  $q_B$  corresponds to the second-order coupling term. Because the resulting  $2\xi C$  term was relatively large, a centrifugal constant for this term

TABLE I. The assigned transitions of the 4.1 THz band of the water tetramer-d8.

$J'$	$K'$	$n'$	$J''$	$K''$	$n''$	Frequency (MHz)	O-C (MHz)
19	19	2	20	-20	0	4 070 133.7	3
18	18	2	19	-19	0	4 073 248.7	0
17	17	2	18	-18	0	4 076 360.3	-1
16	16	2	17	-17	0	4 079 465.9	-1
15	15	2	16	-16	0	4 082 565.9	-1
14	14	2	15	-15	0	4 085 660.0	0
13	13	2	14	-14	0	4 088 747.6	0
12	12	2	13	-13	0	4 091 828.5	0
11	11	2	12	-12	0	4 094 903.0	-1
10	10	2	11	-11	0	4 097 971.9	-1
9	9	2	10	-10	0	4 101 034.3	0
8	8	2	9	-9	0	4 104 089.8	-1
7	7	2	8	-8	0	4 107 141.1	1
6	6	2	7	-7	0	4 110 183.9	0
5	5	2	6	-6	0	4 113 221.1	0
4	4	2	5	-5	0	4 116 251.4	0
3	3	2	4	-4	0	4 119 275.7	0
2	2	2	3	-3	0	4 122 293.1	0
2	2	1	1	-1	0	4 140 426.2	-2
3	3	1	2	-2	0	4 143 398.9	0
4	4	1	3	-3	0	4 146 359.7	-2
5	5	1	4	-4	0	4 149 317.8	-1
6	6	1	5	-5	0	4 152 268.9	0
7	7	1	6	-6	0	4 155 212.7	-1
8	8	1	7	-7	0	4 158 150.6	0
9	9	1	8	-8	0	4 161 080.9	-1
10	10	1	9	-9	0	4 164 007.0	0
11	11	1	10	-10	0	4 166 925.5	0
12	12	1	11	-11	0	4 169 837.6	1
13	13	1	12	-12	0	4 172 743	1
14	14	1	13	-13	0	4 175 642.5	1
15	15	1	14	-14	0	4 178 535.3	1
16	16	1	15	-15	0	4 181 419.8	0
17	17	1	16	-16	0	4 184 302.3	2
18	18	1	17	-17	0	4 187 176.5	3
19	19	1	18	-18	0	4 190 038.0	-2
20	20	1	19	-19	0	4 192 902.4	2
21	21	1	20	-20	0	4 195 754.5	-1
3	2	1	2	-1	0	4 146 537.0	2
4	3	1	3	-2	0	4 149 489.1	-1
5	4	1	4	-3	0	4 152 437.4	0
6	5	1	5	-4	0	4 155 378.2	0
7	6	1	6	-5	0	4 158 311.5	0
8	7	1	7	-6	0	4 161 239.3	0
9	8	1	8	-7	0	4 164 161.0	1
10	9	1	9	-8	0	4 167 075.9	1
11	10	1	10	-9	0	4 169 983.4	0
12	11	1	11	-10	0	4 172 885.6	1
13	12	1	12	-11	0	4 175 776.5	-4
14	13	1	13	-12	0	4 178 669.9	1
15	14	1	14	-13	0	4 181 553.2	2
16	15	1	15	-14	0	4 184 431.0	3
17	16	1	16	-15	0	4 187 300.8	3
18	17	1	17	-16	0	4 190 158.8	-3
18	17	1	17	-16	0	4 190 158.8	-3
19	18	1	18	-17	0	4 193 019.1	0
20	19	1	19	-18	0	4 195 867.7	-2
17	16	2	18	-17	0	4 073 051.7	2
16	15	2	17	-16	0	4 076 161.6	-1
15	14	2	16	-15	0	4 079 268.2	-2

TABLE I. (*Continued.*)

$J'$	$K'$	$n'$	$J''$	$K''$	$n''$	Frequency (MHz)	O-C (MHz)
14	13	2	15	-14	0	4 082 369.9	-2
13	12	2	14	-13	0	4 085 463.3	-5
12	11	2	13	-12	0	4 088 551.6	-6
11	10	2	12	-11	0	4 091 640.5	0
10	9	2	11	-10	0	4 094 717.8	0
9	8	2	10	-9	0	4 097 789.2	0
8	7	2	9	-8	0	4 100 855.2	1
7	6	2	8	-7	0	4 103 913.4	1
6	5	2	7	-6	0	4 106 967.0	2
5	4	2	6	-5	0	4 110 012.0	1
4	3	2	5	-4	0	4 113 052.4	1
3	2	2	4	-3	0	4 116 085.4	2
4	2	1	3	-1	0	4 152 621.1	-2
5	3	1	4	-2	0	4 155 563.7	1
6	4	1	5	-3	0	4 158 493.1	-1
7	5	1	6	-4	0	4 161 418.6	0
8	6	1	7	-5	0	4 164 336.8	1
9	7	1	8	-6	0	4 167 247.4	1
10	8	1	9	-7	0	4 170 150.5	-1
11	9	1	10	-8	0	4 173 050.3	1
12	10	1	11	-9	0	4 175 936.0	-4
13	11	1	12	-10	0	4 178 826.5	1
14	12	1	13	-11	0	4 181 700.1	-4
15	13	1	14	-12	0	4 184 580.4	4
16	14	1	15	-13	0	4 187 444.6	2
17	15	1	16	-14	0	4 190 299.2	-3
18	16	1	17	-15	0	4 193 155.5	0
19	17	1	18	-16	0	4 196 001.8	-1
20	18	1	19	-17	0	4 198 840.5	-3
18	16	2	19	-17	0	4 066 615.8	-3
17	15	2	18	-16	0	4 069 746.9	1
16	14	2	17	-15	0	4 072 866.3	-1
15	13	2	16	-14	0	4 075 981.3	-2
14	12	2	15	-13	0	4 079 093.0	1
13	11	2	14	-12	0	4 082 195.9	0
12	10	2	13	-11	0	4 085 295.0	1
11	9	2	12	-10	0	4 088 386.9	1
10	8	2	11	-9	0	4 091 473.5	1
9	7	2	10	-8	0	4 094 553.6	1
8	6	2	9	-7	0	4 097 626.8	1
7	5	2	8	-6	0	4 100 695.0	1
6	4	2	7	-5	0	4 103 756.4	1
5	3	2	6	-4	0	4 106 812.0	2
4	2	2	5	-3	0	4 109 857.8	2
18	15	1	17	-14	0	4 196 156.0	1
16	13	1	15	-12	0	4 190 461.2	-2
15	12	1	14	-11	0	4 187 605.8	-2
14	11	1	13	-10	0	4 184 745.6	-0
13	10	1	12	-9	0	4 181 873.9	-4
12	9	1	11	-8	0	4 179 002.6	-1
11	8	1	10	-7	0	4 176 118.4	-4
10	7	1	9	-6	0	4 173 235.6	1
9	6	1	8	-5	0	4 170 340.1	-1
8	5	1	7	-4	0	4 167 438.9	-1
7	4	1	6	-3	0	4 164 530.0	-2
6	3	1	5	-2	0	4 161 618.1	2
5	2	2	6	-3	0	4 103 609.8	0
7	4	2	8	-5	0	4 097 482.4	0
8	5	2	9	-6	0	4 094 407.5	1
9	6	2	10	-7	0	4 091 325.7	2

TABLE I. (Continued.)

$J'$	$K'$	$n'$	$J''$	$K''$	$n''$	Frequency (MHz)	O-C (MHz)
10	7	2	11	-8	0	4 088 235.7	1
11	8	2	12	-9	0	4 085 141.8	1
12	9	2	13	-10	0	4 082 041.1	1
13	10	2	14	-11	0	4 078 934.3	1
14	11	2	15	-12	0	4 075 821.0	0
15	12	2	16	-13	0	4 072 704.2	1
16	13	2	17	-14	0	4 069 580.2	1
17	14	2	18	-15	0	4 066 452.0	2
18	15	2	19	-16	0	4 063 319.8	4
17	13	2	18	-14	0	4 063 163.1	0
16	12	2	17	-13	0	4 066 300.1	0
15	11	2	16	-12	0	4 069 431.8	0
14	10	2	15	-11	0	4 072 559.1	1
13	9	2	14	-10	0	4 075 680.4	2
12	8	2	13	-9	0	4 078 795.1	2
11	7	2	12	-8	0	4 081 904.4	2
10	6	2	11	-7	0	4 085 005.8	0
9	5	2	10	-6	0	4 088 103.0	1
8	4	2	9	-5	0	4 091 192.1	-1
7	3	2	8	-4	0	4 094 277.0	2
6	2	2	7	-3	0	4 097 343.0	-2
8	4	1	7	-3	0	4 170 544.5	-5
9	5	1	8	-4	0	4 173 438.3	-3
10	6	1	9	-5	0	4 176 323.8	-2
11	7	1	10	-6	0	4 179 201.9	-1
12	8	1	11	-7	0	4 182 075.2	2
13	9	1	12	-8	0	4 184 941.2	4
14	10	1	13	-9	0	4 187 798.4	4
15	11	1	14	-10	0	4 190 645.5	0
18	13	2	19	-14	0	4 056 735.6	2
17	12	2	18	-13	0	4 059 883.4	0
16	11	2	17	-12	0	4 063 027.9	-1
15	10	2	16	-11	0	4 066 167.5	-1
14	9	2	15	-10	0	4 069 302.3	0
13	8	2	14	-9	0	4 072 431.3	0
12	7	2	13	-8	0	4 075 554.7	0
11	6	2	12	-7	0	4 078 672.3	1
10	5	2	11	-6	0	4 081 781.5	-1
9	4	2	10	-5	0	4 084 880.8	-5
8	3	2	9	-4	0	4 087 983.9	4
7	2	2	8	-3	0	4 091 061.6	7
10	5	1	9	-4	0	4 179 416.5	-4
11	6	1	10	-5	0	4 182 285.5	-3
12	7	1	11	-6	0	4 185 151.3	3
14	9	1	13	-8	0	4 190 848.7	0
15	10	1	14	-9	0	4 193 693.8	5
12	6	1	11	-5	0	4 188 228.6	1
13	7	1	12	-6	0	4 191 070.8	-1
15	9	2	16	-10	0	4 062 910.5	-1
14	8	2	15	-9	0	4 066 053.7	0
13	7	2	14	-8	0	4 069 188.4	-2
12	6	2	13	-7	0	4 072 318.2	-2
16	9	2	17	-10	0	4 056 504.6	-1
15	8	2	16	-9	0	4 059 659.8	-1
14	7	2	15	-8	0	4 062 807.1	-3
2	2	1	2	-1	0	4 128 109.8	-1
3	2	1	3	-1	0	4 128 059.8	1
4	2	1	4	-1	0	4 127 988.2	-1
3	3	1	3	-2	0	4 124 922.4	0
4	3	1	4	-2	0	4 124 856.4	1

TABLE I. (*Continued.*)

$J'$	$K'$	$n'$	$J''$	$K''$	$n''$	Frequency (MHz)	O-C (MHz)
5	3	1	5	-2	0	4 124 770.2	-1
6	3	1	6	-2	0	4 124 670.8	2
7	3	1	7	-2	0	4 124 544.6	-2
5	4	1	5	-3	0	4 121 646.1	1
6	4	1	6	-3	0	4 121 547.0	1
7	4	1	7	-3	0	4 121 429.4	1
8	4	1	8	-3	0	4 121 290.7	-2
9	4	1	9	-3	0	4 121 131.4	-4
5	5	1	5	-4	0	4 118 526.1	0
6	5	1	6	-4	0	4 118 430.3	2
7	5	1	7	-4	0	4 118 316.1	2
8	5	1	8	-4	0	4 118 181.9	0
9	5	1	9	-4	0	4 118 031.6	1
10	5	1	10	-4	0	4 117 861.4	2
6	6	1	6	-5	0	4 115 318.6	0
7	6	1	7	-5	0	4 115 206.5	1
8	6	1	8	-5	0	4 115 078.0	2
9	6	1	9	-5	0	4 114 930.6	2
10	6	1	10	-5	0	4 114 764.4	2
11	6	1	11	-5	0	4 114 578.4	1
3	2	2	3	-3	0	4 140 717.0	-2
4	2	2	4	-3	0	4 140 647.2	-1
5	2	2	5	-3	0	4 140 555.2	-3
6	2	2	6	-3	0	4 140 442.6	-6
7	2	2	7	-3	0	4 140 313.5	2
4	3	2	4	-4	0	4 143 847.1	3
5	3	2	5	-4	0	4 143 762.4	3
6	3	2	6	-4	0	4 143 655.9	0
7	3	2	7	-4	0	4 143 534.5	1
8	3	2	8	-4	0	4 143 392.9	3
5	4	2	5	-5	0	4 146 961.0	-1
6	4	2	6	-5	0	4 146 859.6	-1
7	4	2	7	-5	0	4 146 740.8	-1
8	4	2	8	-5	0	4 146 601.3	-4
6	5	2	6	-6	0	4 150 073.0	0
7	5	2	7	-6	0	4 149 956.1	0
8	5	2	8	-6	0	4 149 818.6	-2
9	5	2	9	-6	0	4 149 666.1	-2
7	6	2	7	-7	0	4 153 177.3	0
8	6	2	8	-7	0	4 153 044.1	1
9	6	2	9	-7	0	4 152 892.4	0
10	6	2	10	-7	0	4 152 722.3	-1
8	7	2	8	-8	0	4 156 276.6	2
9	7	2	9	-8	0	4 156 125.5	2
10	7	2	10	-8	0	4 155 957.8	2
11	7	2	11	-8	0	4 155 771.5	1
9	8	2	9	-9	0	4 159 367.4	3
10	8	2	10	-9	0	4 159 200.6	3
11	8	2	11	-9	0	4 159 016.0	3
12	8	2	12	-9	0	4 158 813.2	2
13	8	2	13	-9	0	4 158 592.3	1
10	9	2	10	-10	0	4 162 443.3	-5
11	9	2	11	-10	0	4 162 259.4	-5
4	2	1	5	-1	0	4 097 198.4	1
5	2	1	6	-1	0	4 090 946.4	-6
4	3	1	5	-2	0	4 094 062.9	-1
5	3	1	6	-2	0	4 087 821.0	-3
5	4	1	6	-3	0	4 084 698.8	2



TABLE II. The results of a combined fit of both the 2.03 THz parallel band and the 4.13 THz perpendicular band. All values are in MHz.

Ground state		
$B(=A)$	3079.531 (24)	3079.512 (33) <sup>a</sup>
$C$	1497.007 (18)	1497.0 (3) <sup>b</sup>
$D_J$	0.008 40 (24)	0.0089 (04) <sup>a</sup>
$D_{JK}$	-0.011 42(55)	-0.0177(07) <sup>a</sup>
$D_K$	0.003 18 (33)	0.04 (1) <sup>b</sup>
$\Delta I(\mu\text{\AA}^2)$	9.375	
Excited state of the 2.03 THz band		
$B(=A)$	3091.762 (32)	3091.726 (31) <sup>a</sup>
$C$	1493.522 (21)	
$D_J$	0.009 07 (27)	0.0092 (03) <sup>a</sup>
$D_{JK}$	-0.013 82(58)	-0.0181(06) <sup>a</sup>
$D_K$	0.004 94 (43)	
$\Delta I(\mu\text{\AA}^2)$	11.461	
$E_0$	2 032 688.20 (49)	2 032 688.38 (33) <sup>a</sup>
Excited state of the 4.13 THz band		
$B(=A)$	3071.489 (27)	3070.7 (1) <sup>b</sup>
$C$	1493.867 (18)	1494.5 (3) <sup>b</sup>
$D_J$	0.007 46 (30)	0.007 (1) <sup>b</sup>
$D_{JK}$	-0.011 52(60)	-0.018(3) <sup>b</sup>
$D_K$	0.003 75 (35)	0.035 (8) <sup>b</sup>
$q$	2.31 (20)	
$2\xi C$	126.4 (55)	
$2\xi C_J$	1.721 (96)	
$\Delta I(\mu\text{\AA}^2)$	9.225	
$E_0$	4 132 890.51 (56) <sup>c</sup>	4 132 885 (1) <sup>d</sup>
$N$	357	

<sup>a</sup>Values taken from Refs. 24 and 25.<sup>b</sup>Values taken from Ref. 26.<sup>c</sup> $\sigma$  uncertainties of fitted constants in parenthesis.<sup>d</sup>The rms of the fit is 1.9 MHz.

was also added. Both first- and second-order Coriolis terms are significant and cannot be removed. Equations (1) and (2) apply to the excited states of the 2.03 THz parallel band and the 4.13 THz perpendicular band, respectively. The resulting spectroscopic constants are listed in Table II. The rms of the fit is 1.9 MHz compared to the experimental error of 2–3 MHz. The fitted results also compare well with previous results.<sup>24–26</sup> The use of this effective Hamiltonian allowed the inclusion of most of the observed transitions, although there are still some low- $K$  transitions that are shifted too much to be included in the present fit. These include the  $K = 1 \leftarrow 0$ ,  $K=0 \leftarrow 1$ , and  $K=1 \leftarrow 2$  transitions of the  $Q$  branch, and some  $K \leq 2$  transitions of the  $P$  and  $R$  branches. These transitions are very sensitive to the Coriolis coupling term, but not to the rotational constants. We list these transitions in Table III along with their tentative assignments. A complete analysis that includes these additional splittings and the shifted frequencies would require the development of a new Hamiltonian that is appropriate for the higher symmetry of the water tetramer.

## VIBRATIONAL ANALYSIS

The first parallel band observed for the water tetramer ( $D_2O$ )<sub>4</sub> at 2.03 THz (Refs. 24 and 25) was originally assigned to an  $A_g \rightarrow A_u$  transition, corresponding to the torsional  $A_u$  fundamental calculated by Schütz *et al.*<sup>32</sup> Cruzan *et al.*<sup>23</sup> later reported a parallel band of ( $H_2O$ )<sub>4</sub> at 2.04 THz. The very small isotopic shift, along with the similar tunneling splittings involving  $K=2$  states for both bands, led them to reassign the ( $D_2O$ )<sub>4</sub> band to an  $A_g \rightarrow B_g$  transition. The fact that the experimental frequencies of 67.9 (67.8)  $\text{cm}^{-1}$  for ( $H_2O$ )<sub>4</sub> [( $D_2O$ )<sub>4</sub>] are so close to the theoretical values, 79.4 (77.1)  $\text{cm}^{-1}$  calculated by Schütz *et al.*,<sup>32</sup> 67  $\text{cm}^{-1}$  calculated by Xantheas and Dunning,<sup>41</sup> and 66 (62)  $\text{cm}^{-1}$  calculated by Dunn *et al.*,<sup>42</sup> seems to imply that the water tetramer is considerably more rigid than both the water trimer and the water

TABLE III. Transitions not included in the analysis with their tentative assignments.

Tentative assignments						Frequency	
$J'$	$K'$	$n'$	$J''$	$K''$	$n''$	Upper band (MHz)	Lower band (MHz)
11	1	1	11	0	0	4 128 477.1	4 128 284.8
10	-1	1	10	0	0	4 128 868.0	4 128 677.0
9	1	1	9	0	0	4 129 254.4	4 129 062.2
8	-1	1	8	0	0	4 129 625.7	4 129 435.5
7	1	1	7	0	0	4 129 975.2	4 129 784.2
6	-1	1	6	0	0	4 130 292.8	4 130 101.6
5	1	1	5	0	0	4 130 574.6	4 130 383.0
4	-1	1	4	0	0	4 130 813.5	4 130 623.0
3	1	1	3	0	0	4 131 008.8	4 130 818.5
2	-1	1	2	0	0	4 131 158.4	4 130 966.8
1	1	1	1	0	0	4 131 259.4	4 131 066.4
1	-1	1	0	0	0	4 137 484.7	4 137 294.0
2	1	1	1	0	0	4 143 687.7	4 143 493.7
3	-1	1	2	0	0	4 149 901.6	4 149 709.8
4	1	1	3	0	0	4 156 140.2	4 155 948.8
3	0	1	3	1	0	4 134 387.5	4 134 194.8
2	0	1	2	1	0	4 134 424.6	4 134 232.2

TABLE IV. The currently observed vibrational modes for the water tetramer. (All values are in  $\text{cm}^{-1}$ ).

Vibration type	Cluster type	Band frequency	Schütz <i>et al.</i> <sup>a</sup>	Sabo <i>et al.</i> <sup>b</sup>	Dunn <i>et al.</i> <sup>c</sup>
In-plane ring deformation	(H <sub>2</sub> O) <sub>4</sub>	67.9	79.4		66
	(D <sub>2</sub> O) <sub>4</sub>	67.8	77.1		62
Torsion	(H <sub>2</sub> O) <sub>4</sub>		236.5	228.958	195
	(D <sub>2</sub> O) <sub>4</sub>	137.8	174.7	184.680	147

<sup>a</sup>Reference 32.<sup>b</sup>Reference 34.<sup>c</sup>References 42 and 43.

pentamer. Jung and Gerber<sup>44</sup> studied water clusters using the correlation corrected vibrational self-consistent field approximation. They found that the water tetramer has a much smaller anharmonic effect than the water dimer and trimer. The previous report of the perpendicular band of (D<sub>2</sub>O)<sub>4</sub> at 4.13 THz (137.7  $\text{cm}^{-1}$ ) (Ref. 26) assigned this band to an  $A_g \rightarrow E_g$  transition, which was calculated by Schütz *et al.*<sup>32</sup> to be 174.7  $\text{cm}^{-1}$ . This transition corresponds to the torsional  $E_g$  fundamental. Sabo *et al.*<sup>34</sup> also calculated the torsional levels of the water tetramer from their four-dimensional calculation and reported a value of 184.68  $\text{cm}^{-1}$  for this transition. Recently, Dunn *et al.*<sup>42,43</sup> reported anharmonic calculations of experimental vibrational frequencies for water clusters. Their calculated values of this vibration for (H<sub>2</sub>O)<sub>4</sub> and (D<sub>2</sub>O)<sub>4</sub> are 195 and 147  $\text{cm}^{-1}$ , respectively. Their calculated value of 66  $\text{cm}^{-1}$  for the ring distortion vibration of (H<sub>2</sub>O)<sub>4</sub> agrees well with the experimental value<sup>23</sup> of 67.9  $\text{cm}^{-1}$ . It is also interesting to note that the anharmonic frequencies calculated by Sabo *et al.*<sup>34</sup> are higher than the harmonic frequencies calculated by Schütz *et al.*<sup>32</sup> Table IV lists the experimentally determined frequencies with their respective calculated values for comparison.

## ROTATIONAL ANALYSIS

The rotational constants for water clusters also provide valuable information about their respective structures and dynamics. For all three observed vibrational states of the water tetramer, the rotational constants follow the approximate relation  $A=B \approx 2C$ , which suggests that the structure of the water tetramer is nearly planar. The fitted rotational constant  $C$  of the ground state agrees with the estimate from previous work.<sup>24,25</sup> The  $B$  rotational constants for both the 2.03 THz band and the 4.13 THz band have similar values. The  $B$  rotational constant of the excited state of the 2.03 THz band is larger than that of the ground state, whereas the  $B$  rotational constant of the excited state of the 4.13 THz band is smaller. In the global fit of the water trimer, the  $B$  rotational constants the torsional bands exhibit a decreasing trend with increasing torsional energy levels. This supports the assignment of the 4.13 THz band to a torsional band.

The fitted rotational constants of the ground state lead to a positive inertia defect of 9.375  $\mu\text{Å}^2$ . The inertia defect ( $\Delta I$ ) can be used to gain insight about the planarity of the molecule. It is defined as a linear combination of the principal inertia moments,

$$\Delta I = I_C - I_A - I_B. \quad (3)$$

For a perfectly rigid and planar molecule, the inertia defect  $\Delta I$  should be exactly zero. In reality, molecules are not perfectly rigid, nor completely planar, and  $\Delta I$  is found to be nonzero (typically a small and negative value). The positive inertia defects found for both the ground state and the two excited states of the water tetramer are indicative of “quasi-planar” structures in these states. The large positive values obtained here reflect vibration-rotation contributions to moments of inertia. Table V compares the inertia defects of the trimer and the tetramer. The trimer has large negative inertia defects in all observed states. This is the result of the large amplitude out-of-plane torsional motions of the free deuteron atoms. In contrast, the inertia defects for the tetramer are positive, indicating very different tunneling motions from the trimer. The determined centrifugal distortion constants for the water tetramer are also much smaller than those of the trimer; another indication that the water tetramer is more rigid.

## TUNNELING DYNAMICS

The most characteristic feature of the three bands identified for the water tetramer is the regular doublet splitting of each transition. The inversion motion between the two global minimum structures splits all vibrational levels into two tunneling states with opposite parities, which are symmetric or antisymmetric with respect to the inversion coordinate. Depending on the parities, the observed doublets can be the sum or difference of the ground state and excited state tunneling splittings. For the 2.04 THz (H<sub>2</sub>O)<sub>4</sub> band, the splitting is 2260 MHz, whereas for the analog 2.03 THz (D<sub>2</sub>O)<sub>4</sub> band, the splitting is only 5.6 MHz, about 400 times smaller. This

TABLE V. Inertial defects of the water trimer-d6 and tetramer-d8.

Water trimer (D <sub>2</sub> O) <sub>3</sub>		Water tetramer (D <sub>2</sub> O) <sub>3</sub>	
$E_0$ (MHz) <sup>a</sup>	$\Delta I$ ( $\mu\text{Å}^2$ )	$E_0$ (MHz)	$\Delta I$ ( $\mu\text{Å}^2$ )
0	-10.704	0	9.375
225 977.3(4)	-10.862	2 032 688.20 (49)	11.461
839 187.2(4)	-11.184	4 132 890.51 (56)	9.225
1 232 139.3(5)	-11.433		
2 709 548.8(6)	-11.479		
2 940 937.63(3)	-11.054		
4 284 781.9(3)	-10.860		

<sup>a</sup>Values taken from Ref. 17.



decrease in the tunneling splittings reflects a kinetic isotopic effect resulting from the increase of the reduced mass along the tunneling coordinates. For the 4.13 THz  $(D_2O)_4$  band, the splitting is 192 MHz, 34 times larger than the splittings of the 2.03 THz band. This vibration-assisted effect is in line with our assignment of the vibration to the torsional band, as the torsional motions help facilitate the flipping of the free deuteron atoms. It would be interesting to include the corresponding torsional vibration band of  $(H_2O)_4$  into the comparison, however, the predicted region of this band is currently not accessible due to the limited availability of strong laser lines. These splittings have been interpreted as resulting from the flipping of all free hydrogen (deuteron) atoms from one side of the oxygen plane to the other, resulting in a double minimum potential, similar to the inversion potential of ammonia. Each vibrational state splits into two tunneling states, so the experimentally observed splittings for the 2.04 THz (2.03 THz) band of  $(H_2O)_4$  ( $(D_2O)_4$ ) are probably the sum of the tunneling splittings in the ground and excited states. Although the exact tunneling path remains uncertain, Gregory and Clary<sup>45</sup> studied the tunneling of the water tetramer through diffusion quantum Monte Carlo calculations. They calculated tunneling splittings of 17 MHz (1200 MHz) for the ground state tunneling splittings of  $(D_2O)_4$  ( $(H_2O)_4$ ). Assuming the assignment of the 2.03 THz band to the ring deformation vibration is valid and the contributions of the free D(H) atoms to this vibration are insignificant, i.e., there is little vibration-assisted effect on tunneling splittings, the ground state tunneling splitting should be about half of what were experimentally observed for the 2.03 THz band, still of the same order as the experimental values. Sabo *et al.*<sup>34</sup> four-dimensional calculation based on the modEPEN4B potential energy surface developed by Graf and Leutwyler<sup>36</sup> gave the values of 0.000 12 MHz (21.8 MHz) for the ground state tunneling splittings of  $(D_2O)_4$  ( $(H_2O)_4$ ). They attributed this discrepancy to inaccuracies in the calculated potential.

In the VRT dynamics of the water trimer, the bifurcation tunneling, wherein the bonded and free hydrogen (deuteron) atoms interchange, splits each transition into a characteristic quartet. This type of tunneling is completely absent from the water tetramer  $(D_2O)_4$  spectra, although Cruzan *et al.*<sup>23</sup> observed line broadening in their  $(H_2O)_4$  study, which might be attributed to unresolved bifurcation tunneling. The largely quenched bifurcation tunneling again reflects the very different tunneling dynamics occurring in the water trimer and tetramer.

## CONCLUSION

In this work, we reported the combined analysis of the 4.13 THz perpendicular band and the 2.03 THz parallel band of  $(D_2O)_4$ . More experimental and theoretical efforts, including new torsional band measurements and the development of a more appropriate Hamiltonian for the water tetramer, are required to obtain an understanding of dynamics of the water tetramer comparable to that existing for the water trimer.

There have been several proposed pair potentials<sup>46–48</sup> developed from fitting the terahertz VRT spectroscopic data that reproduce many properties of bulk liquid water very

well. These advances, along with those described in the Introduction, are very encouraging. It will soon be possible to include the many-body dispersion and exchange terms in the potential by fitting to the water trimer, tetramer, and pentamer VRT spectroscopic data. Precise characterization of the water trimer and the water tetramer by VRT spectroscopy is the first step in this direction. Further progress will require new foundations of the high-dimensional VRT dynamics that are sufficiently efficient to enable calculation from global potential surfaces. Meanwhile, the detailed understanding of the water tetramer evolving from this work illustrates efforts to quantify the nature of many-body forces in the condensed phases of water. These efforts can be viewed in twofolds. The gas-phase spectroscopy of water clusters provides insights into the interactions between each water molecule in the cluster and the intrinsic properties of each water molecule. The results of these studies also provide good validity check for the theoretical calculations that intend to be used toward understanding of the condensed phase of water, as have been evidenced in the studies of water dimer.

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