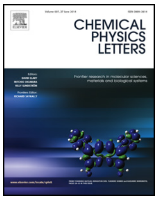
Chemical Physics Letters 610–611 (2014) 369–374

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett



Low temperature heat capacity of water clusters

Hongshan Chen [a,*], Klavs Hansen [b]

[a] College of Physics & Electronic Engineering, Northwest Normal University, Lanzhou 730070, China
[b] Department of Physics, University of Gothenburg, SE-41296 Gothenburg, Sweden

ARTICLE INFO

Article history:
Received 22 February 2014
In final form 28 July 2014
Available online 2 August 2014

ABSTRACT

Geometry optimization and vibrational frequency calculation are carried out at the MP2/6-31G(d,p) level for 35 low-energy isomers of $(H_2O)_n$ clusters in the size range $n = 6–21$. The heat capacities of the clusters are calculated using quantum statistical theories based on the harmonic approximation. The specific heat capacity increases with the cluster size but the difference diminishes gradually with increasing size. The heat capacities divided by the number of intermolecular vibrational modes are very close for all the clusters. The overall picture of the heat capacity of the clusters is bulk-like and it agrees well with the experimental results of size-selected clusters.

1. Introduction

Water clusters are important objects of current experimental and theoretical studies because of their importance in understanding atmospheric chemistry, solution chemistry, and a large number of biochemical processes [1,2]. Substantial progress has been made in the study of the structure of water clusters. From a theoretical point of view, unbiased global minima searches based on different model potentials have been studied with the aim of understanding the characteristics of hydrogen bonds [3–5]. A number of *ab initio* calculations have also been carried out to investigate the strength of the hydrogen bonds and their cooperativity [6–13]. Experimentally, laser infrared and far-infrared vibration–rotation–tunneling spectroscopic studies demonstrated conclusively cyclic structures for $n = 3–5$ [14,15], and different isomers were observed for $n = 6$ [15–17]. Experiments involving pure water clusters as well as hydrated molecules were also carried out for $n = 7–10$ [18–21]. There now exists a general consensus about the global minima up to $n = 8$. *Ab initio* calculations also agree on the structure of the lowest energy isomers for $n = 10$, 12, 15, 16, and 20. The low-energy structures have been well established up to the size around 20 even though the global minima based on different models differ at some sizes. The structures and energetics of water clusters have been recently reviewed [22,23].

Relative to the extensive studies on the structure, investigations on the thermal behavior were limited, and we know little about the property of water clusters at finite temperature. Molecular dynamics and Monte Carlo simulations have been widely used to study the thermal properties of water clusters [24–34]. However, the reliability of the simulations depends on the model potentials used and the results can be different markedly. Moreover, the conventional MD and MC simulations were performed at the level of classical dynamics to treat the motion of atoms or rigid molecules. As the discrete vibration energy levels are allowed to change continuously, the calculations strongly overestimate the energy of the system and the heat capacities obtained from classical MD or MC simulations are expected to be much larger than the true value. We are aware of three literature studies that were carried out to simulate water clusters and treated atomic motion quantum mechanically [35–37], but only one was aimed to calculate the heat capacity. The variational GAUSSIAN wavepacket combined with a model potential SPC was applied to calculate the heat capacities of $(H_2O)_8$ and $(H_2O)_{10}$ [37]. The results show that the classical heat capacity is about one order larger than the quantum value. Simulations dealing with both the motion of the mass center and interatomic interactions in quantum mechanics are beyond the computation ability at present. Experimentally, the heat capacity of water cluster anions consisting of 48 and 118 molecules were measured using photofragmentation technique [38], and the protonated water clusters with 60–79 molecules were studied by multi-collision excitation of the accelerated clusters with helium [39]. While the phase transition temperatures are higher for the protonated clusters, the measured caloric curves of the anions and the protonated clusters coincide at the temperatures before the phase transition occurs and the overall picture is bulk-like.

In this Letter, we turn to the quantum statistical theory to calculate the heat capacity of water clusters. Geometry optimization and vibrational frequencies were computed by the MP2/6-31G(d,p)

---

* Corresponding author.
E-mail addresses: chenhs@nwnu.edu.cn, chenhsyz@sina.com (H. Chen).

http://dx.doi.org/10.1016/j.cplett.2014.07.063

method for the low energy isomers of water clusters from size 6 to 21. The heat capacities of the clusters were obtained using the quantum statistical theories. The Letter was organized as follows. The computation methods are described in Section 2 and the main results reported in Section 3. After the discussion Section 4, the article ends with a brief summary.

2. Calculation methods

In the harmonic approximation, the normal modes are independent and the vibrational motion is the superposition of the normal modes. At normal temperatures (say about 300 K), the modes with high frequencies remain frozen at the vibrational ground levels while the low frequency modes are partially populated at the excited states with probability $\exp(-h\gamma/k_BT)$. When temperature changes, the heat capacity contributed from the vibrational degrees of freedom will change dramatically. For a system having N normal modes of frequencies γ_i ($i = 1 - N$), the energy states are

$$E = \sum_{i=1}^{N}\left(n_i + \frac{1}{2}\right) h\gamma_i \qquad (1)$$

For a canonical ensemble, the partition function is defined as [40]

$$Z = \sum_{n_i=0}^{\infty} e^{-\beta\sum_{i=1}^{N}\left(n_i+\frac{1}{2}\right)h\gamma_i} = \prod_{i=1}^{N}\frac{e^{-\beta h\gamma_i/2}}{1-e^{-\beta h\gamma_i}} \qquad (2)$$

Here $\beta = 1/k_BT$. At temperature T, the average energy of the system is given by

$$U = -\frac{\partial}{\partial\beta}\ln Z = U_0 + \sum_{i=1}^{N}\frac{h\gamma_i}{e^{h\gamma_i/k_BT} - 1} \qquad (3)$$

where U_0 is the zero point energy. The heat capacity of the system can be derived as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = k_B\sum_{i=1}^{N}\left(\frac{h\gamma_i}{k_BT}\right)^2\frac{e^{h\gamma_i/k_BT}}{\left(e^{h\gamma_i/k_BT} - 1\right)^2} \qquad (4)$$

The heat capacity is the sum of the individual oscillator heat capacities.

Møller–Plesset 2nd order perturbation theory (MP2) was adopted to calculate the frequencies in our computation. The basis set used is the double split basis including polarization functions on both oxygen and hydrogen (6-31G(d,p)). The calculation was carried out using the GAUSSIAN 03 program [41]. Comparison with the experimental IR spectra of water clusters shows that the frequencies calculated at MP2/6-31G(d,p) level are quite satisfying [9,16,18,20]. The comparison of the calculated frequencies of the water octamer with the experimental IR spectra is given in supplementary material Figure S1. Experimental spectra are only available for the OH stretching band and the calculated frequencies are 2.0–5.6% higher. We also computed the vibrational frequencies of the water tetramer using a very large basis set 6-311++g(3df,3pd). The results are given in the supplementary material Table S1, and it shows the frequencies calculated at the two basis sets agree well.

The water clusters considered in the present study are the sizes $n = 6–21$. The isomers of the clusters include the global minima structures based on empirical TIPnP ($n = 3$, 4, 5) potentials [3,5] and HF/6-31G(d,p) calculations [6]. $(H_2O)_6$ has a few low energy isomers with competing energies. For $n = 7–9$, optimization based on different empirical potentials and *ab initial* calculations lead to same global minima structure. In the size range $n = 10–21$, the lowest energy structure based on different models differs amongst a few isomers. Totally we computed the frequencies of 35 structures.

Table 1
Binding energy E_b and averaged over the number of molecules for $(H_2O)_n$ ($n = 6–21$).

Clusters	E_b(eV) (without ZPE)	E_b (eV)	E_b/n
w6(prism)	−2.89	−2.22	−0.37
w6(cage)	−2.83	−2.17	−0.36
w6(ring)	−2.57	−1.98	−0.33
w7	−3.51	−2.72	−0.39
w8	−4.43	−3.47	−0.43
w9	−4.92	−3.86	−0.43
w10	−5.60	−4.40	−0.44
w10(3p)	−5.30	−4.21	−0.42
w11	−6.18	−4.86	−0.44
w11(HF)	−6.16	−4.83	−0.44
w11(5p)	−6.05	−4.76	−0.43
w12	−7.18	−5.66	−0.47
w12(3p)	−6.82	−5.37	−0.45
w12(5p)	−6.79	−5.36	−0.45
w13	−7.68	−6.06	−0.47
w13(5p)	−7.40	−5.84	−0.45
w14	−8.44	−6.68	−0.48
w14(HF)	−8.13	−6.42	−0.46
w14(5p)	−8.03	−6.35	−0.45
w15	−8.94	−7.23	−0.48
w15(5p)	−8.75	−7.11	−0.47
w16	−9.93	−8.04	−0.50
w16(5p)	−9.26	−7.56	−0.47
w17	−10.46	−8.48	−0.50
w17(5p)	−10.22	−8.31	−0.49
w18	−11.20	−9.07	−0.50
w18(5p)	−10.77	−8.77	−0.49
w19	−11.80	−9.62	−0.51
w19(HF)	−11.71	−9.50	−0.50
w20	−12.74	−10.33	−0.52
w20(4p)	−12.60	−10.23	−0.51
w20(5p)	−12.38	−10.11	−0.51
w21	−13.24	−10.77	−0.51
w21(5p)	−13.09	−10.70	−0.51

The initial coordinate parameters of TIP4P/5P and HF isomers were taken from the Cambridge Cluster Database posted by Wales and his colleagues [42]. The TIP3P structures are based on our genetic algorithm optimization and they agree with those reported by Kabrede and Hentschke [4]. All the structures are illustrated in the supplementary material Figure S2. The isomers of water clusters in this Letter are denoted as following: Wn is the lowest energy structure of $(H_2O)_n$ based on the present calculation and Wn(kp) ($k = 3, 4, 5$) or Wn(HF) refers to the global minima isomers based on model potentials TIPkP ($k = 3$, 4, 5) or HF/6-31G(d,p) calculations, respectively.

3. Results

3.1. Structure and stability of $(H_2O)_n$ ($n = 6–21$)

In order to study the correlation of the heat capacities with the stability of the clusters, the binding energies of the clusters are presented first but briefly. The binding energy is defined as the energy difference of the cluster at the equilibrium structure and the H_2O molecules building up it:

$$E_b = E_0((H_2O)_n) - n \times E_0(H_2O) \qquad (5)$$

The binding energies corrected and uncorrected with zero point energy (ZPE) are presented in Table 1. *Ab initio* calculations have been previously carried out for water hexamer [6–8,12], for the sizes $n = 7–10$ [6,10,12], $n = 11–13$[9,10,12,13], $n = 14–16$ [10,12], and $n = 17–21$ [10–12]. Even the binding energies calculated at different levels may be different slightly, the order of the stability of the isomers is in good agreement. Water hexamer is the smallest size that has 3D structures as global minimum isomer. Calculations at high levels show that the prism and cage forms are nearly isoenergetic [8]. The global minimum structure for $n = 7$, 8, 9 have