Energy landscapes for water clusters in a uniform electric field

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(Received 29 June 2006; accepted 5 December 2006; published online 5 February 2007)

The behavior of small water clusters, \((\text{H}_2\text{O})_n\), \(n=2-5\) and \(n=8\), in a uniform electric field is investigated for three related rigid-body models. Changes in the properties of the low-lying potential energy minima and the rearrangement pathways between them are examined. Results for certain structural transitions are compared with recent \textit{ab initio} calculations. The models are found to give qualitatively similar trends, and there is some evidence that as the applied field strength is increased the quantitative differences between the models are also reduced. © 2007 American Institute of Physics. [DOI: 10.1063/1.2429659]

I. INTRODUCTION

The influence of external electric fields on aqueous media is important in many areas of chemical and biophysical interest. In particular, the structure of water near electrode surfaces is of fundamental importance in our understanding of electrochemical processes. For example, considerable electrostriction in the first layer of water on a charged Ag (111) surface has been observed in x-ray studies.\(^1\) In a biochemical context, voltage gating is thought to be important in controlling the transport of ions through hydrophobic pores.\(^2,3\) The application of an electric field is known to affect the growth of ice filaments,\(^4\) and this observation may have meteorological significance in the study of cloud electrification during thunder storms. The freezing point of water on amino acid crystals is observed in most cases to differ for the racemic and optically resolved materials.\(^5,6\) This phenomenon has been attributed to electric field promoted nucleation of ice crystallites in cracks on the crystal surface for those structures with a polar axis.\(^6,7\) Ferroelectric ice is a proton-ordered phase which recent experiments suggest can be produced in thin films under laboratory conditions.\(^8-10\) The electric field generated by such a structure may be important in, for example, the agglomeration of interstellar ice particles.\(^7\)

There have been numerous simulation studies of water under the influence of a uniform electric field. Svischev and Kusalik\(^11\) found that an applied field of 0.5 V Å\(^{-1}\) was sufficient to induce formation of a polar form of ice from supercooled water at 250 K. This structure was not mechanically stable in the absence of the field but could be made so by further reducing the temperature to 200 K. Kiselev and Heinzinger\(^12\) modeled a bulk electrolyte solution at 300 K. These authors found that field strengths of up to 2 V Å\(^{-1}\) were insufficient to induce crystallization at this temperature, and although the field did enhance the water structure, no anisotropy in the self-diffusion coefficient was detected. Sutmann\(^13\) employed a flexible model at 300 K and, despite issues with the box size, observed that above a threshold field strength of 2.5–4 V Å\(^{-1}\) a complete transition to a polar, crystal-like structure with two-layer periodicity could be achieved. Jung \textit{et al.}\(^14\) found that the threshold for induced structural change at 243 K lies in the region 0.15–0.2 V Å\(^{-1}\).

These authors found that above this field strength a water structure analogous to cubic ice could be formed, but that even at 0.5 V Å\(^{-1}\) the diffusion constants were too high to be characteristic of the solid. Simulations have also been performed on bulk water between parallel plates, with electric fields both parallel\(^15\) and perpendicular\(^16\) to the surfaces. Such studies may be at least partly motivated by the observation that, unlike organic solvents, simply confining water to very thin films in the subnanometer range does not lead to a divergence of the viscosity.\(^17\) Provided the plate separation is commensurate with the structure,\(^15\) crystallization is relatively easy to achieve during simulations under such conditions. This contrasts with the difficulty of simulating the freezing transition in pure bulk water systems.\(^18\)

There have been fewer calculations on the properties of water clusters under the influence of electric fields. In the absence of an applied field, molecules in liquid water tend to align so as to increase the total dipole moment, whereas in clusters they exhibit the opposite behavior.\(^19,20\) This difference arises because of the difference in boundary conditions for the two types of system. Cluster properties are dominated by the existence of the free surface, and one would therefore expect to observe different behavior from the bulk. For example, Vegiri and Schevkanov\(^21\) observed partial formation of square nanotube structures, not seen in the bulk, in \((\text{H}_2\text{O})_{32}\) at intermediate field strengths of 0.15–0.275 V Å\(^{-1}\). Higher fields (\(\geq 0.6\) V Å\(^{-1}\)) were found, however, to lead to a formation of a quasicrystalline phase analogous to cubic ice. The same authors in a different study\(^22\) observed that for \((\text{H}_2\text{O})_{40}\) at field strengths in the range of 0.07–0.7 V Å\(^{-1}\) the cluster polarization was found to increase with temperature. As a consequence of this increase the field strength required to cause a transition to a saturated polarization state was found to decrease with temperature, a result that was attributed to the presence of nonequilibrium states in the simula-
tions. Investigations of smaller cluster sizes have also been reported, but these have focused in detail on a limited number of structures in each case.

In the present contribution we have attempted to make a systematic assessment of the effect of a constant, uniform electric field on the potential energy landscapes of the water trimer through pentamer, plus the low energy regions for the octamer. The model we have employed is the rigid, nonpolarizable TIPnP family of effective pair potentials developed by Jorgensen and co-workers. We compare results for three members of this family, namely, TIP3P, TIP4P, and TIP5P. The importance of various improvements to this type of description has been much discussed, including flexibility, polarizability, and quantum corrections. Despite the development of models that are both polarizable and flexible, these have yet to see widespread application. This may be partly because such potentials are computationally more demanding than their less sophisticated predecessors, but there are also acknowledged difficulties with the definition of molecular multipole moments within a condensed phase environment. Nonlinear polarization responses at high applied fields have also been reported to be problematic for model potentials. For these reasons, we have chosen to use the TIPnP models to investigate the most basic type of response to an applied field, namely, reorientation of fixed charge distributions under the constraint of a hydrogen-bonding network.

II. METHODS

The TIPnP models represent water through a Lennard-Jones (LJ) site on the oxygen atom, plus various partial charge sites, and they share a common monomer geometry. The interaction between two monomers, \(a\) and \(b\), is thus of the form

\[ U_{ab} = \sum_{ij} \frac{q_i q_j e^{2}}{4\pi\epsilon_0 r_{ij}} + 4\epsilon \left[ \left( \frac{\sigma}{r_{OO}} \right)^{12} - \left( \frac{\sigma}{r_{OO}} \right)^{6} \right], \]

where \(q_i\) and \(q_j\) are the partial charges on site \(i\) of monomer \(a\) and site \(j\) of monomer \(b\), respectively, \(r_{ij}\) is the Cartesian separation of the two sites, and \(r_{OO}\) is the distance between the two oxygens. The positive partial charge sites always lie on the hydrogen atoms. The qualitative difference between the models lies in the location of the negative partial charge site(s). For TIP3P, the negative charge lies on the oxygen atom. For TIP4P, it is shifted away from the oxygen along the vector bisecting the two hydrogen atoms. For TIP5P, there are two negative partial charge sites positioned to mimic the lone pairs on the oxygen atom. The specific parameters for each model are given in Ref. 26. We are principally interested in the qualitative differences in the responses of the three models to an applied electric field; hence we choose to retain the original parametrization of the TIP5P model rather than the subsequent reparametrization.

We apply a uniform electric field to the systems in the \(z\) direction. The appropriate expression for the total potential energy within a consistent approximation is then

\[ U_{total} = \sum_{a<b} U_{ab} - E \sum_{i} q_i z_i, \]

where \(E\) is the field strength and \(z_i\) is the \(z\) Cartesian coordinate of partial charge \(i\).

We have used angle-axis coordinates to represent the rigid-body orientational degrees of freedom. The advantage of this coordinate system compared with Euler angles is that it does not suffer from the problems associated with reduced dimensionality due to rotational axes becoming equivalent.

A. Integrating the steepest-descent paths

Stationary points are identical in all coordinate systems that are related by true transformations (ones that are both integrable and invertible). Hence, for the purposes of locating such points we may retain our standard tools, which are LBFGS (Refs. 47 and 48) for energy minimization and eigenvector-following for optimizing transition states (TSs). However, in a Riemannian space such as that defined by the angle-axis coordinate system, we are required to consider the metric tensor when calculating second derivatives and normal modes and when following steepest-descent paths.

We have integrated the generalized form of the steepest-descent equation using an appropriately modified version of a fifth order Runge-Kutta scheme with adaptive step size control. While there are certainly more sophisticated methods of integrating ordinary differential equations, we have found the performance of the Runge-Kutta algorithm to be generally acceptable in terms of the required magnitude of the step away from the TS and the root-mean-square force achievable at the end points. However, we did find that for some paths with particularly low curvature our integration was rather inefficient. Such paths typically occurred at low field strengths and possessed large degrees of overall rotational character. In certain cases, we were forced to use energy minimization as an approximation to steepest-descent path integration.

We have analyzed our paths in terms of the integrated path length \(S\), the distance between the end points, \(D\) and the moment displacement ratio \(\gamma\) (or the related property \(N=N/\gamma\), where \(N\) is the number of atoms). We calculate the first of these properties using the covariant arc length, while the latter two were calculated using the Cartesian coordinates of the end points.

We are further encouraged in our use of the Runge-Kutta method by its ability to locate steepest-descent paths with valley-ridge inflection, or branch, points. Typically such paths form a small minority of the total population for any given system and show no particular trends with field strength. We have visually assessed all of the steepest-descent paths that terminate at stationary points of index 1 and confirmed the presence of conserved symmetry elements. The majority of cases involve conservation of a mirror plane, with a smaller number showing a conserved \(C_2\) rotation axis. We also observed a very small number of paths...
that terminated at stationary points of index 2. These we have excluded from our analysis for the present time. For the purposes of this report, we have expanded our definition of a fundamental rearrangement step to be any stationary point-TS-stationary point triplet connected by steepest-descent paths.

**B. Locating global minima**

We have used the basin-hopping method\textsuperscript{59,60} to locate global minimum structures. For system sizes up to the pentamer, a single run with fixed step size was considered sufficient for reliable determination of the lowest energy structure. Searches were performed at applied field strengths of \(0.0001\), \(0.01\) and \(0.1–1\) V Å\(^{-1}\) in 0.1 V Å\(^{-1}\) intervals and 10 V Å\(^{-1}\). For the octamer we omitted the search at the lowest field strength because the results for the smaller systems were not topologically different from those at 0.01 V Å\(^{-1}\). Otherwise, multiple runs were performed from different starting structures at each field strength, in the manner described in Ref. \textsuperscript{61}. We used variable step sizes and separated the translational and angular degrees of freedom into blocks of moves, which was previously found to be effective for molecular clusters.\textsuperscript{62} The only system for which we experienced significant difficulty was TIP4P \((\text{H}_2\text{O})_8\) at 0.5 V Å\(^{-1}\),

<table>
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<th>(H\textsubscript{2}O\textsubscript{4})</th>
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**TABLE I.** Disconnectivity graphs for three sizes of water cluster, as described by the TIP5P potential, subject to uniform electric field strengths of 0.0, 0.1, 1 and 10 V/Å (top to bottom). The scale bars indicate an energy range of 10 kJ mol\(^{-1}\) for (H\textsubscript{2}O\textsubscript{5}), and of 5 kJ mol\(^{-1}\) otherwise.
TABLE II. Landscape statistics for water clusters of various sizes, as described by the TIP5P potential, under the action of uniform electric fields of strength $E$ (V Å\(^{-1}\)), \(n_{\text{im}}\), and \(n_{\text{TS}}\) are the numbers of minima and TS in the database, respectively. \(U_{\text{range}}\) is the energy range spanned by the minima. \(U_{\text{gap}}\) is the energy gap between the two lowest minima. \(\langle \mu \rangle\) is the average geometric mean normal mode frequency for the minima. \(\langle |\mu| \rangle\) is the average imaginary normal mode frequency for the transition states. \(\langle E_{\text{up}} \rangle\) is the average dipole moment per molecule for the minima, in units of the monomer dipole. \(b_{\text{up}}\) and \(b_{\text{down}}\) are the average uphill and downhill barriers for elementary rearrangements, respectively, and \(\langle \Delta U \rangle = (b_{\text{up}}) - (b_{\text{down}})\). \(S\), \(D\), and \(\tilde{N}\) are described in the text. All energies are in kJ mol\(^{-1}\), frequencies in cm\(^{-1}\), and distances in Å.

| System | \(E\) | \(n_{\text{im}}\) | \(n_{\text{TS}}\) | \(U_{\text{range}}\) | \(U_{\text{gap}}\) | \(\langle \mu \rangle\) | \(\langle |\mu| \rangle\) | \(\langle b_{\text{up}} \rangle\) | \(\langle b_{\text{down}} \rangle\) | \(\langle \Delta U \rangle\) | \(S\) | \(D\) | \(\tilde{N}\) |
|--------|-------|---------------|---------------|----------------|-------------|---------------|---------------|----------------|----------------|----------------|-------|-------|-------|
| \((\text{H}_2\text{O})_3\) | 0.0   | 6             | 16            | 12.8           | 1.8          | 272           | 134           | 0.37           | 6.9            | 3.7            | 3.2   | 5.5   | 2.3   | 3.6   |
|       | 0.1   | 4             | 18            | 5.0            | 3.0          | 187           | 96            | 0.54           | 4.8            | 4.0            | 0.8   | 11.1  | 4.7   | 5.3   |
|       | 1     | 3             | 9             | 11.2           | 10.0         | 232           | 66            | 1.00           | 7.7            | 4.1            | 3.6   | 8.7   | 4.5   | 5.1   |
|       | 10    | 6             | 12            | 10.9           | 1.2          | 323           | 84            | 1.00           | 6.4            | 4.5            | 1.9   | 6.0   | 3.4   | 4.5   |
| \((\text{H}_2\text{O})_4\) | 0.0   | 15            | 107           | 38.3           | 5.0          | 287           | 124           | 0.41           | 23.0           | 14.4           | 8.6   | 14.5  | 3.9   | 5.7   |
|       | 0.1   | 18            | 133           | 27.4           | 1.5          | 202           | 111           | 0.57           | 13.3           | 7.3            | 6.0   | 16.5  | 6.1   | 7.0   |
|       | 1     | 7             | 35            | 23.6           | 0.3          | 215           | 52            | 0.99           | 10.6           | 6.2            | 4.4   | 10.7  | 5.1   | 6.3   |
|       | 10    | 16            | 45            | 22.9           | 1.3          | 302           | 55            | 1.00           | 7.6            | 3.9            | 3.7   | 8.1   | 4.5   | 6.3   |
| \((\text{H}_2\text{O})_5\) | 0.0   | 89            | 707           | 54.9           | 6.86         | 256           | 104           | 0.35           | 22.0           | 10.3           | 11.7  | 15.3  | 5.3   | 7.0   |
|       | 0.1   | 136           | 1159          | 42.9           | 3.91         | 199           | 104           | 0.56           | 14.6           | 6.7            | 8.0   | 20.7  | 7.2   | 8.2   |
|       | 1     | 34            | 204           | 57.0           | 0.81         | 222           | 60            | 0.95           | 19.6           | 9.1            | 10.5  | 14.6  | 6.3   | 7.4   |
|       | 10    | 41            | 181           | 38.3           | 0.03         | 295           | 50            | 1.00           | 12.2           | 6.2            | 6.0   | 11.5  | 5.5   | 7.2   |
| \((\text{H}_2\text{O})_6\) | 0.0   | 4981          | 13 036        | 75.7           | 1.86         | 290           | 128           | 0.24           | 16.4           | 8.2            | 8.3   | 10.0  | 4.5   | 6.9   |
|       | 0.1   | 5000          | 12 141        | 64.1           | 2.00         | 246           | 131           | 0.35           | 15.0           | 7.6            | 7.3   | 18.3  | 7.8   | 13.3  |
|       | 1     | 1423          | 11 500        | 79.6           | 0.53         | 222           | 55            | 0.97           | 19.4           | 8.9            | 10.5  | 17.4  | 7.0   | 9.7   |
|       | 10    | 950           | 7 268         | 77.4           | 0.29         | 290           | 42            | 1.00           | 18.6           | 7.9            | 10.6  | 17.2  | 7.3   | 9.8   |

where even runs of \(2 \times 10^5\) basin-hopping steps only located the lowest energy structure in 6/10 cases. Further examination of the potential energy landscape under these conditions revealed that it has a triple funnel\(^{57}\) motif in which a large majority of the low energy structures are associated with the funnel containing the second-lowest minimum. We have examined the thermodynamics of this system in more detail in a separate investigation.\(^{63}\)

C. Generating disconnectivity graphs

Disconnectivity graphs\(^{64}\) are a useful way of visualizing potential energy landscapes. However, to calculate them is computationally intensive, and so we have limited ourselves to a subset (0.0, 0.1, 1, and 10 V Å\(^{-1}\)) of the field strengths that were probed in terms of global minima. We have generated our databases of stationary points using the methods outlined in Ref. \(^{65}\). In particular, we used eigenvector-following\(^{49,50}\) to locate transition states. Energy minimization with LBFGS was used to generate initial approximate paths, which were later refined using the methods described in Sec. II B.

For system sizes up to the pentamer, we continued to expand the stationary point database until no new stationary points were encountered. For the octamer such exhaustive sampling was not practical, and we have chosen to focus our attention on the low energy regions of the landscapes. To facilitate this study, we have monitored the ratio of the number of TSs to the number of minima in our databases. This value rises as a function of the number of TSs located, indicating that the algorithm gradually spends less time finding new minima and more time making extra connections between existing structures. For complete samples, in the independent subsystem limit, the ratio is expected to scale linearly with system size,\(^{66,67}\) and even for small clusters this prediction holds quite well.\(^{66}\) Extrapolating our results from smaller cluster sizes suggests that most of our octamer landscapes are considerably undersampled, particularly those at the lower field strengths. However, we have additionally compared the minima in our database to those generated during our global optimization runs. As we employ a stochastic global optimization algorithm we usually succeed in locating many alternative low energy structures, and we use these to judge how well we have explored the lower regions of the landscape during disconnectivity graph generation. In all cases our databases contain at least the lowest 180 minima recorded during the global optimization searches, corresponding to an energy range of at least 15 kJ mol\(^{-1}\) above the putative global minima. We are therefore satisfied that our graphs provide a reasonable representation of the low energy minima for each landscape, although the connections between them, especially those involving large barriers, are probably less complete.

III. RESULTS

We present results for the water dimer through pentamer and for the octamer. Disconnectivity graphs for the largest three systems at various applied field strengths are shown for the TIP5P potential in Table I. We have omitted the trimer graphs for brevity, as they do not show any extra features beyond those exhibited by the larger cluster sizes. Selected landscape statistics, also for the TIP5P potential, are given in Table II. Properties or trends that vary significantly amongst the different model potentials are noted in the text; otherwise the results for the TIP3P and TIP4P potentials are qualitatively similar to those for TIP5P. Full details are available in the supplementary material.\(^{53}\)
A. Water dimer

We begin our investigation with an assessment of the behavior of the water dimer in an applied electric field. Although computationally trivial, these systems provide us with a great deal of information about the models due to their strictly pairwise formulation. The monomer dipole moments for the three models are given in Table III. In order to facilitate comparisons between the models, all dipole moments will be reported in units of the corresponding monomer value.

The behavior of the TIP3P and TIP4P dimers is qualitatively similar. For each system there is a single minimum with \( C_s \) symmetry at all field strengths up to 1000 V Å\(^{-1}\). With increasing field strength, the hydrogen bond becomes increasingly nonlinear as the monomer dipoles become aligned (Fig. 1). There is also a small accompanying increase in the separation of the oxygen atoms. At zero field strength the TIP4P dimer dipole is significantly lower than the corresponding TIP3P value. However, dipolar saturation in both systems occurs in approximately the same range (0.1–1 V Å\(^{-1}\)), indicating that the TIP4P system has the greater average polarizability prior to saturation.

At zero field strength the clusters have six normal modes with zero frequency, corresponding to overall translations and rotations of the system. For finite electric fields two of the (initially) rotational modes acquire nonzero frequencies. In general, the frequencies of the nonzero normal modes increase with increasing field strength (Fig. 2). There are two contributions to this effect, namely, changes in the intermolecular interactions and the dipole variations along each normal mode coordinate. In many cases the dipole decreases as the system moves away from the equilibrium structure, and this makes a significant contribution to the increase in curvature. The exception is the mode with the greatest hydrogen-bond stretching character, which shows a small decrease in frequency above approximately 0.2 V Å\(^{-1}\). This effect is largely determined by changes in the geometry of the minimum energy structure, because the system dipole is essentially constant along this mode.

As the applied field increases and the system tends towards dipolar saturation (and constant structure for the potential energy minimum), there are two limiting possibilities. Firstly, the dipole can decrease along the normal mode coordinate, resulting in a monotonically increasing frequency. This increase occurs for the four highest frequency modes. Secondly, the dipole can remain constant along the normal mode coordinate, resulting in a field-independent frequency. This behavior occurs for the remainder of the normal modes in each case. The limiting frequencies are 56, 124, 202, and 343 cm\(^{-1}\) (64, 155, 209, and 422 cm\(^{-1}\)) for TIP3P (TIP4P).

We also observe that at high field strengths the motion in many of the modes is localized in one of the molecules, whereas lower field modes tend to involve movement of both monomers. The exceptions are the lowest frequency mode, which is largely rotational in character, and the hydrogen-bond stretching mode. There, the motion is almost equally

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<th>( \sigma ) (Å)</th>
<th>( q_H ) (e)</th>
<th>( \mu ) (D)</th>
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</tr>
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<td>TIP5P</td>
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**FIG. 1.** Geometric parameters of the TIPnP (H\(_2\)O\(_2\)) minima as a function of the applied electric field.
divided between the two bodies at high field strengths (as measured by the magnitudes of the displacement vectors).

The TIP5P potential shows behavior that is somewhat different. For this model there are three distinct minima that exist over different ranges of field strength. At zero field there is a single minimum with $C_{s}$ symmetry [min 1 in Fig. 3(a)]. This structure shows qualitatively similar variation in its geometric properties to the TIP3P and TIP4P minima at low field strengths. However, at approximately 0.422 V Å$^{-1}$, a fold catastrophe$^{68,69}$ occurs, resulting in a non-Morse point$^{68,69}$ where this minimum coalesces with a TS structure, and the system possesses an additional zero Hessian eigenvalue. Hence, at higher field strengths, this structure is no longer a stationary point. Another non-Morse point was located for this potential near 0.171 V Å$^{-1}$, this time corresponding to a cusp catastrophe$^{68,69}$ in which a transition state changes Hessian index to become a second $C_{s}$ minimum [min 2 in Fig. 3(a)]. This minimum is initially higher in energy than the first but becomes the global minimum above approximately 0.28 V Å$^{-1}$. It is stable up to at least 1000 V Å$^{-1}$, with only small changes in geometry occurring even at very high field strengths. The third minimum has $C_{2v}$ symmetry [min 3 in Fig. 3(b)]. This structure is a TS for the TIP3P and TIP4P potentials at all field strengths considered in this work, as it is for the TIP5P potential up to approximately 1.622 V Å$^{-1}$. At this point a second cusp catastrophe occurs, and the TS becomes a minimum. The geometry of

![Fig. 2](image1.png)

**Fig. 2.** Normal mode frequencies for the water dimer minimum as a function of applied field. Modes with $A'$ symmetry are shown with solid lines, and those with $A''$ symmetry are shown with dashed lines. The modes with visually the most hydrogen-bond stretching character at each field strength are identified with crosses. The greatest magnitude for a "zero" frequency is in all cases less than 0.07 cm$^{-1}$. The two modes with frequencies that tend to zero in zero field are both pure rotational modes in that limit.

![Fig. 3](image2.png)

**Fig. 3.** Evolution of (a) fold and (b) cusp catastrophes for the TIP5P water dimer as a function of applied field strength. The lines are labeled with the corresponding values of $E$ in V Å$^{-1}$. The structures depicted are those at (a) 0.3 V Å$^{-1}$ and (b) 1.4 V Å$^{-1}$.
this structure does not change at all with applied field. As a minimum, it is always higher in energy than the $C_s$ structure by approximately 1.3 kJ mol$^{-1}$.

The behavior of the normal mode frequencies for the first TIP5P minimum is qualitatively different from that for the TIP3P and TIP4P cases. Five of the modes show an overall decrease in frequency on increasing the field from zero to the strength at which the minimum disappears, although the variation is nonmonotonic in two of those instances (Fig. 4). A quadratic polynomial cannot describe a fold catastrophe, and the lowest frequency is therefore discontinuous at the non-Morse point. The relatively rapid change in the geometric properties of this minimum as a function of field strength means that the changes in intermolecular interaction make a large contribution to the frequency variation. Additionally, above zero field the hydrogen-bond stretching character is increasingly shared between the two intermediate frequency modes of $A'$ symmetry, rather than remaining localized to a single mode.

As a result of their constant, or near-constant, geometries, the behavior of the normal modes for the other TIP5P minima is relatively simple. All of the frequencies either increase monotonically with field strength or are independent of the field (Fig. 5). This behavior is qualitatively similar to the high field variation of the TIP3P and TIP4P frequencies, for the same reasons. Again, at high field strengths, the four lowest modes reach constant frequencies in each case. These frequencies are 60, 212, 230, and 402 cm$^{-1}$ for the $C_s$ structure, and 13, 66, 172, and 181 cm$^{-1}$ for the $C_{2v}$ structure. The particularly low frequency mode in the latter case involves a sliding motion in which the two bodies move in the plane perpendicular to the system dipole, translating in directions perpendicular to the oxygen-oxygen vector.

B. Water trimer

For the water trimer there are essentially three different global minimum topologies that are observed with changing field strength. Representative structures for each are shown in Fig. 6. Previous studies employing a model polarizable potential$^{23}$ and density functional theory (DFT) at the B3LYP/6-311+ +G** level$^{24}$ have suggested that the global
minimum progresses from an up-up-down (UDU, referring to the orientations of the non-hydrogen-bonding hydrogen atoms relative to the plane of the ring\(^\text{23}\)) ring to an up-up-up (UUU) ring and finally to a chain as the field strength is increased. The field strengths at which the changes between different morphologies being lowest in energy are reported to take place are given in Table IV. A comparison with the model potentials considered here is complicated by the fact that only TIP4P shows the same progression of global minimum structures. For TIP4P we find that the transition field strengths are slightly lower than those reported for the more sophisticated calculations, which we would attribute to the high static dipole moment of the fixed point-charge model. For TIP3P the zero field global minimum is planar (C\(_{3v}\)), and any finite field produces a distortion to a UUU ring. The subsequent transition to a chain global minimum occurs at a lower field strength than for TIP4P, probably due to the larger TIP3P dipole moment. The three-membered ring is particularly strained for the TIP5P potential, as shown, for example, by the small energy gap to the second-lowest structure (a chain) at zero field. Hence, although the energetic ordering of the two homodromic ring structures changes at approximately 0.10 V Å\(^{-1}\), chain structures are the global minimum above 0.05 V Å\(^{-1}\). The TIP5P value in Table IV is shown in italics to indicate this.

Given the small number of stationary points and the large fraction of degenerate rearrangements (between permutation-inversion isomers of the same structure\(^\text{20}\)), it is difficult to draw any meaningful conclusions from the landscape statistics for the trimers. Hence, we restrict ourselves to commenting on trends that we see reproduced at larger system sizes. The most straightforward of these trends is the onset of dipolar saturation in the local minima with increasing field strength. If we (somewhat arbitrarily) choose to define dipolar saturation as having occurred when the dipole moment exceeds 0.95 monomer units per molecule, we find that dipolar saturation of the global minimum structures occurs in the range of 0.2–0.4 V Å\(^{-1}\) for all three models and between 0.1 and 1 V Å\(^{-1}\) for the average of all the minima. Secondly, the average mean geometric normal mode frequency for the minima, \(<\nu>\), decreases as the field strength increases from 0 to 0.1 V Å\(^{-1}\) but increases thereafter. This result can be understood from our analysis of the dimer, where we see that upon application of an electric field, two modes that are initially purely rotational in character acquire nonzero frequencies. These frequencies are initially close to zero but increase with applied field strength, as, on average, do the frequencies for the other normal modes. The increasingly positive curvature with field strength is also responsible for the general decrease in magnitude of the imaginary frequencies for the TS, \(\langle |\nu|\rangle\).

In common with larger system sizes, the low energy region of the TIP5P trimer landscape at an applied field strength of 10 V Å\(^{-1}\) is complicated by the stability of the bifurcated hydrogen-bonding arrangement shown for the dimer. This additional minimum gives rise to different chain morphologies not available to the other two models.

### C. Water tetramer

Choi et al.\(^\text{24}\) have previously characterized the field strengths at which the non-hydrogen-bonding hydrogen atoms for the homodromic tetracycle become aligned along the field direction and at which chain structures become lower in energy than this ring. We find that the model potentials again give transition field strengths lower than those predicted by the DFT calculations and that the field strength at which chain structures become lower in energy than the homodromic ring decreases with increasing static dipole moment. However, the variation in the TIP global minima cannot be described in terms of these two structural transitions alone, as shown in Table V. In particular, both TIP4P and TIP5P show a nonhomodromic tetracycle over certain ranges of field strength, and for TIP4P chain structures remain at least 1 kJ mol\(^{-1}\) higher in energy than this alternative ring minimum at all field strengths examined here.

From Table II it can be seen that the variation of the minimum dipole moments and geometric mean frequencies for the tetramer is qualitatively similar to that observed for the trimer. We also see that at a TS the magnitude of the curvature along the normal mode with imaginary frequency generally decreases with increasing field strength. The range of energies spanned by the minima, the value of \(<\Delta U>\), and the gap between the global minimum and the next lowest structure also show a consistent reduction with field strength. However, we do not find these trends to be so well reproduced at larger system sizes, so we do not attach too much significance to them. We note that the number of distinct minima and the number of distinct TSs show maxima at 0.1 V Å\(^{-1}\) for all three models. We suggest the following explanation for this observation. At low field strengths the allowed stationary point structures are determined largely by the intermolecular interactions. At high field strengths they are determined mainly by the interactions with the field. At some intermediate field strength there will be a balance be-

![FIG. 6. Representative structures for the different (H\(_2\)O\(_3\)) global minimum topologies found as a function of applied field strength.](image)
between the two types of forces, giving greater scope for structural variation. Below the thermodynamic limit the average intermolecular interaction varies with system size; hence we would also expect this balance point to vary. However, we would not expect to detect this variation with such a limited sample of applied field strengths.

For the tetramer we only located paths involving branch points for the TIP5P potential and then only as a minority of the total population. From the disconnectivity graphs we observe that the TIP5P model again typically exhibits more local minima in close energetic proximity to the global minimum than the other two models. At low field strength, this occurs because homodromic tetracycles with different arrangements of the dangling hydrogen atoms relative to the ring plane are close in energy for TIP5P. At high field strength, bifurcated chains are responsible.

D. Water pentamer

For the water pentamer none of the potentials give a planar global minimum structure at zero field (see Table VI). With the TIP3P and TIP4P models at low field strength the structures are oriented such that their ring planes approximately contain the field vector. At intermediate field strengths the parallel TIP3P orientation is replaced by one perpendicular to the field, which briefly attains a high symmetry $C_3$ configuration before being supplanted by a chair structure. Unlike the high field structures observed for (H$_2$O)$_4$, these chains do not really show helical character. Instead, the global minima at high field strengths are based on a $C_1$ ring geometry with a single dangling molecule. The TIP4P model is unique in that it gives bridged-ring structures as the global minima at intermediate field strengths. The other two models do support such structures as relatively low energy minima but never as the global minimum. In contrast, the TIP4P potential does not seem to give chain structures as the global minima at any field strength, passing straight from the bridged rings to the $C_1$ structure previously described for TIP3P. For TIP5P, the low field ring structures remain approximately perpendicular to the field vector. The $C_1$ ring structure becomes the global minimum for this potential at roughly the same field strength as for the TIP4P potential. However, at very high field strengths chain structures are observed to be lowest in energy. Unlike the intermediate-field TIP3P minima, these chains do show helical character.

Characterization of the field strengths required to cause the specific topological changes previously discussed for the trimer and tetramer has also been carried out for the pentamer. Our analysis of the corresponding values for the model potentials considered here is complicated by the existence of structural isomers that were apparently not considered in Ref. 24. We find, however, that some of the transition field strengths predicted by the model potentials are now larger than those calculated using the electronic structure method. Most notably, a field strength of approximately 0.37 V Å$^{-1}$ is required to cause the non-hydrogen-bonding hydrogen atoms to align along the field vector in the TIP5P homodromic pentacyle, as compared to a DFT value of 0.2 V Å$^{-1}$. We believe that the relatively close proximity of the lone-pair charge sites is what disfavors the aligned ring structure for this potential.
By measuring the ratio of the highest and lowest principal moments of inertia, we can examine how the shapes of the minima change. We find that typically this ratio increases with field strength, indicating that as the dipoles are aligned along the external field, extended planar or linear structures become favored over more compact arrangements, due to the hydrogen-bonding restrictions. In terms of fundamental rearrangement steps, the average barrier heights are greatest at zero field for all three models (Table II). The integrated path lengths show maxima at \( E=0.1 \ \text{V} \ \text{Å}^{-1} \), which can be understood in terms of the shallow curvatures introduced along the low frequency normal modes at each minimum. The values of \( S \) are largest in magnitude for TIP5P, but the differences between the models are again reduced at high field strength. The trends in \( (D) \) with field strength are similar, although the difference between the models is not very large.

The disconnectivity graphs for this system are characterized by an increased level of branching at low energies with increasing field strength. These regions become less “palm-tree-like” and more “banyan-tree-like” as the field strength increases. At high field strengths there are three competing morphologies for each potential. Two of these are based on the nonhomodromic four-membered ring depicted in Table IV, and the third is a linear chain. The chain structures are usually the most numerous, especially for the TIP5P potential where the bifurcated arrangements are also local minima. Rearrangements between minima with different morphologies typically involve greater disruption of the hydrogen-bonding network than rearrangements between minima with the same morphology, and therefore the former have higher potential energy barriers. This gives the landscape a hierarchical pattern. This trend is also visible to a lesser extent in the disconnectivity graphs for the tetramer system, except that there are only two competing morphologies (ring and chain) at high field.

### E. Water octamer

The water octamer is of particular interest because, in the absence of an applied field, there are two competing cubic morphologies at low energy. For the TIP3P and TIP5P models the \( D_{2d} \) structure is lower by \( 1-2 \ \text{kJ} \ \text{mol}^{-1} \), whereas for TIP4P the \( S_4 \) structure is favored but only by \( 0.11 \ \text{kJ} \ \text{mol}^{-1} \). At field strengths up to \( 0.1 \ \text{V} \ \text{Å}^{-1} \) distorted versions of these structures remain the lowest two minima. The distortions do not, however, occur in the same way for the different model potentials. For TIP3P and TIP4P the \( D_{2d} \) minimum distorts along one of the two equivalent rotation axes to give a \( C_2 \) structure, whereas for TIP5P the distortion occurs along the unique rotation axis to give a \( C_{2v} \) minimum. Conversely, for TIP4P the \( S_4 \) structure distorts along the rotation axis to give a \( C_2 \) minimum, whereas with TIP3P and TIP5P the distortion occurs along a perpendicular axis, resulting in a structure with \( C_1 \) symmetry. These changes are illustrated in Table VII. For TIP3P and TIP4P the energy gap between the two morphologies decreases slightly with field strength, but for TIP5P it increases. This difference occurs primarily because for TIP5P the dipole moment of the lower energy minimum increases faster with field strength, whereas for the other two models the opposite is true.

In the range \( 0.1-0.2 \ \text{V} \ \text{Å}^{-1} \) there occur significant changes in the ordering of the lowest energy configurations. At \( 0.2 \ \text{V} \ \text{Å}^{-1} \), the structures derived from the zero field global minima lie at least \( 12 \ \text{kJ} \ \text{mol}^{-1} \) above the new global minimum, which for all three models is the same cubic arrangement in which the dangling hydrogen atoms are no longer maximally separated. In this structure the system dipole is directed along a body diagonal of the cube. For the TIP4P and TIP5P models alternative cubic structures in which all four dangling hydrogen atoms share a single face are the most stable at \( 0.3 \ \text{V} \ \text{Å}^{-1} \). Unlike the TIP3P model, these potentials also have irregular polyhedral global minima at intermediate field strengths. At high field strengths the dominant global minimum topology is an extended structure with two approximately perpendicular rings, very similar to the high field pentamer structures. The only exception occurs for TIP5P at \( 10 \ \text{V} \ \text{Å}^{-1} \), where the lowest energy configuration is a netlike structure qualitatively similar to arrangements that have previously been observed at high field strengths for the 32-molecule cluster. Chain structures are no longer competitive at this system size for any of the potentials, lying at least \( 7 \ \text{kJ} \ \text{mol}^{-1} \) above the global minima even at 10 \( \text{V} \ \text{Å}^{-1} \).

Despite the incomplete nature of the samples, some of the landscape trends from the smaller system sizes are reproduced in the octamer systems (Table II). The values of \( \langle \bar{v} \rangle \) are again largest for TIP5P and smallest for TIP3P, although
the variations with field strength are less well conserved. $\langle |p^{(2)}| \rangle$ typically decreases with field strength. Dipolar saturation is again observed with increasing field strength, although in contrast to some of the smaller clusters the standard deviation of the dipole moments for local minima shows a maximum at $E=0.1$ V Å$^{-1}$ for all three models (data not shown). In addition to exhibiting maxima for the integrated path length and the distance between the end points at $E=0.1$ V Å$^{-1}$, the fundamental rearrangement steps are also most cooperative at this field strength.

To visually simplify the disconnectivity graphs for this system size, we have shown only the lowest 150 minima at each field strength (Table I). In the absence of an applied field all of the models give double potential energy funnels, as previously discussed. The funnel containing the $S_4$ structure contains more minima in each case, although we note that for TIP3P and TIP5P there is approximately an order of magnitude difference between the two populations, whereas for TIP4P the difference is only a factor of 2. All of the models show an increase in the potential energy density of minima at low energy on going from zero field to $E=0.1$ V Å$^{-1}$. For TIP3P this increase becomes apparent at around 6 kJ mol$^{-1}$ above the global minimum, whereas for TIP4P and TIP5P it does not begin until approximately 12 kJ mol$^{-1}$ above the global minima. At $E=0.1$ V Å$^{-1}$ cubic minima still dominate the low energy regions of the landscape, but alternative hydrogen-bonding arrangements with higher dipole moments become more favored. The double funnel pattern is lost for TIP4P, although it is still discernable for the other two models. As the applied field strength is increased further, ring structures (both single and fused) become lowest in energy. The energy density close to the global minimum continues to increase for TIP5P. This landscape becomes increasingly banyan-tree-like at lower energy, as for (H$_2$O)$_5$. For the other two models the trends are less clear. The energy gaps between the lowest structures are smaller than at zero field, but the barriers for conversion to the global minimum remain high. The degree of branching is less than for the TIP5P potential.

IV. CONCLUSIONS

The variation in cluster properties with system size and field strength is different in detail for each of the three empirical potentials, but certain trends are apparent. We observe that there is a change from favoring compact structures at low applied field strengths to more extended structures at high fields, because the latter are better able to support aligned dipoles. In terms of the field strength required to induce dipolar saturation in the minima, we see that there is a general increase in this threshold as the number of molecules in the cluster increases. Given the size regime that we are operating in, this result is expected because the average binding energy per molecule (in the absence of a field) increases in magnitude towards the bulk value. There are systematic and rational variations in the geometric mean normal mode frequency for the minima and the average imaginary frequency for the TS as a function of field strength. Finite temperature dynamical studies have found electric fields to be structure enhancing, increasing the average number of hydrogen bonds per molecule.$^{12,13,78}$ In contrast, we find that increasing the field strength consistently decreases the average number of hydrogen bonds for the minima because the interaction with the field restricts the orientational freedom of the molecules. Here we have used a geometric criterion to define our hydrogen bonds ($r_{\text{O-H}} \leq 2.5$ Å and O–H–O $\geq 110^\circ$), but we believe that the trends would be qualitatively the same with other definitions.

In terms of the numbers of distinct minima and TS, for the complete samples these values are always maximal at $E=0.1$ V Å$^{-1}$ and lower at higher fields. High field strengths essentially remove two of the rotational degrees of freedom for each molecule, so one might expect to see fewer stationary points under such conditions. Looking at the arrangement of the minima on the potential energy surface, we have identified a weak trend towards a more hierarchical structure at low energies with increasing field strength. Such a landscape topology has previously been observed for a larger water cluster in the absence of an applied field.$^{71}$ The trend is less readily identifiable for the largest cluster that we have considered in this study, although in that case it may be obscured by the strong double funnel character of the zero field landscapes. We would therefore need to undertake further examination before attempting to make a connection between this reorganization and, for example, electrofreezing behavior.

For the fundamental rearrangement steps, there are fewer clear trends. The fraction of degenerate rearrangement paths decreases with system size, and the TIP5P values are typically the largest. The average integrated path length is influenced by the average curvature of the surface, typically reaching a maximum at $E=0.1$ V Å$^{-1}$ and decreasing thereafter. The barrier heights do not appear to show any consistent variation. We have also characterized the paths to the global minimum from all the other minima for each of the stationary point databases, but we do not find any noteworthy patterns.

Despite their qualitatively similar behavior, there are certain consistent differences between the models. The existence of multiple dimer minima for the TIP5P potential at relatively low field strengths can be explained, we believe, by the overstructuring of the energy curve as a function of tilt angle.$^{26}$ From the model parameters shown in Table III, it can be seen that the TIP3P potential has the shallowest LJ well. For TIP4P, the equilibrium LJ separation is the same, but the well is deeper, while TIP5P has the strongest, shortest range interaction. For TIP4P the magnitudes of the partial charges are additionally greater than those for TIP3P. TIP5P has the smallest magnitude partial charges, but because of the explicit representation of the lone pairs the average separation between charged sites on different bodies is significantly reduced in this model. The curvature of the potential energy surface increases as the interaction range decreases$^{79,80}$ and also as the strength of the interactions increases. The above factors lead to the TIP5P model having the largest average curvature and the TIP3P model having the smallest. As a result, the average geometric mean frequencies for the minima typically occur in the order TIP3P < TIP4P < TIP5P. We observe that as the applied field...
strength increases the range of values of $\langle \vec{p} \rangle$ exhibited by the three potentials shows a systematic decrease. We also note that typically the largest number of distinct stationary points at a given system size is observed for the TIP5P potential, and the fewest is observed for TIP3P.

There is also a consistent trend that the average integrated path lengths of fundamental rearrangement steps for the different models occur in the same order as the frequencies. This contrasts with previous results where the path length decreased with increasing curvature (we note that the results in Ref. 81 are for nondegenerate rearrangements only, whereas the figures reported here are for all rearrangements; the results are not qualitatively different if we consider only nondegenerate pathways for the current study).

The relationship between the barrier heights $S$ and $D$ and the curvature is apparently nontrivial for the current systems.

There are relatively few higher level calculations for water clusters in an electric field in the literature. We have compared our findings to those of Choi et al., who report threshold field strengths for transitions to ring structures in which the dangling hydrogen atoms are aligned along the electric field vector and for the crossover between ring and chain structures. We find that, while these transitions are reasonably good at describing the changes observed for the water trimer global minimum, more isomers should probably be considered for the larger systems. The transition field strengths calculated for the model potentials are generally lower than those predicted by the DFT calculations, except for the pentamer. We also find that the field strength at which chain structures become lower in energy than the homodromic ring typically decreases as the static dipole moment of the model increases.

In the absence of more systematic higher level calculations, it is difficult to conclude which of the models considered here is best able to describe the field-dependent behavior of water clusters. There are obvious deficiencies of the TIP5P model in its prediction of planar ring structures for the trimer and tetramer and of the TIP5P model in its destabilization of rings with the non-hydrogen-bonding hydrogens on the same side of the ring plane. The existence of bifurcated structures for the TIP5P potential is interesting, but the field strengths required for them to become minima are high, and for the larger systems these geometries are not competitive with the lowest energy structures. We would also point out that while the increased dipole moment of the water monomers relative to the gas phase value may partly offset the neglect of polarization at moderate field strengths in dipole-aligned cluster geometries, the same would not be true in bulk water systems because of the mutual polarization even at zero field.

We have observed changes in the character of certain points in configuration space for the TIP5P dimer as the field strength is varied. Cusp catastrophes occur at $E=0.171$ V Å$^{-1}$ and $E=1.622$ V Å$^{-1}$, and a fold catastrophe occurs at $E=0.422$ V Å$^{-1}$. There are undoubtedly further examples of such features in the energy landscapes of the larger water clusters, although we have not specifically searched for them. As the field strength approaches a value corresponding to a non-Morse point, the local geometric properties of the energy surface can be predicted using catastrophe theory. For example, near a fold catastrophe it is found that

$$\frac{6\Delta U}{\Delta x^2} = 1,$$

where $\Delta U$ is the change in potential energy between the TS and the minimum, $\Delta x$ is the integrated steepest-descent path length, and $\lambda$ is the curvature along the path at the minimum. A similar expression can be obtained for a cusp catastrophe. Calculating the ratio in Eq. (3), known as the fold ratio, at different field strengths allows us to follow the convergence of the landscape properties in the vicinity of a catastrophe. Such analyses have previously been performed for various atomic systems, for phase transitions in liquid crystals, and the Ising spin model. For the TIP5P dimer we observe reasonable convergence of the catastrophe ratios to within approximately 5% of unity. As we approach closer to the non-Morse points the curvature along the steepest-descent paths becomes small, and we eventually experience numerical problems with the integration.

**Acknowledgments**

One of the authors (T.J.) is grateful to Cambridge University for providing financial support via a Millennium Scholarship and to Downing College. Another author (J.H.-R.) gratefully acknowledges the support of the “Ministerio de Educación y Ciencia (Spain)” and “FEDER fund (EU)” under Contract No. FIS2005-02886.
