

# Nuclear Quantum Effects in Water Clusters: The Role of the Molecular Flexibility

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With the objective of establishing the importance of water flexibility in empirical models which explicitly include nuclear quantum effects, we have carried out path integral Monte Carlo simulations in water clusters with up to seven molecules. Two recently developed models have been used for comparison: the rigid TIP4PQ/2005 and the flexible q-TIP4P/F models, both inspired by the rigid TIP4P/2005 model. To obtain a starting configuration for our simulations, we have located the global minima for the rigid TIP4P/2005 and TIP4PQ/2005 models and for the flexible q-TIP4P/F model. All the structures are similar to those predicted by the rigid TIP4P potential showing that the charge distribution mainly determines the global minimum structure. For the flexible q-TIP4P/F model, we have studied the geometrical distortion upon isotopic substitution by studying tritiated water clusters. Our results show that tritiated water clusters exhibit an  $r_{OT}$  distance shorter than the  $r_{OH}$  distance in water clusters, not significant changes in the  $\Phi_{HOH}$  angle, and a lower average dipole moment than water clusters. We have also carried out classical simulations with the rigid TIP4PQ/2005 model showing that the rotational kinetic energy is greatly affected by quantum effects, but the translational kinetic energy is only slightly modified. The potential energy is also noticeably higher than in classical simulations. Finally, as a concluding remark, we have calculated the formation energies of water clusters using both models, finding that the formation energies predicted by the rigid TIP4PQ/2005 model are lower by roughly 0.6 kcal/mol than those of the flexible q-TIP4P/F model for clusters of moderate size, the origin of this difference coming mainly from the geometrical distortion of the water molecule in the clusters that causes an increase in the intramolecular potential energy.

## I. Introduction

Water simulations play a fundamental role in many research areas, such as chemistry, environmental science, biology, etc. In fact, the number of publications related with this topic during the last 5 years amounts to more than 45 000 articles, which indicates the great relevance of water simulation. This fact has boosted the design of more and more precise and versatile computational models used to describe the behavior of water in many different environments, such as in its different phases of ice,<sup>1</sup> liquid water,<sup>2,3</sup> and vapor,<sup>4</sup> in confinement regime,<sup>5–7</sup> water clusters,<sup>8–13</sup> etc. Nowadays we can find nearly a hundred models with this aim, the majority of them being empirical models. Some of these models have been enormously successful, as are the cases of the TIP4P,<sup>14</sup> SPC/E,<sup>15</sup> and TIP5P.<sup>16</sup> These models are rigid and nonpolarizable and were designed to be used within classical simulations.

In recent years, it has been shown that these models could be further improved by forcing them to reproduce a number of water properties. In this way, TIP4P-Ew<sup>17</sup> and TIP4P/2005<sup>18</sup> have been proposed, which overall provide a better description. However, the feeling is that we have reached the limit of what can be described of water by using rigid, nonpolarizable models within classical simulations. To get further improvement, some additional features of water which are neglected in these models

should be incorporated. Let us briefly justify this. First, the dielectric constant of TIP4P-Ew<sup>17</sup> and TIP4P/2005<sup>18</sup> is rather low when compared to the experimental value. The second virial coefficient is too negative,<sup>19,20</sup> and the vapor pressures of water are not described properly by these models.<sup>21</sup> These failures are due to the fact that the model is not polarizable, having the same dipole moment for the vapor and condensed phases. Obviously, the dipole moment of water changes from the vapor to the liquid phase,<sup>22,23</sup> and this cannot be accounted for by a nonpolarizable model. In addition, it seems that to describe the fluctuations of the polarization of a system (which accounts for the dielectric constant), the inclusion of the polarizability is needed. In summary, not including the polarizability prevents properly describing the properties of the vapor and the dielectric constant.

Second, the equation of state of ices at temperatures below 150 K cannot be reproduced by classical statistical mechanics,<sup>24,25</sup> and both the structure and heat capacities ( $C_p$ ) are affected by isotopic substitution, strongly suggesting the importance of nuclear quantum effects when describing water.<sup>26–29</sup> Third, water is a flexible molecule, and that should be incorporated into the description,<sup>30–35</sup> although at this point, the impact of that approximation on the final results is not clear. Ideally, the next generation of water potentials should explicitly include polarizability and flexibility to finally describe the properties of water at all thermodynamic conditions when using quantum statistical

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mechanics. However, it may still be useful to incorporate one by one each of these features missing in the traditional description of water provided by rigid nonpolarizable models treated with classical statistics.

In this paper, we shall incorporate nuclear quantum effects in the description of small water clusters. The purpose is to analyze the magnitude of nuclear quantum effects on clusters and how the properties of small clusters tend to those of the bulk phase. Several authors have already argued the importance of nuclear quantum effects in water.<sup>36–41</sup> One of the most convincing proofs about the importance of this effect comes from the comparison between light water (H<sub>2</sub>O) and heavy water (D<sub>2</sub>O). From the point of view of the Born–Oppenheimer approximation, the potential energy surface (PES) is independent of the isotope considered. Thus, the different behavior of these isotopes is due to how the molecule reacts to this PES. This is known as nuclear quantum effects. For example, the melting point of heavy water is 3.82 K higher than that of light water, and in tritiated water (T<sub>2</sub>O), this difference is 4.49 K, proving that quantum effects modify the hydrogen bond network, reducing the melting point. Another example comes from X-ray diffraction measurements that have shown a clear difference in the structure factors between liquid H<sub>2</sub>O and D<sub>2</sub>O.<sup>42,43</sup> These examples point out that quantum effects cannot be ignored when designing a realistic and precise water model. To incorporate this effect in a computational model, it is useful to employ the Feynman’s path integral (PI) formulation of statistical mechanics.<sup>44</sup> This treatment has been extensively used in liquid and ice water by means of molecular dynamics (MD)<sup>37,45,46</sup> or Monte Carlo simulations (MC).<sup>25,40</sup> Somewhat surprisingly, there are not many studies dealing with nuclear quantum effects in water clusters. Let us just mention some recent studies, all of them focused on how the melting transition in clusters is affected by quantum effects. The first one, carried out by Shin, Son, and Jang,<sup>47</sup> studied the melting of the water octamer using path integral molecular dynamics with the flexible SPC/F<sub>2</sub> model.<sup>48</sup> In addition, Doll and co-workers<sup>49,50</sup> have studied the water octamer, but using rigid models and path integral Monte Carlo simulations. Finally, in a recent article, Frantsuzov and Mandelshtam<sup>51</sup> studied water clusters with  $N = 8$  and 10 using a flexible model with the variational Gaussian wavepacket method.<sup>52</sup>

In this article, we shall perform PI simulations of small water clusters (with up to seven water molecules). Instead of using potential models optimized for classical simulations (SPC,<sup>53</sup> SPC/F),<sup>54</sup> we shall use two models that have provided a good description of liquid water and ices within PI simulations. In particular, we shall use the recently proposed q-TIP4P/F<sup>55</sup> and TIP4PQ/2005<sup>25</sup> models. These models are the quantum counterparts of the TIP4P/2005<sup>18</sup> designed for classical simulations. Since these models provide a good description of bulk water properties when used within PI simulations, one expects that the model would be more reliable as the size of the cluster increases. The comparison between q-TIP4P/F (a flexible model) and TIP4PQ/2005 (a rigid model), which present a similar distribution of charges and parameters, would be quite useful, since it allows one to discriminate how much of the nuclear quantum effects are due to intra- and to intermolecular degrees of freedom. We should emphasize from the beginning that since these models are not polarizable, they cannot reproduce quantitatively the experimental values of the formation energy of water clusters. In this paper, we do not intend to reproduce experimental properties of clusters. Rather, our objectives are the following: first, to analyze how the geometry of the water

molecule changes by increasing the size of the cluster; second, to analyze how nuclear quantum effects change with the size of the cluster; third, by comparing the results of q-TIP4P/F and TIP4PQ/2005 to analyze how much is lost in the description of water clusters (when including nuclear quantum effects) using a rigid model instead of the more sophisticated flexible one. As a subproduct, we shall also determine the geometry of minimum energy of the clusters for these two models.

The present article is organized as follows: In the first part, we briefly describe the rigid and flexible water models and outline the PIMC method for both models. In the second part, we present and discuss the different results, and finally, we highlight the most outstanding conclusions.

## II. Methodology

**A. Rigid and Flexible Water Models.** To compare the nuclear quantum effects in a rigid and in a flexible model, we have employed two models recently proposed and both inspired in the rigid pairwise additive TIP4P/2005 water model developed by Abascal and Vega.<sup>18</sup> Extensive simulations have shown that, among the available nonpolarizable rigid models of water, the TIP4P/2005 potential provides one of the best overall description of water.<sup>56</sup>

The flexible q-TIP4P/F model, developed by Habershon, Markland, and Manolopoulos,<sup>55</sup> is a flexible version of the rigid TIP4P/2005 model and reproduces the correct liquid structure, the infrared adsorption frequencies, the temperature of maximum density, and the diffusion coefficient. This model consists of an intermolecular term plus an intramolecular term; that is,

$$U_{q\text{-TIP4P/F}} = U_{\text{inter}} + U_{\text{intra}} \quad (1)$$

The intermolecular contribution is identical to that of the TIP4P/2005 model with the difference that the positions of the hydrogen and the M-point are not fixed. This contribution has the following form,

$$U_{\text{inter}} = \sum_i \sum_{j>i} \left\{ 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{m \in i} \sum_{n \in j} \frac{q_m q_n}{r_{mn}} \right\} \quad (2)$$

where  $r_{ij}$  represents the distance between the oxygen atoms in molecules  $i$  and  $j$ ;  $r_{mn}$  is the distance between partial charges site,  $q_m$  and  $q_n$ , in molecules  $i$  and  $j$ ; and  $\epsilon$  and  $\sigma$  are the Lennard–Jones parameters. The charged sites are placed on the hydrogen atoms, and on the M-point, placed at the following position,

$$\mathbf{r}_M = \gamma \mathbf{r}_O + (1 - \gamma)(\mathbf{r}_{H_1} + \mathbf{r}_{H_2})/2 \quad (3)$$

where  $\gamma$  is a parameter also given in Table 1.

The intramolecular term that accounts for water flexibility is represented by a quartic expansion of a Morse potential to describe the O–H stretching, and a quadratic harmonic potential in the bending angle,

$$U_{\text{intra}} = \sum_i \left[ V_{\text{OH}}(r_{i1}) + V_{\text{OH}}(r_{i2}) + \frac{1}{2} k_\theta (\theta_i - \theta_{\text{eq}})^2 \right] \quad (4)$$

where the function  $V_{\text{OH}}$  has the following expression:

$$V_{\text{OH}}(r) = D_r \left[ \alpha_r^2 (r - r_{\text{eq}})^2 - \alpha_r^3 (r - r_{\text{eq}})^3 + \frac{7}{12} \alpha_r^4 (r - r_{\text{eq}})^4 \right] \quad (5)$$

where the parameters  $k_\theta$ ,  $\theta_{\text{eq}}$ ,  $D_r$ ,  $\alpha_r$ , and  $r_{\text{eq}}$  are given in Table 1.

It is interesting to point out that the flexibility of the water molecule is usually represented by means of harmonic potentials.<sup>31,40,48,57,58</sup> However, recently, it has been argued that nuclear quantum effects are overestimated by the use of harmonic functions,<sup>55</sup> so if one wants to include both effects explicitly in a computational model, it seems important also to add anharmonic functions in the intramolecular term. In this model, the anharmonicity in the OH bonds seems to be necessary to provide an accurate description of the infrared spectrum.<sup>55</sup>

The rigid TIP4PQ/2005 model developed by McBride et al.<sup>25</sup> is a reparametrization of the TIP4P/2005 to allow the explicit incorporation of the nuclear quantum effects. This model has provided an accurate description of the densities and relative stabilities of most of the ice polymorphs and of the structure of ice  $I_h$  and liquid water. It also reproduces with good accuracy the maximum in the density of water.<sup>59</sup> Its functional form is identical to that of eq 2,

$$U_{\text{TIP4PQ/2005}} = U_{\text{inter}} \quad (6)$$

using the appropriate parameters specified in Table 1.

**B. Path Integral Monte Carlo.** The path integral method is based on Feynman's interpretation of statistical mechanics, which makes it possible to write the partition function  $Q$  in a path integral form.<sup>44,60</sup> For a canonical ensemble of  $N$  rigid water molecules whose positions are described by the center of mass coordinates ( $\mathbf{r}$ ) and the Euler angles ( $\Omega$ ), the partition function is written as<sup>25</sup>

$$Q_N(\beta) \approx \frac{1}{N!} \left( \frac{MP}{2\pi\beta\hbar^2} \right)^{3NP/2} \int \dots \int \prod_{i=1}^N \prod_{t=1}^P d\mathbf{r}_i^t d\Omega_i^t \times \exp \left( - \frac{MP}{2\beta\hbar^2} \sum_{i=1}^N \sum_{t=1}^P (\mathbf{r}_i^t - \mathbf{r}_i^{t+1})^2 - \frac{\beta}{P} \sum_{t=1}^P U^t \right) \times \prod_{i=1}^N \prod_{t=1}^P \rho_{\text{rot},i}^{t,t+1} \quad (7)$$

where  $\beta = 1/k_B T$ ,  $T$  is the temperature of the system, and  $M$  is the mass of the water molecule.

This expression has the same form of a purely classical partition function for a cyclic chain of  $P$  beads coupled by

**TABLE 1: Parameters for the q-TIP4P/F, TIP4PQ/2005, and TIP4P/2005 Models**

	q-TIP4P/F	TIP4PQ/2005	TIP4P/2005
$\epsilon$ (kcal/mol)	0.1852	0.1852	0.1852
$\sigma$ (Å)	3.1589	3.1589	3.1589
$q_H$ (e)	0.5564	0.5764	0.5564
$r_{\text{OM}}$ (Å)		0.1546	0.1546
$\gamma$	0.73612		
$D_r$ (kcal mol <sup>-1</sup> Å <sup>-2</sup> )	116.09		
$\alpha_r$ (Å <sup>-1</sup> )	2.287		
$r_{\text{eq}}$ (Å)	0.9419		
$k_\theta$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )	87.85		
$\theta_{\text{eq}}$ (°)	107.4		

harmonic springs, with spring constant equal to  $k = MP/2\beta^2\hbar^2$ .<sup>61</sup> Molecules of replica  $t$  interact through an intermolecular potential  $U^t$  (divided by  $P$ ). In this work,  $U^t$  is described by the rigid TIP4PQ/2005 potential,

$$U^t = U_{\text{TIP4PQ/2005}}^t \quad (8)$$

The number of beads,  $P$ , also called Trotter number, indicates how many replicas of the classical system will be used to mimic the quantum behavior. For  $P \rightarrow \infty$ , the quantum simulation becomes exact, and for  $P = 1$ , the simulation is classical.

The last term in eq 7 is associated with the rotational degrees of freedom of the rigid water molecules, and it can be exactly evaluated.<sup>62</sup>

The internal energy,  $E$ , can be calculated from the partition function  $Q_N(\beta)$  using the equation:

$$E = - \frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} \quad (9)$$

With some algebra, it can be proved that the internal energy takes the form

$$E = K_{\text{tra}} + K_{\text{rot}} + U \quad (10)$$

where the functional forms of these three factors are<sup>25</sup>

$$K_{\text{tra}} = \frac{3NP}{2\beta} - \left\langle \frac{MP}{2\beta^2\hbar^2} \sum_{i=1}^N \sum_{t=1}^P (\mathbf{r}_i^t - \mathbf{r}_i^{t+1})^2 \right\rangle \quad (11)$$

$$K_{\text{rot}} = \left\langle \frac{1}{P} \sum_{i=1}^N \sum_{t=1}^P \frac{1}{\rho_{\text{rot},i}^{t,t+1}} \left\{ \sum_{J=0}^{\infty} \sum_{M,\bar{K}=-J}^J f_{i,J,M,\bar{K}}^{t,t+1} E_{\bar{K}}^{JM} e^{-\beta/PE_{\bar{K}}^{JM}} \right\} \right\rangle \quad (12)$$

$$U = \left\langle \frac{1}{P} \sum_{t=1}^P U_{\text{TIP4PQ/2005}}^t \right\rangle \quad (13)$$

where  $f_{i,J,M,\bar{K}}^{t,t+1}$  is a function of the relative Euler angles between beads  $t$  and  $t+1$ , whose form is detailed in reference 25 and  $E_{\bar{K}}^{JM}$  is the eigenvalue of the energy of the asymmetric top.

In the case of a flexible water model, the usual set of coordinates is the Cartesian one ( $\mathbf{r}$ ) because there is no need to separate the rotational and translational movement. The partition function is now written as

$$Q_N(P) \propto \prod_{\alpha=1}^n \left( \frac{m_\alpha P}{2\pi\beta\hbar^2} \right)^{3P/2} \int \dots \int \prod_{\alpha=1}^n \prod_{t=1}^P d\mathbf{r}_\alpha^t \times \exp \left( - \frac{P}{2\beta\hbar^2} \sum_{\alpha=1}^n \sum_{t=1}^P m_\alpha (\mathbf{r}_\alpha^t - \mathbf{r}_\alpha^{t+1})^2 - \frac{\beta}{P} \sum_{t=1}^P U^t \right) \quad (14)$$

Here,  $n$  is the number of atoms in the system, and the potential energy  $U^t$  is now given by the flexible q-TIP4P/F potential.

Now again, we can evaluate the internal energy using eq 9, obtaining the following expression,

$$E = K + U \quad (15)$$

These two contributions have a functional form similar to eqs 11 and 13, but now the number of molecules ( $N$ ) must be replaced by the number of atoms ( $n$ ), the water molecule mass ( $M$ ) is replaced by the atomic masses ( $m_\alpha$ ), and the potential term ( $U^n$ ) is defined now by the flexible q-TIP4P/F water–water interaction potential; that is,

$$K = \frac{3nP}{2\beta} - \left\langle \frac{P}{2\beta^2\hbar^2} \sum_{\alpha=1}^n \sum_{i=1}^P m_\alpha (\mathbf{r}_\alpha^i - \mathbf{r}_\alpha^{i+1})^2 \right\rangle \quad (16)$$

$$U = \left\langle \frac{1}{P} \sum_{i=1}^P U_{\text{q-TIP4P/F}}^i \right\rangle \quad (17)$$

**C. Simulation Details.** Path integral Monte Carlo simulations require the specification of several parameters, some related to the path integral method and others related to the Monte Carlo sampling.

For the first method, the number of beads,  $P$ , is the fundamental parameter. This number needs to be large enough to correctly describe the quantum properties, but it also must be small enough to simulate in a reasonable computational time. It is also important to notice that quantum effects are enhanced as the temperature decreases, and therefore, a larger number of replicas are needed at low temperatures. For this reason, we kept the rule  $PT = \text{constant}$  in our simulation. We took  $PT = 1500$  K for the rigid model (following ref 25) and  $PT = 6000$  K for the flexible one because the number of beads needed is usually higher for flexible models.<sup>40,46</sup> For this reason, the calculations of the flexible model are, in principle, more expensive computationally than those of the rigid one, although the computational effort can be reduced significantly by using the ring polymer contraction techniques proposed recently by Manolopoulos and co-workers.<sup>63–65</sup>

We performed simulations at the temperature  $T = 50$  K. This temperature should be low enough to avoid the evaporation of molecules from the cluster, which was estimated around  $T = 150$  K for the rigid dimer, and it also must give us some confidence that the cluster structures keep close to the global minima structures during the simulation. This is because we are not interested in exploring the whole potential energy surface, but in the different behaviors of the clusters while using a flexible or rigid model in a specific configuration (i.e., the global minima structures). On the other hand, a too low temperature will require an excessive number of replicas, making the simulation unapproachable. Following the rule of  $PT = \text{constant}$ , the respective Trotter numbers at temperature  $T = 50$  K are  $P = 30$  for the rigid model and  $P = 120$  for the flexible model.

For the Monte Carlo sampling, we have used four different trial moves for the rigid model with a probability indicated in parentheses: first, displacement of a single replica of a particular molecule (30%); second, rotation of a single replica of a particular molecule (30%); third, translation of all the replicas associated with a single molecule (20%); and fourth, rotation of all the replicas associated with a single molecule (20%). In the case of the flexible water model, we have used three trial moves: first displacement of a single replica of a particular molecule (20%); second, rotation of a single replica of a particular molecule (20%); and third, translation of a randomly selected atom of a particular replica of a specific molecule

**TABLE 2: Predicted Global Minima Energies (in kcal/mol) for Water Clusters Using the TIP4P, TIP4P/2005, TIP4PQ/2005 and q-TIP4P/F Models<sup>a</sup>**

$N$	TIP4P	TIP4P/2005	TIP4PQ/2005	q-TIP4P/F
2	-6.235	-6.862	-7.516	-6.547
3	-16.729	-18.397	-20.165	-17.768
4	-27.866	-30.655	-33.584	-29.863
5	-36.355	-39.987	-43.774	-39.005
6	-47.271	-52.099	-57.034	-50.645
7	-58.215	-64.175	-70.235	-62.396
8	-73.021	-80.502	-88.150	-78.442
9	-82.322	-90.722	-99.295	-88.451
10	-93.457	-103.012	-112.754	-100.377
11	-103.128	-113.701	-124.403	-110.710
12	-117.808	-129.934	-142.200	-126.549
13	-127.383	-140.489	-153.777	-137.044
14	-139.338	-153.656	-168.136	-149.717
15	-150.185	-165.603	-181.162	-161.314
16	-162.809	-179.608	-196.514	-174.893
17	-172.994	-190.828	-208.809	-186.083
18	-184.807	-203.851	-223.035	-198.620
19	-196.233	-216.474	-236.770	-211.344
20	-208.649	-230.105	-251.740	-224.487

<sup>a</sup>For comparison, the global minima found from ab initio calculations is  $-4.98$  kcal/mol for the dimer,  $-36.3$  kcal/mol for the pentamer, and  $-72.7$  kcal/mol for the octamer.<sup>74</sup>

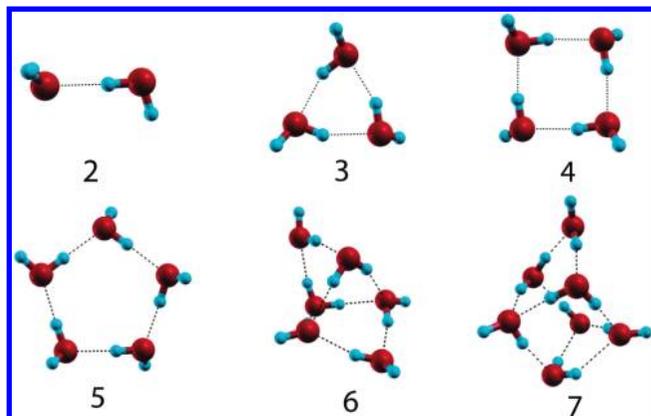
(60%). The maximum displacement or rotation in each move was adjusted to get a 40% acceptance probability.

In general, a simulation consists of a million Monte Carlo cycles of equilibration and typically 80 or 100 million Monte Carlo cycles to collect data for the rigid or flexible model. Notice that we define a Monte Carlo cycle as the attempt of  $N$  Monte Carlo moves.

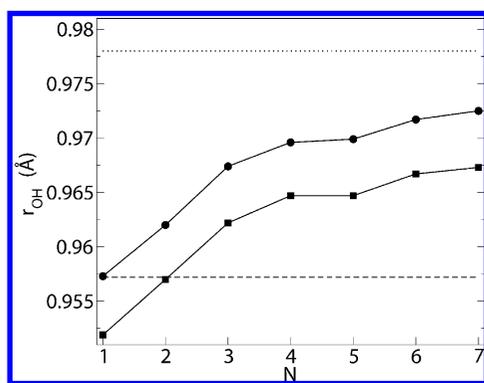
### III. Results

To generate a starting configuration for our PIMC simulations, we have calculated the global minima of the potential energy for water clusters up to  $N = 20$ . For this purpose, we have used the Basin–Hopping global optimization algorithm,<sup>66</sup> starting the search from random configurations and also from the TIP4P global minima structures.<sup>67</sup> The structures obtained from both types of search were found to be coincident, which gives us some confidence that a global minimum was, indeed, found. In Table 2, we present the energies for the water clusters up to  $N = 20$  for three rigid models—TIP4P, TIP4P/2005, and TIP4PQ/2005—and also for the flexible q-TIP4P/F model. For the rigid models, the decrease in energy in the order TIP4P, TIP4P/2005, TIP4PQ/2005 just reflects the increase in the magnitude of the proton charge in these rigid models. Figure 1 represents the global minima structure of the water cluster up to  $N = 7$  for the TIP4PQ/2005 model. The global minima structures up to  $N = 20$  for the rigid TIP4P/2005 and TIP4PQ/2005 models and for the flexible q-TIP4P/F model are given as Supporting Information and will be available in the SklogWiki.<sup>68</sup>

The energies at the minima found in this work for TIP4P/2005 are in agreement with the values recently reported by Kiss and Baranyai.<sup>69</sup> The geometry of the cluster at the minima is the same for these three rigid models—TIP4P, TIP4P/2005 and TIP4PQ/2005—and also in the flexible q-TIP4P/F model (although slight differences in the distances and angles appear). This is not surprising, since these models present the same charge distribution. It seems that the charge distribution within the water molecules determines the configuration of the minimum energy of a cluster. That may explain why the



**Figure 1.** Global minima configurations of the  $(\text{H}_2\text{O})_N$ ,  $N = 2-7$  for the TIP4PQ/2005 water model. For  $N = 3, 4, 5$ , the cyclic geometry was found to be the global minimum, whereas for  $N = 6$ , the cage geometry was the global minimum (the same structures were found to be the global minimum for q-TIP4P/F, TIP4P/2005, and TIP4P).

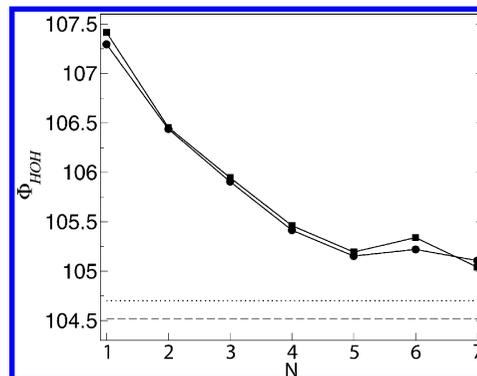


**Figure 2.** Average  $r_{\text{OH}}$  distances for water clusters ( $\bullet$ ) and tritiated water clusters ( $\blacksquare$ ) having  $N$  molecules obtained from PIMC simulations with the flexible q-TIP4P/F model at temperature  $T = 50$  K. The dashed line indicates the  $r_{\text{OH}}$  distance for the rigid TIP4PQ/2005 model, and the dotted line is the value obtained by Habershon et al. for the liquid phase of water using the q-TIP4P/F model.<sup>55</sup>

minimum energy configuration of water clusters described by the TIP5P model<sup>70</sup> or the TIP3P model<sup>9</sup> is quite different from those obtained when using the TIP4P models.

To study the geometrical distortion of the water molecule by the formation of hydrogen bonds, we have determined the variation of the bond distances, angles and molecular dipolar moment with the cluster size by performing PIMC simulations with the flexible q-TIP4P/F model at the temperature  $T = 50$  K. We also performed PI simulations of tritiated water clusters (using the same model potential) to analyze the geometrical changes caused by substitution of the hydrogen by a heavier isotope. Because we are including nuclear quantum effects, the present simulations will allow us to determine changes in the molecular geometry due to isotopic substitution. Notice that energy minimization of water and tritiated water clusters would not be very useful for this purpose, since the configuration of the cluster at the minimum energy is not affected by isotopic substitution and, in addition, the effects of vibrations on the molecular geometry are not incorporated.

Figure 2 shows the average O–H covalent bond distance,  $r_{\text{OH}}$ , as a function of the cluster size. At this temperature ( $T = 50$  K), the average  $r_{\text{OH}}$  bond length in the monomer was found to be 0.957 Å, which is a bit larger than the bond length in the monomer at the global minimum (0.9419 Å, see Table 1). The cubic term in eq 5 introduces asymmetry in the stretching potential, which provokes an increase in the average bond length



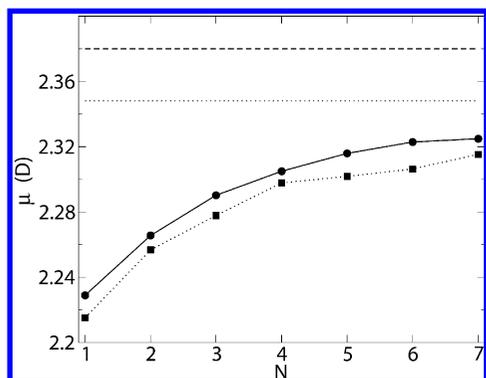
**Figure 3.** Average  $\Phi_{\text{HOH}}$  angles for water clusters ( $\bullet$ ) and tritiated water clusters ( $\blacksquare$ ) having  $N$  molecules obtained from PIMC simulations with the flexible q-TIP4P/F model at temperature  $T = 50$  K. The dashed line indicates the  $\Phi_{\text{HOH}}$  angle for the rigid TIP4PQ/2005 model, and the dotted line is the value obtained by Habershon et al. for the liquid phase of water using the q-TIP4P/F model.<sup>55</sup>

of the monomer with respect to the value at the global minimum. As can be seen, the  $r_{\text{OH}}$  distance increases with the cluster size, reflecting the fact that the intermolecular hydrogen bonds increase the  $r_{\text{OH}}$  distance. As the size of the cluster increases, the bond length gets closer to the bond length of 0.978 Å found in the liquid phase for the q-TIP4P/F.<sup>55</sup> Similarly, in the tritiated clusters, the bond length  $r_{\text{OT}}$  also increases with the cluster size. However, for a certain size, the  $r_{\text{OT}}$  is not identical to the  $r_{\text{OH}}$  distance but somewhat smaller.

The difference between the  $r_{\text{OH}}$  distances in water and  $r_{\text{OT}}$  distances in tritiated water clusters is almost constant with a value of 0.005 Å. These results are in line with the experimental trends, where it has been found from microwave and infrared spectroscopies that for an isolated single molecule, the distance  $r_{\text{OT}}$  in tritiated water (0.967 Å) is slightly smaller (by 0.005 Å) than the  $r_{\text{OH}}$  distance in water (0.972 Å).<sup>71</sup> It has also been recently suggested that this difference in the geometries is even larger in the liquid, where it was found that the  $r_{\text{OD}}$  in deuterated water is 0.98 Å, whereas in water, it has been estimated to be 1.01 Å.<sup>72</sup> In summary, the  $r_{\text{OH}}$  increases with the cluster size (due to hydrogen bond formation) and decreases with the mass of the hydrogen isotope. Most rigid models of water use an  $r_{\text{OH}}$  bond length taken from the geometry of the gas (i.e., 0.9574 Å). It appears from the previous discussion that to model the condensed phases of water with a rigid model, a bond length around 0.98 Å would be more appropriate.

In Figure 3, we present the average  $\Phi_{\text{HOH}}$  angles in water and tritiated water clusters. The differences in the bond angle between water and tritiated water are rather small (less than 0.1°). Even for a cluster having just a few molecules, the bond angle differs by only 0.5° of the value found for the liquid phase by the q-TIP4P/F model. Most rigid models use a bond angle taken from the geometry of the molecule in the gas phase (i.e., 104.5°). This value is close to the value adopted in the liquid phase by the q-TIP4P/F model.

Figure 4 shows the average dipole moment of the water molecule as a function of the cluster size. Results are presented for water and tritiated water. The dipole moment of the molecule of water in the liquid phase has been taken from the PIMC results of Manolopoulos and co-workers for the q-TIP4P/F.<sup>55</sup> In tritiated clusters, the dipole moment of the molecule is about 0.01–0.02 D lower than in water clusters. This smaller value of the dipole moment is related to the shorter (O–T) bond length when compared to the (O–H) bond length. Even for a cluster having just a few molecules, the dipole moment differs by only



**Figure 4.** Average dipole moment for water clusters (●) and for tritiated water clusters (■) as obtained from PIMC simulations with the flexible q-TIP4P/F model at temperature  $T = 50$  K. The dashed line indicates the dipole moment for the rigid TIP4PQ/2005 model, and the dotted line is the value obtained by Habershon et al. for the liquid using the q-TIP4P/F model.<sup>55</sup>

**TABLE 3: Average Energy Components (in kcal/mol) Per Water Molecule for Water Clusters Using the Rigid TIP4PQ/2005 Model and PIMC Simulations at Temperature  $T = 50$  K<sup>a</sup>**

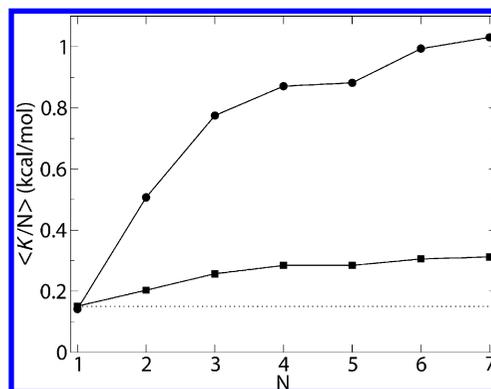
$N$	$\langle K_{\text{rot}}/N \rangle$	$\langle K_{\text{tra}}/N \rangle$	$\langle U/N \rangle$	$\langle K_{\text{rot}}^{\text{cl}}/N \rangle, \langle K_{\text{tra}}^{\text{cl}}/N \rangle$	$\langle U^{\text{cl}}/N \rangle$
1	0.14	0.15	0.00	0.15	0.00
2	0.51	0.20	-3.07	0.15	-3.27
3	0.77	0.26	-5.65	0.15	-6.62
4	0.87	0.28	-7.12	0.15	-8.28
5	0.88	0.28	-7.49	0.15	-8.52
6	0.99	0.30	-8.05	0.15	-9.38
7	1.03	0.31	-8.44	0.15	-9.90

<sup>a</sup>  $K_{\text{rot}}$  and  $K_{\text{tra}}$  represent the rotational and translational kinetic energy components, and  $U$  is the potential energy. The superscripts cl indicate the classical values as obtained from classical simulations. The errors (in kcal/mol) are  $O(0.02)$  in the kinetic components and  $O(0.02)$  in  $U$ .

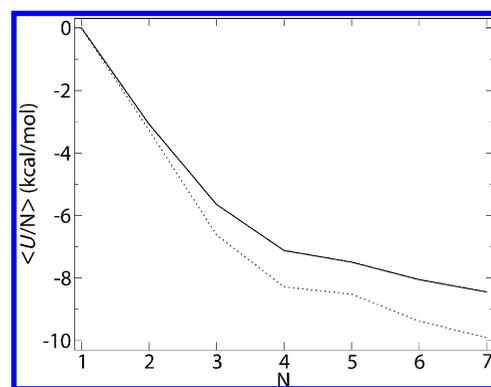
0.03 D of the value found for the liquid phase by the q-TIP4P/F model. The model predicts a small increase in the dipole moment with the size of the cluster. However, because polarizability has not been included, the model cannot simultaneously describe the dipole moment of the isolated molecule (experimentally 1.85 D) and that of the liquid phase. In fact, first principle calculations have shown that the dipole moment of water in clusters increases from 1.85 D for the monomer to a value close to 2.7 D for the hexamer.<sup>73</sup>

We shall now compare energetic results for clusters, as described with the rigid TIP4PQ/2005 and the flexible q-TIP4P/2005 models. Before doing this comparison, it is interesting to see if the impact of nuclear quantum effects on clusters (for the rigid model) is similar to that found in our previous work for condensed phases.<sup>25</sup> In Table 3, the different contributions to the energy for clusters obtained at  $T = 50$  K from PIMC simulations and from classical simulations are presented. Several conclusions can be obtained.

For the monomer, the results of classical and PIMC simulations are coincident. For a free particle, the translational kinetic energy is still given by  $3/2 RT$ , even within a quantum treatment (only confinement would modify that). The rotational energy obtained from the PIMC is very close to  $3/2 RT$ , indicating that at this temperature, the water free asymmetric rotor behaves almost classically. For clusters with two or more molecules, the quantum and classical contributions to the energy no longer coincide due to the presence of hydrogen bonds. As expected, the differences between the quantum and classical systems tend



**Figure 5.** Quantum and classical kinetic energy per water molecule for several water clusters predicted by the rigid TIP4PQ/2005 model at temperature  $T = 50$  K as a function of size. Squares represent the quantum translational kinetic energy, circles represent the quantum rotational kinetic energy, and the dotted line represents the classical translational or rotational kinetic energy (i.e.,  $3/2 RT$ ).



**Figure 6.** Quantum and classical potential energy per water molecule for several water clusters predicted by the rigid TIP4PQ/2005 model at temperature  $T = 50$  K as a function of size. The solid line represents the quantum potential energy, and the dotted line represents the classical potential energy.

to increase with the size of the cluster, reflecting the fact that quantum effects increase with the number of hydrogen bonds in the system.

At the largest studied sizes, the translational kinetic energy of the quantum system is slightly larger (by about 0.16 kcal/mol) than that obtained from classical simulations (see Figure 5), whereas the rotational kinetic energy of the quantum system is much larger than that of the classical system (by about 0.88 kcal/mol). This is not surprising, because quantum effects arise from the interplay between the atomic masses and intermolecular forces. The strength of the hydrogen bond causes a hindered rotation libration that it is quantized. Thus, quantum effects are reflected mainly in the rotational degrees of freedom.

Finally, the potential energy is systematically higher in quantum simulations than in classical simulations (see Figure 6). The results found here for the clusters are in line with those found for ices using the same model. For ices, we found that the potential energy of the classical system is lower than that of the quantum system and also that it is the rotational kinetic energy that deviates mostly from the classical value. The magnitude of the differences between classical and quantum systems found here for small clusters is similar to those found for ices (although slightly smaller). In fact, at  $T = 50$  K, the differences in  $U$ ,  $K_{\text{tra}}$  and  $K_{\text{rot}}$  between quantum and classical systems are (for  $N = 7$ ) 1.46, 0.16, and 0.88 kcal/mol, to be compared with the differences obtained for ice  $I_h$  at temperature

**TABLE 4: Average Energy Components (in kcal/mol) Per Water Molecule for Water Clusters Using the Flexible q-TIP4P/F and the Rigid TIP4PQ/2005 Models Obtained from PIMC at Temperature  $T = 50$  K<sup>a</sup>**

N	q-TIP4P/F			TIP4PQ/2005		
	$\langle K/N \rangle$	$\langle U_{\text{intra}}/N \rangle$	$\langle U_{\text{inter}}/N \rangle$	$\langle K/N \rangle$	$\langle U_{\text{intra}}/N \rangle$	$\langle U_{\text{inter}}/N \rangle$
1	6.27	6.14	0	0.29	0	0
2	6.65	6.32	-2.88	0.71	0	-3.07
3	6.90	6.58	-5.53	1.03	0	-5.65
4	7.01	6.76	-7.06	1.15	0	-7.12
5	7.02	6.79	-7.43	1.16	0	-7.49
6	7.14	6.82	-7.95	1.29	0	-8.05
7	7.16	6.85	-8.39	1.34	0	-8.44

<sup>a</sup>  $U_{\text{intra}}$  and  $U_{\text{inter}}$  are the intramolecular and intermolecular potential energy components, and  $K$  represents the kinetic energy. The errors for the flexible model (in kcal/mol) are  $O(0.04)$  in  $K$ , and  $O(0.06)$  in the  $U$  components.

$T = 77$  K: 1.66, 0.23, and 1.20 kcal/mol.<sup>25</sup> The similarity in the trends for both systems is evident.

We shall now present results for the flexible q-TIP4P/F model. In Table 4, the average energy components for the flexible q-TIP4P/F model at a temperature of 50 K are presented. Let us start with the results for the monomer. The total kinetic energy of the monomer has a contribution arising from the translation and rotation of the molecule as a whole. For a free particle, these are given by the classical value  $3/2 RT$  (exactly for the translation and approximately for the rotation), which at this temperature amounts to 0.15 kcal/mol each. Thus, the vibrational kinetic energy of the monomer is given by  $6.27 - 0.3 = 5.97$  kcal/mol. Concerning the potential energy, there is no intermolecular contribution, and the intramolecular contribution is 6.14 kcal/mol. For a harmonic oscillator in the fundamental state, the kinetic energy should be identical to the vibrational one. The difference found here just reflects the unharmonic character of the vibrations. By adding the two contributions 5.97 and 6.14 kcal/mol, we obtain 12.11 kcal/mol for the intramolecular energy of the molecule at 50 K. This value is close to the experimental zero point energy of the isolated molecule (which amounts to 12.87 kcal/mol when using the experimental values of the three fundamental vibrational frequencies of the water monomer).

As can be seen in Table 4, the intramolecular potential energy increases from 6.14 kcal/mol in the monomer to about 6.82 kcal/mol in the hexamer. This increase is due to the deformation of the water molecule in the cluster with respect to the isolated molecule, which occurs when hydrogen bonds are formed. This behavior is in line with the increase in the bond length and the decrease in the bond angle discussed previously.

In Table 4, results for the rigid TIP4PQ/2005 model are also presented and compared with the results for the flexible model. Two conclusions emerge from the comparison. The first one is that the intermolecular energies are quite similar in both models. Thus, fixing the molecular geometry does not modify much the intermolecular energy. Second, the intramolecular energy is obviously zero for the rigid model, whereas it is not zero for the flexible one. More significantly, the intramolecular energy does not change with the cluster size in the rigid model, whereas it increases with size in the flexible one.

The rigid model cannot account for the molecular deformation that occurs when clusters are formed, which provokes a larger covalent bond length,  $r_{\text{OH}}$ ; smaller bending angle; and larger intramolecular energies. The comparison of the absolute values of the kinetic energies is not so useful, since we are comparing

**TABLE 5: Formation Energies (in kcal/mol) Per Water Molecule,  $\Delta E$ , at Temperature  $T = 50$  K for the q-TIP4P/F and TIP4PQ/2005 Models As Obtained from PI Simulations<sup>a</sup>**

N	$\Delta E_{\text{q-TIP4P/F}/N}$	$\Delta E_{\text{TIP4PQ/2005}/N}$	$\Delta E_{\text{q-TIP4P/F}}^{\text{cl}}/N$
2	-2.32	-2.66 (-0.34)	-3.11 (-0.79)
3	-4.45	-4.91 (-0.46)	-5.73 (-1.28)
4	-5.70	-6.26 (-0.56)	-7.21 (-1.51)
5	-6.03	-6.62 (-0.59)	-7.56 (-1.53)
6	-6.40	-7.05 (-0.65)	-8.18 (-1.78)
7	-6.79	-7.39 (-0.60)	-8.63 (-1.84)

<sup>a</sup> Results for the q-TIP4P/F from classical simulations are also shown. For the quantum simulations with the rigid TIP4PQ/2005 model and the classical simulations with the flexible q-TIP4P/F model, the differences with respect to quantum simulations with the q-TIP4P/F model (taken as the reference) are also shown in parentheses.

systems with a different number of degrees of freedom. Instead of comparing term by term the energies of a flexible and of a rigid model, it is more useful to compare formation energies. We shall define the formation energy of a cluster of  $N$  molecules as the energy change  $\Delta E$  in the process,

$$N(\text{H}_2\text{O}) \rightarrow (\text{H}_2\text{O})_N \quad \Delta E = E((\text{H}_2\text{O})_N) - NE(\text{H}_2\text{O}) \quad (18)$$

when done at constant volume and temperature.

In Table 5, we present the formation energies for water clusters obtained using the q-TIP4P/F and the TIP4PQ/2005 models. These formation energies can be calculated easily from the numbers presented in Table 4. As can be seen, for clusters of moderate size, the formation energies of the rigid model tend to be about 0.6 kcal/mol lower than those of the flexible one. The difference does not seem to increase with the cluster size. We can analyze the contribution of the different terms to the energy of formation. Let us discuss the results for  $N = 6$ . For the q-TIP4P/F, the formation energy is -6.40 kcal/mol, 0.87 kcal/mol arising from the kinetic term (i.e.,  $7.14 - 6.27$ ), 0.68 kcal/mol from the intramolecular energy (i.e.,  $6.82 - 6.14$ ) term and -7.95 kcal/mol from the intermolecular energy (i.e.,  $-7.95 - 0$ ) contribution. For the rigid model, the formation energy is -7.05 kcal/mol, 1.0 kcal/mol arising from the kinetic term (i.e.,  $1.29 - 0.29$ ), 0 kcal/mol from the intramolecular energy, and -8.05 kcal/mol from the intermolecular energy (i.e.,  $-8.05 - 0$ ). It is obvious from these results that the kinetic contribution to the energy of formation is quite similar in the flexible and in the rigid models.

The main difference between the two models arises from the intramolecular contribution, which is null for the first and about 0.68 kcal/mol for the flexible model. Thus, formation energies of water clusters are about 0.6 kcal/mol lower in rigid models than in flexible ones, due mainly to the fact that rigid models cannot account for the molecular deformation that causes an increase in the intramolecular energy. A similar difference (of the rigid TIP4PQ/2005 model with respect to the flexible q-TIP4P/F model) is expected for the vaporization energy of the liquid. Notice that an error of about 0.6 kcal/mol in the energy of formation is an error of about 6% for sufficiently large clusters. One conclusion of the previous results is that vaporization and sublimation energies obtained from the rigid TIP4PQ/2005 should be corrected by about 0.6 kcal/mol to include in an effective way the effect of flexibility, which is not incorporated explicitly in the model.

Although the main goal of this work was to consider the differences between a rigid and a flexible water model within PI simulations, let us finish by presenting the impact of using classical statistical mechanics on the formation energies of clusters. For this purpose, we have performed classical simulations of the q-TIP4P/F model. Formation energies are presented in Table 5 and compared with those obtained with the same model using PI simulations. As can be seen, the impact of using classical statistical mechanics is to yield formation energies about 1.8 kcal/mol lower than those from quantum statistics, as compared to the error of about 0.6 kcal/mol of quantum simulations with the rigid TIP4PQ/2005 model. Thus, the energy of formation is strongly affected by nuclear quantum effects, and one wonders whether classical simulations should be used at all to estimate this property, especially when the true PES of water is used in the calculations. Notice, however, that a flexible model (treated with classical statistical mechanics) could yield smaller errors for the formation energies of clusters, provided that the potential parameters were determined to reproduce this property (so that some quantum effects are incorporated effectively through the values of the parameters of the potential).

#### IV. Conclusions

In this work we have performed PI simulations of the rigid TIP4PQ/2005 and the flexible q-TIP4P/F water models. The global minimum energy configurations for clusters with up to 20 molecules were also obtained for these two models. The main conclusions are the following:

The global minima of TIP4PQ/2005 and q-TIP4P/F water clusters are quite similar to those of the TIP4P model.

When clusters form, the bond angle  $\Phi_{\text{HOH}}$  reduces significantly. There is also an increase in the OH bond length with respect to that of the gas. This lengthening of the OH bond length increases with the cluster size. The bond length is affected by isotopic substitution so that it is about 0.005 Å lower for tritiated water than for water clusters.

For the rigid water model, the deviation between classical simulations and PI simulations of clusters is similar to those found for ices. The main contribution to quantum effects arises from the hindered rotation of the molecules (libration) when forming hydrogen bonds.

The formation energies of water clusters for the rigid model are about 0.6 kcal/mol lower than those for the flexible one. This is due to the fact that the rigid model cannot account for the geometrical distortion of the water molecule that occurs when forming hydrogen bonds. However, the difference seems to be constant and could be corrected, although in an ad hoc way.

For flexible models, using classical statistical mechanics to obtain formation energies of clusters yields an error of about 1.8 kcal/mol when compared to the quantum results of the same potential model. This is the magnitude of the error that one would expect for the formation energy of clusters, when combining the true potential energy surface of water and classical statistical mechanics.

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**Supporting Information Available:** Energies and geometries of the clusters at the minima for TIP4P, TIP4PQ/2005, and q-TIP4P/F. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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