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Terahertz VRT Spectroscopy of the Water Hexamer-h12 Cage: Dramatic Libration-Induced Enhancement of Hydrogen Bond Tunneling Dynamics

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Abstract

We report the assignment and analysis of 176 transitions belonging to a librational band of the $(H_2O)_6$ cage isomer near 525 cm^{-1}(15 THz). From a fit of the transitions to an asymmetric top model we observe both dramatic changes in the rotational constants relative to the ground state, indicating significant non-rigidity, and striking enhancement in the tunneling motions which break and reform the hydrogen bonds in the cluster. This is the fifth water cluster system to display such an enhancement in the15 THz librational region, the details of which may help to elucidate the hydrogen bond dynamics occurring in bulk liquid water.

Introduction

The challenge in developing a predictive molecular-scale description of water is essentially that of correctly describing its extended and highly dynamic hydrogen-bonded network [1–6]. High-resolution spectroscopy of water clusters provides a means of systematically untangling its complexities. In this context, the water hexamer is of particular interest, as it is the smallest cluster exhibiting a 3-D hydrogen bond network [4,7–20]. Previous studies have revealed the existence of low energy cage, prism, and book hexamer isomers produced in a supersonic expansion [14,21–24]. It has been established that the cage isomer is the global minimum energy structure [14,25], although the prism lies in close energetic proximity [4,22,26–33]. Additionally, cyclic hexamer clusters have been observed in frozen rare gas matrices [34,35].

The first detailed experimental study of a water hexamer cluster was reported in 1996 by Liu et al, who observed and characterized the cage isomer in a supersonic expansion [14,21]. From those experiments, the cage structure was determined, as shown in Figure 1, along with the “feasible” tunneling motions of the cluster. Liu determined that the tunneling splitting of the cage cluster can be described by the molecular symmetry group G_4, comprising three “feasible” tunneling motions. Two tunneling motions, $ß_1$ and $ß_2$, are described by a switching of the hydrogens of the two single donor- single acceptor (SDA) hydrogen bonded monomers. The third pathway, $ß_3$, is described as the simultaneous exchange of the hydrogens of both doubly hydrogen bonded monomers.

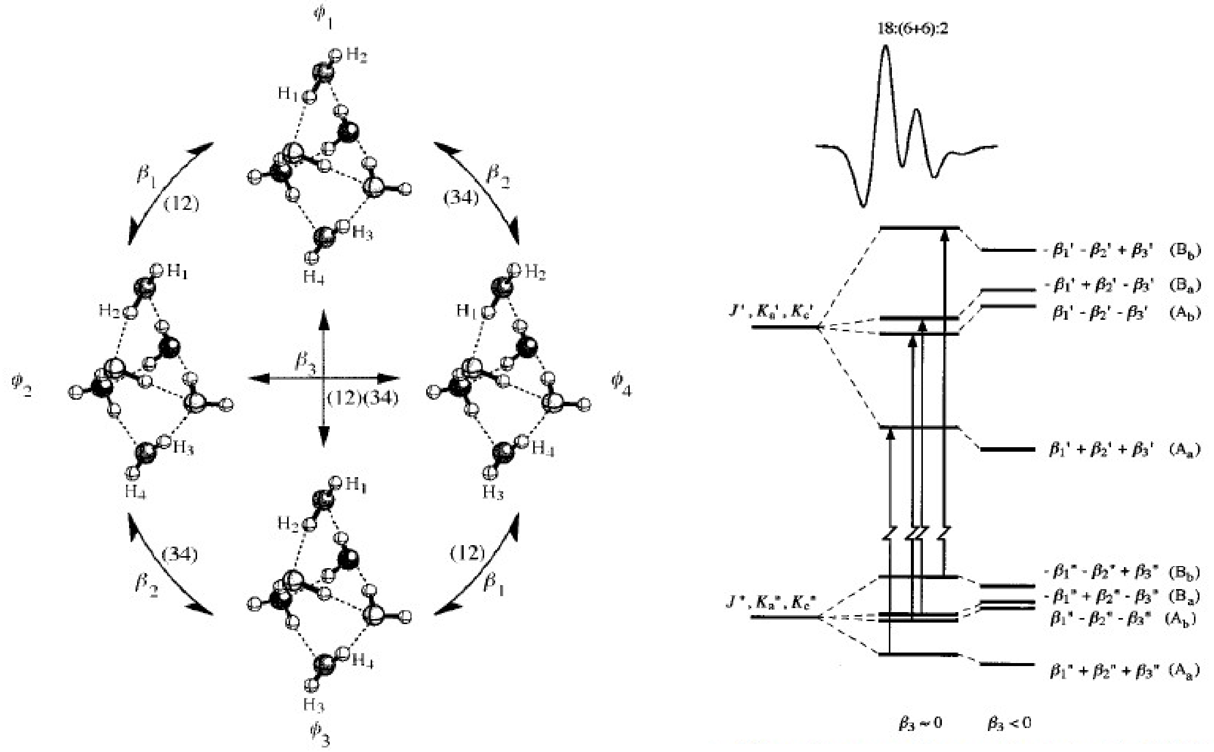

Figure 1: (Left) The structure of the water cage hexamer along with the "feasible" tunneling motions. The labels in parentheses correspond to the group elements of the molecular symmetry group, G_4. **(Right)** The expected spectral pattern caused by the tunneling of the cluster system. Liu et al observed that the splitting between the A_bA_b and B_aB_a was below the experimental resolution of the experiment indicating that the magnitudes of $ß_1$ and $ß_2$ are quite similar. Reproduced with permission from Ref. 9.

More recently, Perez et al observed the cage, prism, and book isomer (in addition to heptamer and nonamer clusters) in a supersonic expansion using broadband microwave spectroscopy [22,23,36]. This study characterized the ground state structures of these isomers at high resolution and provided critical insight into the associated hydrogen bond network tunneling motions.

Most recently, we reported the measurement and analysis of 142 VRT transitions of the fully deuterated hexamer prism in the 15 THz librational band region, which revealed a thousand-fold enhancement in the bifurcation tunneling splitting upon single quantum excitation of this librational vibration[40]. Here, we report the assignment of 176 VRT transitions belonging to four a-type ($\Delta K_a=0$) librational subbands originating from the $(H_2O)_6$ cage structure near 520 cm^{-1}. The tunneling splittings in the excited vibrational state also show a dramatic enhancement, consistent with our previous results for the hexamer-d6, as well as for the water dimer, trimer, and pentamer clusters in this 15 THz librational band region [37–40].

Experimental

Our previous investigations of water dimer, trimer, and pentamer librational motions in the 15 THz region prompted us to search for similar transitions in larger clusters [39]. The Berkeley diode laser/supersonic beam spectrometer used in this study has been described in detail elsewhere and only a short description is provided here [41,42].

A helium-cooled spectrometer (Spectra Physics) using lead-salt diodes (Laser Photonics) was used to produce infrared radiation from 515-528 cm^{-1}. The beam was multipassed 18-22 times through a pulsed planar supersonic expansion of a mixture of H_2O and He using a Herriot cell and detected using a helium-cooled (Si:B) photoconductive detector (IR Labs). The supersonic expansion was produced by bubbling pure He gas, with a backing pressure of 1-2 atm through liquid H_2O and then expanding through a 101.6 mm long slit at a repetition rate of 35 Hz into a vacuum chamber maintained at ~200mTorr by a Roots blower (Edwards 4200) backed by two rotary pumps (E2M 275) [43]. The nominal rotational temperature of the expansion is 4-10K. Simultaneously, the fringe spacing of a vacuum-spaced etalon and an OCS reference gas spectra were detected with a liquid He cooled (Cu:Ge) detector (Santa Barbara Research Center) and recorded to enable precise frequency calibration. The observed linewidths of ~ 30-40 MHz full-width half maximum (FWHM) are somewhat larger than the Doppler-limited linewidths extrapolated from earlier experiments using argon expansions. Typical frequency measurement accuracy is 10-20 MHz, limited by both linewidths of the cluster absorptions and laser drift. Spectra were detected in direct absorption using a time-gated phase sensitive signal processing approach.

Accessing the 15 THz (500 cm^{-1}) region of the electromagnetic spectrum has generally been notoriously difficult. The spectra reported here required the use of 10 separate laser diodes, each scanned across several modes to cover the specified spectral range. Moreover, large laser gaps are present in the spectra, which causes considerable difficulty in the assignment. The laser diodes also exhibited intensity fluctuations, which renders the intensities quite arbitrary.

Results

Experimental Assignment

We have assigned 176 of 364 precisely measured transitions in the 515-528 cm^{-1} region to the $(H_2O)_6$ cage cluster. The transitions belong to 4 a-type ($\Delta K_a=0$) type subbands which are determined to originate from tunneling splitting of the rigid rotor energy levels. The transitions were fit to a standard S-reduced Watson Hamiltonian energy level expression using the PGOPHER platform [44,45]. Fixed ground state constants were obtained from the work of Liu et al and Perez et al [21,22] for which we assume the lower intermolecular vibrational state to be the ground state, consistent with the low temperature of the supersonic expansion. The fitted constants for the four measured subbands are given in Table 1. Correlation matrices of the fit and a list of all assigned transitions are given in the Supplementary Information for this article. Figure 2 shows transitions assigned to subband 1, in addition to all observed transitions.

Anharmonic Excited State Vibrational Calculations

To elucidate the nature of the observed vibration, anharmonic frequencies and rotational constants were calculated by applying generalized second-order vibrational perturbation theory (GVPT2)[46,47] to the second-order Moller-Plesset (MP2) perturbation theory potential energy surface using Gaussian 09 D.01 package [48]**.** The geometry of the lowest energy H_2O cage was optimized at the MP2/aug-cc-pVDZ level of theory, enforcing “very tight” convergence criteria, following which a GVPT2 calculation was performed at the same level of theory using the parameters recommended by Temelso and Shields [12]. The Gaussian input file, the full list of calculated harmonic and anharmonic frequencies, and the rotational constants are listed in the Supplementary Information.

Table 1: Fitted constants for assigned transitions. All values are given in MHz. The uncertainties in the last two significant digits are shown in parentheses. Number of transitions per subband and RMS of the fits are shown below. Values for the ground state are taken from Liu et al and Perez et al [21,22].

	Subband 1	Subband 2	Subband 3	Subband 4	Ground State[a]
Origin	15693333.2(14)	15698512.9(16)	15703420(10)	15708936.3(11)	NA
A	2060.18(88)	2057.62(24)	2058.97(25)	2059.78(84)	2162.12(13)
B	1121.28(139)	1124.67(17)	1121.06(10)	1121.41(78)	1129.07(05)
C	1060.76(13)	1058.67(20)	1060.38(11)	1060.03(68)	1066.88(05)
D_K[b]	-0.039(37)	-0.032(79)	0.022(56)	-0.037(31)	0.0083(15)
D_{JK}	0.020(30)	-0.120(71)	-0.032(29)	0.012(24)	-0.00221(89)
D_J	0.010(10)	0.051(25)	5.0(85)e-3	3.3(62)e-3	0[#]
Δ_K	-1(20)e-4	3.5(36)e-3	-7.8(89)e-4	-2.20(43)e-3	-1.43(46)e-4
Δ_J	-1.5(77)e-3	-0.020(11)	-1.9(24)e-3	-2.4(11)e-3	4.28(92)e-4
H_K	-7.8(18)e-5	-5.2(11)e-3	8.5(36)e-4	-3.3(27)e-4	0[#]
H_{KJ}	-2.0(45)e-4	5.0(18)e-3	-7.3(53)e-4	2.0(14)e-4	-5.36(61)e-5

H_{JK}	1.7(24)e-4	-2.18(82)e-3	9.0(12)e-5	-2.9(83)e-5	5.7(18)e-6
H_J	2.6(45)e-5	4.0(16)e-4	3.0(23)e-7	3.8(18)e-6	0[#]

Number of Transitions	53	34	38	51
RMS	22.8	16.5	21.5	26.4

a) Ground state constants taken from Liu et al and Perez et al [21,22]

b) Description of the fit constants can be found in references 21 and 22.

#) Constants not include in fit

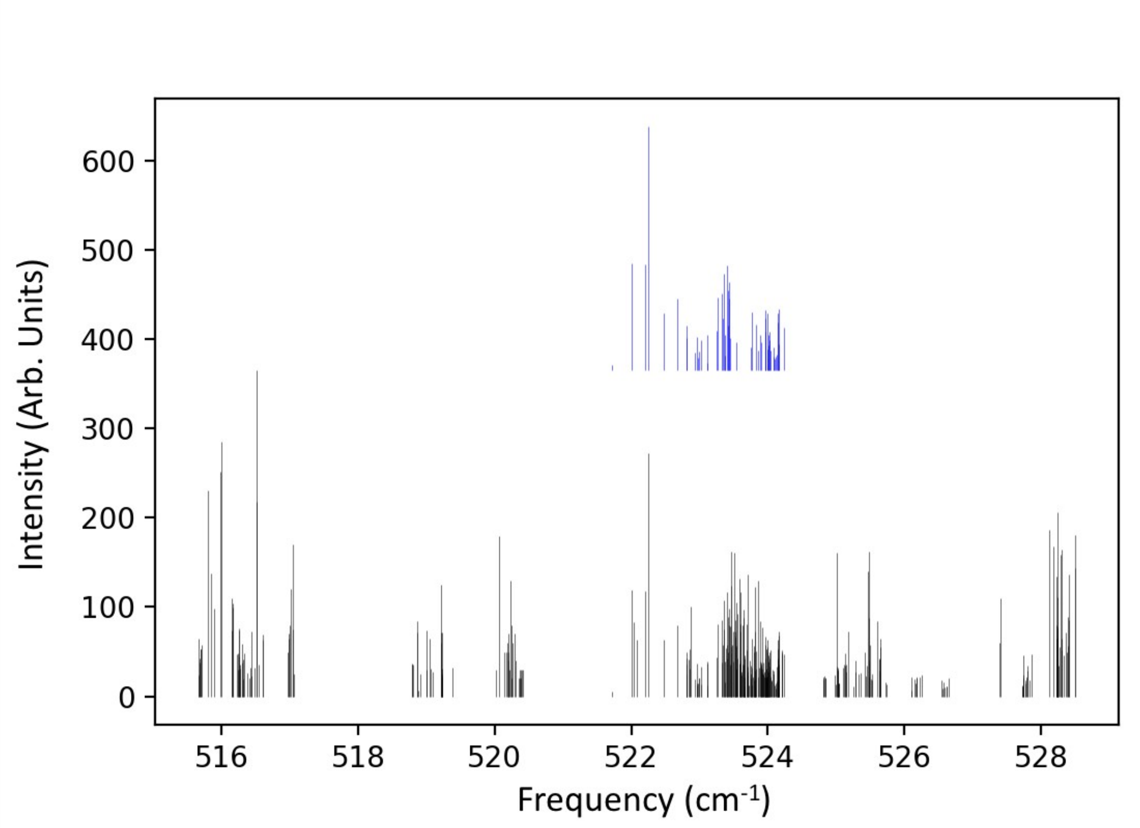

Figure 1: Stick spectrum of all observed transitions is shown in black. Transitions assigned to Subband 1 are shown in blue. The assignment was complicated by large laser gaps, which are apparent across the experimental range.

Fit Analysis

We obtained a high quality fit with an average RMS of 21.8 MHz, which is below the observed linewidth of 30-40 MHz and on the order of the frequency accuracy of the experiment (~20 MHz). The similarity of the rotational constants for the 4 assigned subbands' implies that the transitions originate from a common vibrational state. Additionally, we report the ground state constants from Liu et al [21], which show good agreement with those recently observed by Perez et al [22].

Subband Tunneling Assignment

From Figure 1 we see that the observation of 4 subbands fits with the predicted tunneling pattern of the cage clusters. This pattern is produced by 3 tunneling motions, $ß_1$, $ß_2$, and $ß_3$, with the first two pathways corresponding to permutation of the hydrogens of one of the single donor, single accepter (SDA) water monomers and $ß_3$ is the simultaneous permutation of the hydrogens of both SDA monomers. The predicted spacings between the 4 theoretical subbands are given in Equations 1-3:

$$\Delta\left(B_b - B_a\right) = 2\left[-ß_2^{'} + ß_2^{\text{\} + \{ß\} rsub \{3\} rsup \{'\} - \{ß\} rsub \{3\} rsup \{}}\right](1)$$

$$\Delta\left(B_a - A_b\right) = 2\left[-ß_1^{'} + ß_2^{'} + ß_1^{\text{\} - \{ß\} rsub \{2\} rsup \{}}\right](2)$$

$$\Delta\left(A_b - A_a\right) = 2\left[-ß_2^{'} + ß_2^{\text{\} - \{ß\} rsub \{3\} rsup \{'\} + \{ß\} rsub \{3\} rsup \{}}\right](3)$$

Liu et al previously found the magnitude of $ß_3$ to be below experimental resolution in lower energy transitions, as a result of the need to simultaneously break and reform two hydrogen bonds. Also, Liu et al found the relative magnitude of $ß_1$ and $ß_2$ to be nearly identical, resulting in the predicted quartet collapsing to a triplet.

Spin statistics predict the A_a:A_b:B_a:B_b intensity ratio to be 18:6:6:2; but due to laser intensity fluctuations and the large laser gaps, we find an experimental intensity ratio for subbands 1:2:3:4 of 40:55:36:38, which we do not consider realistic due to the above reasons. The four subbands are about equally spaced, with the values of Δ(4-3), Δ(3-2), and Δ(2-1) of 5516.3, 4907.1, and 5179.7 MHz, respectively. The middle two subbands are closer together, and the quartet is asymmetric, which would be expected if $ß_3$ was non-negligible (see Figure 1). It is clear, regardless of the assignment, that the magnitudes of the splitting are greatly enhanced relative to the lower energy states previously measured [14,21]. Hence, we will assume the ground state splittings as being much smaller than the excited state values, which allows us to ignore them and obtain an estimate of the enhanced excited state values. An assumption also has to be made as to whether subband 1 is A_a or B_b, but this only affects the sign of the $ß_3$ term; we arbitrarily assign subband 1 to B_b symmetry, as that makes all of the tunneling motions positive in sign.

Thus, with the assignment of subbands 1/2/3/4 as $B_b/B_a/A_b/A_a$ and assuming $ß_1$”, $ß_2$”, and $ß_3$” to be ~0, from Equations 1-3 we obtain $ß_1$’= 5127.55 MHz, $ß_2$’= 2674 MHz, and $ß_3$’= 84.15 MHz. This analysis yields several insights; first, the values for $ß_1$ and $ß_2$ are different by nearly a factor of two. This observation would indicate that the local environments of the two SDA monomers are no longer identical in the excited state. We also see that all of the tunneling motions are indeed greatly(by $>10^3$) enhanced relative to the ground state values, which were previously observed to be ca. 1 MHz [14,21]. This is in keeping with previous observations in this experimental range [3,37–40].

Discussion

Vibrational Origin

Since the rotational temperatures of a He supersonic expansion are ~10K, whereas the vibrational temperatures can be somewhat higher, it is reasonable to assume that the observed transitions originate from the vibrational ground state. Upon inspection of the calculated anharmonic vibrational frequencies, we find that there are 3 modes predicted at 497.903, 516.356, and 574.222 cm^{-1}, which lie close to the average band origin of 523.731 cm^{-1}. The 3 bands at 497.903, 516.356, and 574.222 cm^{-1} have the calculated values of ΔA: -10.2, -10.6, and -3.7 MHz, respectively. Our observed value of ΔA is -103.0, nearly an order of magnitude greater than the calculated results. This is similar to our recent results for the fully deuterated water hexamer prism[40] in the same experimental range. This provides more evidence that the intermolecular vibrations of clusters in the 500 cm^{-1} region deviate significantly from the predictions for “semi-rigid” clusters [5,6,37,38,40]. Further investigation of this experimental region by theory is warranted.

From the observed changes in rotational constants, we can say that the vibration exhibits significant motion about the A-principal axis, which connects the two SDA water monomers (Figure 1). Any motion about that axis will engender changes in the local environment of those monomers, which, in turn, are expected to affect the barriers of tunneling motions. The higher-order constants of the fit also show an increase in magnitude relative to the ground state, which is consistent with the vibrational motions of a “floppy” cluster molecule.

Librational Tunneling Enhancement

While our analysis of the excited state tunneling dynamics is clearly subject to several assumptions, some observations are significant, viz. the tunneling motions which break/reform the hydrogen bonds are dramatically enhanced relative to the ground state, similar to our previous results for the water dimer, trimer, pentamer, and prism hexamer in this experimental range [37-40]. Definitive determinations of the ground state tunneling splittings have not, to our knowledge, been made experimentally, but the earlier observations of Liu et al showed that $(-ß_2'+ß_2'') \sim 0.9$ MHz for an intermolecular vibration near 83 cm^{-1}, and likewise $|ß_3'-ß_3''| < 25$kHz. We find ca. 3 orders of magnitude enhancement for all three tunneling motions, subject to our assumption that the ground state tunneling splittings are negligible. This $\sim 10^3$ enhancement is greater than that observed for the water dimer (40x) and trimer (100x), but similar to that for the pentamer and prism hexamer [37-40].

The most interesting observation of this study is this striking libration-induced enhancement in the tunneling splittings, and the finding that $ß_1$ and $ß_2$ are no longer approximately equal, indicating an asymmetric vibration with respect to the two SDA monomers. While this is supported by the large change in rotational constant A, it would be enlightening to characterize the actual vibrational motion associated with this transition. However, it should be noted that the large observed tunneling splittings combined with the large changes in rotational constants indicates the deviation from a semi-rigid cluster to a more floppy (non-rigid) structure, which provides additional complications for the theory.

Conclusions

In summary, we have assigned 176 transitions to the cage isomer of the H_2O water hexamer near 15 THz (500 cm^{-1}). The tentative tunneling assignment of the transitions indicates a significant enhancement of the hydrogen bond breaking tunneling motions of the cluster, consistent with our previous studies on other water clusters [37-40,49]. As indicated by the rotational constants measured here, the excited states display significant motion about the A-principal axis, which has interesting consequences for the tunneling pathways.

As this cluster is the fifth system to display unusual behavior in the 15 THz region, further detailed study seems warranted; this region obviously contain vital information about the hydrogen bond breaking/reformation dynamics of water clusters, and as such, may provide useful insight into the associated dynamics that occur in the bulk liquid [2,3,49,50]. Of particular interest is the point in which the local dynamics observed in clusters transition to the dynamics more relevant to the liquid [51], and we note that it is the thermal excitation of librational motions that have been invoked as the essential hydrogen bond breaking mechanism in the liquid [50].

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