

Cluster collisions of water tetramers: a classical dynamical study

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Abstract

The collision of two water tetramers is investigated with classical molecular dynamics and an empirical potential function. Varying the impact parameter, collision and internal energies of the two colliding tetramers we explore the possibility of forming the cubic structure isomers of the octamer. We find that such events are favored under small collision energies and impact parameters with cold, low internal energy, tetramers. Large impact parameter collisions may lead to an orbiting pair of the two tetramers. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Water clusters remain an important topic of research, both experimentally and theoretically, in spite of the extensive work carried out in the last decades [1]. High quality ab initio calculations for the identification of the global and local minima as well as transition states of small water aggregates have been performed by several groups [2–5]. At the same time sophisticated experiments [6–10] made possible the identification of the minimum energy structures predicted by the ab initio methods. Indeed, trimers, tetramers, pentamers, hexamers [6–8], heptamers [10] and octamers [4,9] of

water molecules have been isolated and their structures have been characterized in detail. From the knowledge accumulated up to now, there is no doubt that the lowest energy minima of small water clusters with a number of monomers $n \leq 5$ are cyclic, quasi-planar rings. The transition to three-dimensional structures occurs for the hexamer for which the cage-like geometry is considered as the global minimum of the complex and this is supported by both experiment and quantum Monte Carlo simulations [11].

Analytical functions which describe the water–water interactions in a cluster have also been used in investigating the most stable structures of these systems. In spite of the fact that these functions have been constructed mainly by fitting data from the bulk phases of water, some of the predicted global minima of small water complexes are correct. Such an analytical function has been used by us in previous studies [12–16]. The potential

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function was produced by Cieplak–Kollman–Lybrand (CKL) [17] and it was based on data from the water dimer, ice and liquid. It reproduces the square and cubic minimum energy geometries of the tetramer and octamer respectively predicted by ab initio calculations [18]. In a systematic study of small water clusters and using the CKL potential we showed the significant stability of the tetramer and octamer [12]. This conclusion is based on the melting temperatures and the relatively large energy gaps between the global minimum and excited metastable structures of the clusters. In contrast, the pentamer, hexamer and heptamer have lower melting points, large density of metastable states close to the global minimum and they are more floppy [10].

Experimental evidence [4] supports the structural stability of the two cubic isomers of S_4 and D_{2d} symmetry of the octamer found theoretically. This is deduced from the small fragmentation rate of octamers compared to heptamers. However, apart from that, there are no experimental observations that the tetramers and octamers can give magic numbers. On the contrary, it has been found that an enhanced peak appears in the mass spectra only for the cluster with $n = 21$ water molecules, which corresponds to a clathrate structure [19]. Guven and Anderson [20] have carried out an extended comparison among the energetics and structures of the minima predicted by several empirical potential functions.

If we rely on the theoretical results, the four-membered ring seems to constitute a stable building unit for the formation of larger clusters. The S_4 and D_{2d} symmetry low energy cubes [12,21] and all the other cubic structures [22,23] result from the fusion of tetramer squares. The lowest energy stable dodecamers [13] can be obtained from the fusion of a S_4 or a D_{2d} cube with a tetramer ring. The addition of an extra tetramer results into three fused cubic 16-mers [13] which have lower energy than the structures with five-membered rings. The building up of stable cubic conformations stops at the 18-mer [13] which has a non-cubic geometry for its lowest energy minimum, as is predicted from the CKL model potential function. Low energy face-sharing cubes with 20 water molecules have been identified [21,23], where the lowest en-

ergy minimum is described as a three face-sharing pentagonal prism.

Cubic structures must be very common in $(H_2O)_{27}$ clusters [14] as an investigation with the CKL potential has shown. They consist of eight face-sharing cubes arranged into a larger hypercube. Extension of this type of calculations to $(H_2O)_{64}$ [15] concluded, that deformed cubic sub-units may be formed in large water aggregates.

A central question in the cluster field is how complexes are formed, especially in freely expanding molecular beam jets. Models regarding nucleation processes give incompatible results, so one cannot tell with certainty about the formation mechanism of small and large water clusters. Generally, there are two schemes, either they are built up through three-body collisions, where the third body removes the excess energy and stabilizes the cluster, or through the disintegration of larger clusters, formed at the initial stage of the beam production, close to the nozzle. An experimental study concerning the formation process of the water clusters [24] in a vapor beam, concludes that small clusters, $n \leq 5$, are created in three-body collisions, a process that is in accordance with the observation that these clusters are in thermal equilibrium with the monomers. Larger clusters are in thermal equilibrium with clusters of the same size, and as a consequence, they are probably created through two-body collisions. Also, the concentration of small clusters is independent of their sizes and the source conditions (temperature and pressure).

The purpose of this article is to study the mechanisms of the collisions of water tetramers. Our study is very far from delivering a complete picture of water cluster formation under free jet expansion conditions. There is a small number of studies simulating cluster formation and growth under real conditions and these mainly concern Lennard-Jones particles [25,26]. As a first step we simply pose the question as to whether cubic water clusters can be formed and survive, by letting tetramer rings to collide. This is not an improbable situation to happen, since four-membered rings must exist in abundance in expanding water vapor flows. Under what conditions cubic octamers are formed by the tetramer fusion, how long do they

live and how is the excess energy accommodated, are few of the questions to be answered. This paper is the first in a series of a systematic investigation of the structural stability of the cubic conformers and the possibility of creating larger cubic water clusters by simple fusion of tetramer rings and cubic octamers.

The paper is organized in the following way. In Section 2 the potential and the methods are described. Section 3 deals with results and discussion. Finally, in Section 4 we summarize our results.

2. Potential function and numerical method

The potential function used is that of Cieplak et al. [17], which is a modification of the Reimers, Watts and Klein RWK2 [27] potential for water–water interactions and rigid monomers. This is the sum of a pairwise potential consisting of the electrostatic interactions, based on a model with charges placed on the two hydrogens and on the bisector of the HOH angle, oxygen–oxygen repulsion and Morse-type interactions among hydrogens and oxygens, plus polarization terms. Comparison of the CKL potential with other potential functions can be found in Refs. [12,20]. In view of the recent ab initio calculations and experimental results on small water clusters, the CKL potential correctly predicts the global structures of the tetramer and octamer. The S_4 and D_{2d} energy ordering is the same as in the widely used TIP4P potential, but according to MP2 ab initio calculations [18] the D_{2d} minimum has lower energy than the S_4 isomer. We estimate that for the present study the CKL potential is adequate.

If one compares the binding energies per water monomer for the tetramer and octamer as is done in Ref. [20] for different potential models and ab initio calculations, the CKL plus polarization potential function gives the lowest value for the tetramer and one of the smaller values for the octamer. Therefore, we believe that the results presented here regarding the probability of long lived cubic structures formation from the direct fusion of tetramer rings, represent a lower bound,

since stronger bonds would allow for less distortion of the structures for the same internal and collision energies.

We perform constant energy molecular dynamics simulations where the coupled Newton–Euler equations for the motion of rigid water molecules are integrated in time. The motion of each water molecule is described by three Cartesian coordinates of its center of mass and three Euler angles. To avoid well known singularities in the Hamiltonian we have adopted the quaternion formalism of Evans [28,29]. The integration step was set at 0.0242 ps. The colliding tetramers were randomly selected from a gradually heated and thermally equilibrated for 50 000 time steps gas, at two temperatures. The first ensemble of tetramers was chosen at $T = 47.4$ K, hereafter termed as the cold ensemble, and the second one at $T = 174$ K, named the hot ensemble. Both temperatures are below the melting temperature of the cluster (186 K) [12]. The vibrational and librational temperatures (see next section for their definition) were $T_{\text{vib}} = 32.5$ K and $T_{\text{lib}} = 62$ K for the cold ensemble and $T_{\text{vib}} = 121.6$ K and $T_{\text{lib}} = 225.7$ K for the hot one. The isolated tetramers were produced with zero total linear and angular momentum.

The collision was initiated with the pair of the colliding clusters set at a distance of $45a_0$, a distance which guarantees that the interaction energy is zero. Prior to the collision the tetramers were randomly rotated. We examined two sets of impact parameters, one at $b = 0$ (head-on collisions) and another at $b = 15a_0$ (mostly skew collisions). Some intermediate impact parameters were also examined at $b = 5a_0$ for example. Collision energies at the laboratory system of reference were set at $E = 0.001, 0.05, 0.15, 0.3$ and 1.0 eV. For each set of initial conditions (impact parameter, collision energy and temperature of the initial ensemble) 10 trajectories were examined. All trajectories were run in the center of mass coordinate system for 40 ps. Only a few events of cluster dissociate, especially at higher collision energies, during this evolution time. This time however, is long enough for many rearrangements to take place within the octamer and for the thermalization of energy among the internal degrees of freedom. Eventually, at long collision times all trajectories will

break up. The trajectories were visually examined by the animation program MOVIE MOL [30].

3. Results and discussion

3.1. Mechanisms for a collision complex formation

The pathway of approach is monitored by the impact parameter and the collision energy. Head-on collisions result with a high probability in fused octamers at low energies. On the other hand, at higher energies, above 1.0 eV, the complex dissociates to a heptamer and monomer in a short time interval. Collisions at large impact parameters may result in scattered or orbiting dimer-like $[(\text{H}_2\text{O})_4]_2$ octamers. In these cases fusion events become rare even for longer times. With large impact parameters collision complexes are favored at low energies, even less than 0.001 eV.

Our work shows that cubic octamers can indeed be formed under a wide range of initial conditions. Cubic structures are abundant and long lived the lower the collision energy is, the smaller the impact parameter and the less internally excited the colliding tetramers are. Such cubes are created either directly at the entrance channel or at a later time and their characteristic is that once formed, they are not easily destroyed, despite the large deformations the cubic structure experiences at some times. Such deformations are caused either by the large amplitude concerted vibrations of the structure or by independent motions of single monomers.

The above observations apply only to the cold initial ensemble. Collisions between the hot tetramers lead to fused octamers more easily, even at large impact parameters and collision energies, but cubic structures are very rare and short lived. The resultant octamers are energy rich and liquid-like. To give an idea about how common the event of a cube formation is at the entrance channel, we report that for the cold species at $b = 0$ and $E = 0.001$ eV, three out of 10 trajectories result in a cube, at $b = 5$ and $E = 0.15$ eV, five out of 10 and at $b = 0$ and $E = 0.3$ eV, two trajectories out of 10. Also, the range of lifetimes of the formed cubes is between 10 and 30 ps.

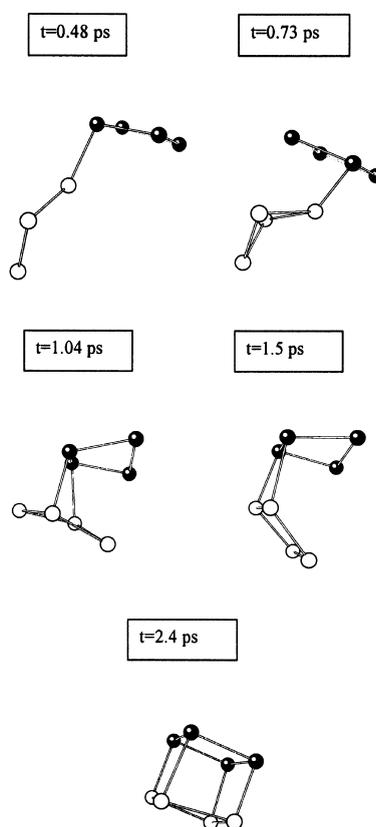


Fig. 1. Snapshots from a trajectory of two colliding square tetramers which leads to the formation of a cubic structure octamer. Only the oxygen atoms are drawn to simplify the picture. Notice that the initial contact of the two tetramers is via the formation of a single hydrogen bond.

The most common pathway of approach for the cold ensemble is shown in Fig. 1. The two tetramers approach each other at skew position where one hydrogen bond is first formed. This bond formation exerts torsional vibrational excitations in the tetramers which in the meantime rotate relatively to each other until a favorable parallel orientation of the two rings is achieved. Four additional bonds are then formed. The complete ring fusion and the cubic structure is completed within 2 ps.

Head-on collisions can also result with a high probability to other types of conformations, termed here as “open book” and “prism structures.” The initial phase of approach is the same as before, i.e. tetramers approach each other at skew

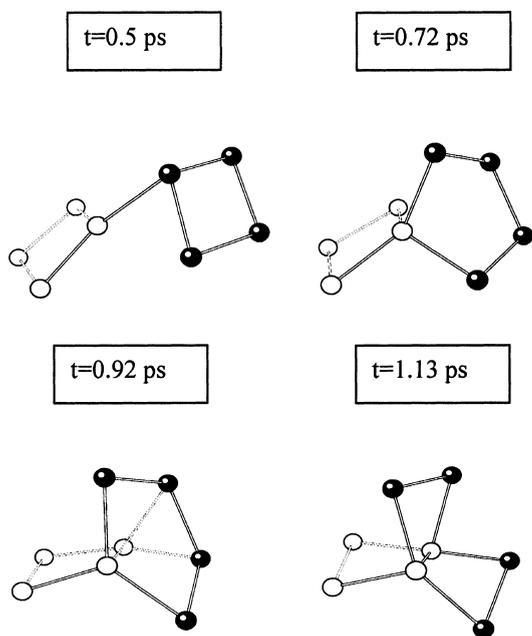


Fig. 2. As Fig. 1 but for a trajectory which leads to the formation of an “open book” geometry octamer via the initial formation of a bifurcating hydrogen bond.

positions and they first interact via one hydrogen bond. Then, either one tetramer bond is broken and a bifurcating hydrogen bond [31] is created with a single monomer of the second tetramer giving rise to an “open book” structure, Fig. 2, or the tetramers, without any of the bonds being broken, are directly captured in an “edge sharing” structure which can eventually lead to a “prism type” or “open book” conformation, Fig. 3. These processes are completed within 1–1.5 ps. Of course, after the initial collision the geometry of the octamer continuously changes visiting several minima depending on the collision and the internal energy. From all local minima where a trajectory was trapped, those corresponding to cubes were the longest lived. Cubes appear less and less frequently at higher collision energies.

Collisions at large impact parameters ($b = 15a_0$) have a high probability to lead to scattering states, especially with an increase in the collision energy. For example, at $E = 0.3$ eV, four out of 10 trajectories were scattered, whereas at $E = 1.0$ eV and beyond all trajectories lead to scattering. For

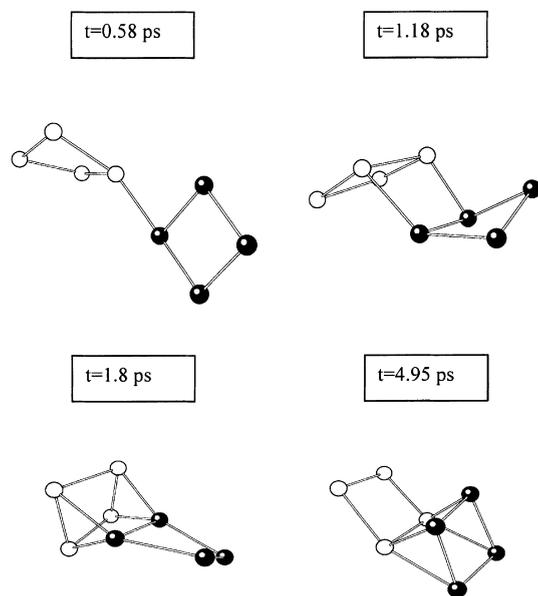


Fig. 3. As Fig. 1 but for a trajectory which leads to “prism type” octamers.

those not scattered, a long-lived dimer-like collision complex was formed. At smaller collision energies, the tetramers rotate relative to each other for times ranging from 2 to 4 ps, before merging occurs.

Collisions with hot tetramers, lead to an immediate break up of the rings and to the formation of open conformations, where the pentagonal rings prevail. The migrations of a water molecule along the volume of the cluster is not uncommon. The tetramer rings lose their identity very quickly, even at large impact parameters and collision energies.

3.2. Energy redistribution

The quantities monitored through the molecular simulation are the translational kinetic energy of one tetramer in the center of mass coordinate system,

$$E_{\text{trans}}^{\text{cm}} = \frac{1}{2}(4m_{\text{H}_2\text{O}})\vec{v}_{\text{cm}}^2, \quad (1)$$

where $m_{\text{H}_2\text{O}}$ is the mass of one water molecule and \vec{v}_{cm} is the center of mass velocity of the whole tetramer

$$\vec{v}_{\text{cm}} = \frac{1}{4} \sum_{i=1}^4 \vec{v}_i. \quad (2)$$

\vec{v}_i is the translational velocity of i th molecule.

The librational energy is defined by

$$E_{\text{lib}} = \frac{1}{2} \sum_{k=1}^N I_k \omega_k^2, \quad (3)$$

where $N = 3 \times 8$ is the total number of the rotational degrees of freedom for the two clusters, I_k the moment of inertia and ω_k the angular velocities of each molecule.

The vibrational–rotational kinetic energy of the a th tetramer oxygen ring, ($a = 1, 2$), is defined by subtracting from the velocity of each molecule the velocity of the center of mass of the tetramer;

$$E_{\text{vib-rot}}^a = \frac{1}{2} \sum_{i=1}^4 m_{\text{H}_2\text{O}} (\vec{v}_i^a - \vec{v}_{\text{cm}}^a)^2. \quad (4)$$

Signatures of the different types of reaction channels are provided by the distributions of the translational kinetic energy averaged in time and over a 10-trajectory ensemble. Such histogram distributions are presented in Figs. 4 and 5 for the cold and hot initial ensemble respectively. Whenever fusion is the dominant effect, the kinetic energy distributions peak at zero irrespectively of its initial value, which means that all relative kinetic energy is lost and is redistributed within the internal degrees of freedom. However, at large impact parameters, the kinetic energy transfer becomes less and less effective, as the collision energy increases. We have to mention, that the collision energy includes not only the radial translational

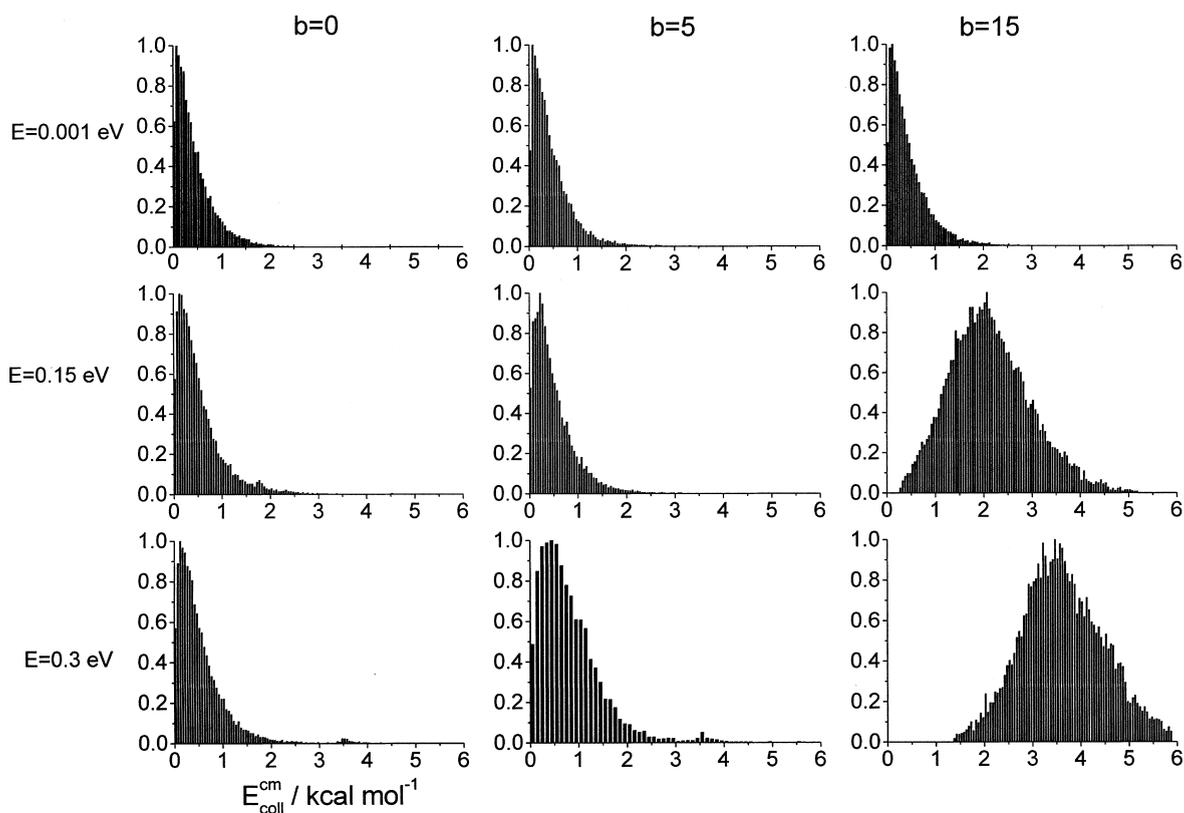


Fig. 4. Distributions of the translational kinetic energy (Eq. (1)) averaged in time and over a 10-trajectory ensemble. The initial tetramers have low internal energy (cold ensemble) with a temperature of $T = 47.4$ K. The distributions are arranged in columns and rows for different impact parameter and relative collision energy, respectively.

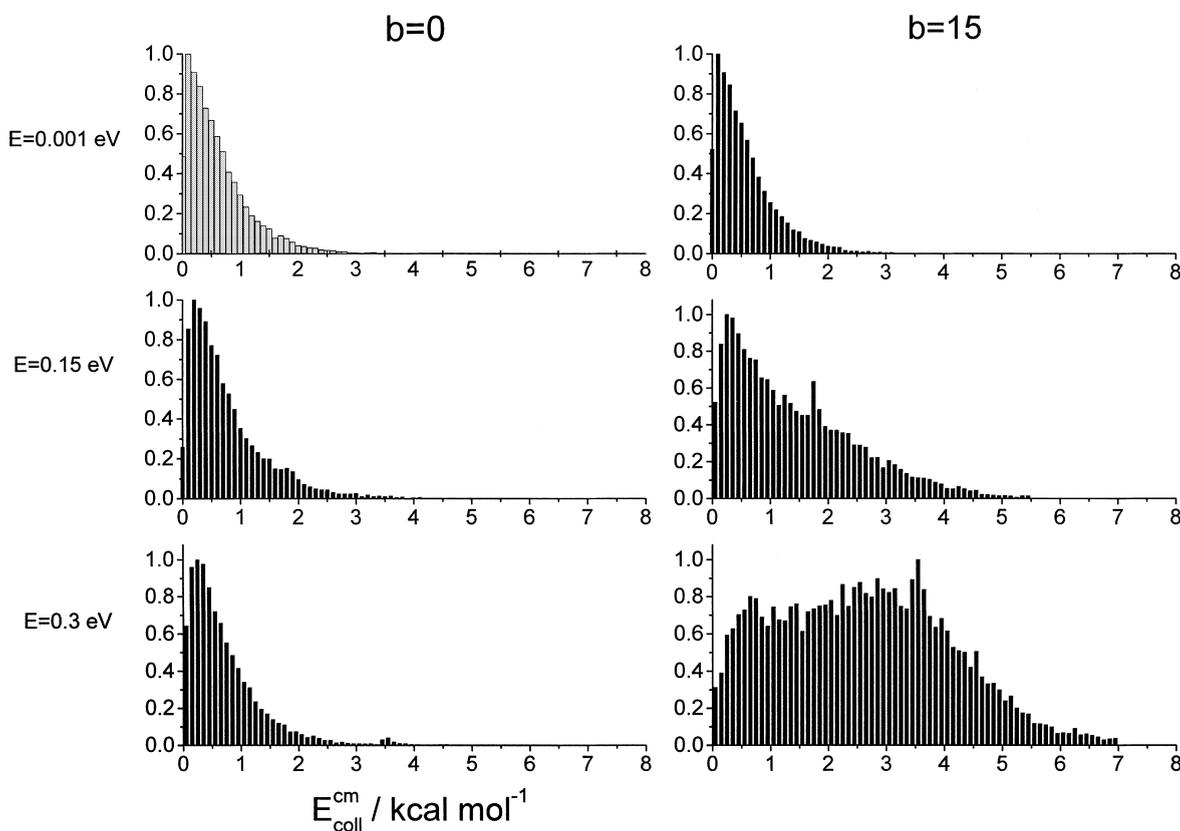


Fig. 5. As Fig. 4 but for hot tetramers (see text) with an initial temperature of $T = 174$ K.

energy, but the overall rotation of the cluster as well for impact parameters greater than zero. At $b = 15$ and $E = 0.3$ eV, the kinetic energy distribution has a mean value very close to its initial value (see Fig. 4). These are the trajectories that correspond to the rotating dimer-like octamer. The relative kinetic energy is soon transformed to overall rotation of the cluster, the cluster is trapped behind large centrifugal barriers and the flow of the rotational energy to the internal degrees of freedom is inefficient or very slow. Also, the kinetic energy transfer in the scattered trajectories, last frame of the third column, is minute. Similar distributions are obtained for the hot ensemble (see Fig. 5), the only difference is that they are broader. At large impact parameters, we observe a significant percentage of aggregates with zero energy contributions, indicative of an ongoing fusion process together with scattering.

The next question, is how fast the relative collision energy is lost and is redistributed among the internal degrees of freedom. In Fig. 6, we plot the ensemble-averaged collision energy as evolves in time for the cold tetramers. The energy loss is apparent for the fused trajectories, which loss becomes larger with the initial collision energy. We see that this process is very fast and terminates in a time interval between 1 and 3 ps. On the other hand, for large impact parameters, the relative collision energy oscillates close to its initial value. The initial increase in the kinetic energy seen in Fig. 6 is due to the initial acceleration of the clusters because of the attractive potential between them.

The oscillatory behavior in the distributions are attributed to the bouncing-off of the rings before obtaining a more favorable orientation. We have to mention that the parallel orientation is

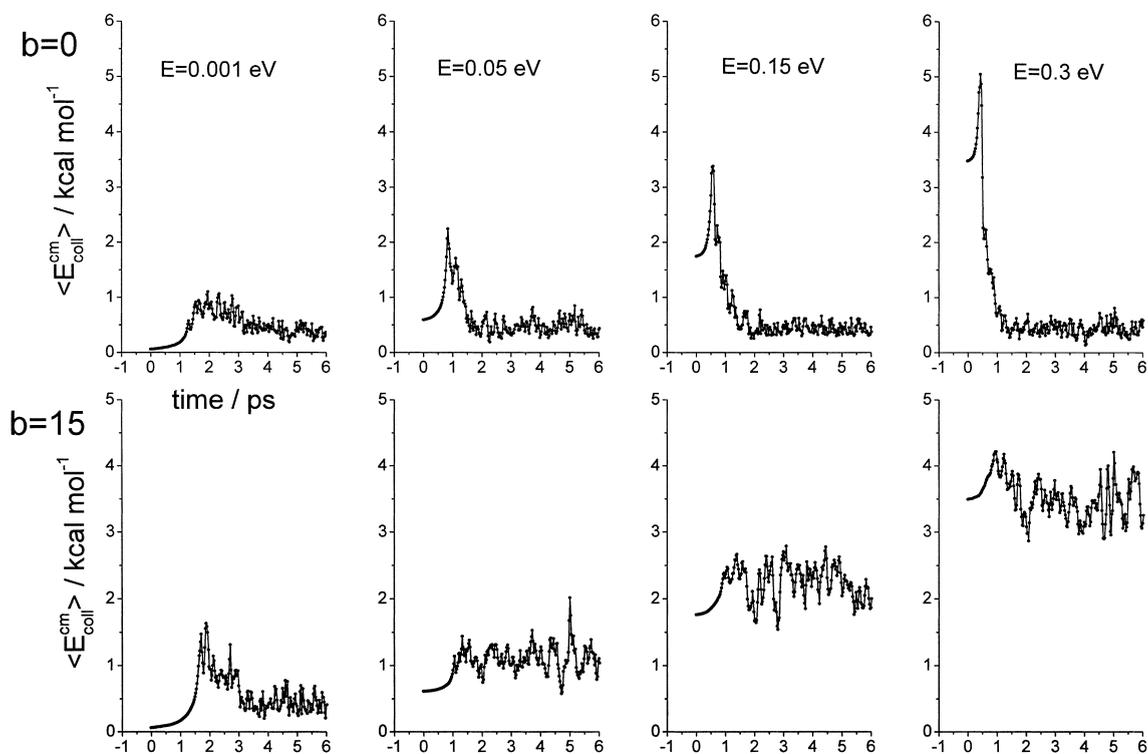


Fig. 6. The ensemble-averaged translational energy as a function of time for initially cold tetramers, for two impact parameters and several initial collision energies.

energetically favored compared to the perpendicular one, although many times such attempts for parallelization lead to misaligned rings, which delay or completely inhibit formation of the cubic structures. At small collision energies, the process of collision energy redistribution is slower than at higher energies, an effect that permits the two tetramers to adjust themselves for the most favorable, low potential energy, orientation.

Another issue is the librational energy excitation during the collisions. In Fig. 7, we plot the time evolution of the ensemble-averaged librational energy (Eq. (3)) for the initially cold tetramers. The upper row is for head-on collisions where we observe an increase of E_{lib} with collision energy. The lower row is for the large b case ($b = 15a_0$), where the opposite trend is observed. This is in accordance with the increased probability of the creation of dimer-like collision complexes, where the relative collision energy is mainly

trapped in overall rotational energy and rotational energy of the individual tetramers (large total angular momentum).

The trend is more apparent in the following figure, Fig. 8, where time and ensemble averaged of the librational energy differences from its initial value are shown. The librational energy transfer is larger for the cold tetramers at $b = 0a_0$ and increases with collision energy. On the other hand, for $b = 15a_0$, a decrease of librational energy transfer is observed, which is larger again for the cold ensemble.

The decisive step in the creation of a fused or of a dimer-like collision complex is the rotation of the individual tetramers in order to obtain a more favorable parallel orientation. This motion is included in the vibrational energy content, together with the torsional and stretching vibrations of the tetramers. As shown in Fig. 9, where the ensemble-averaged time evolution of the total

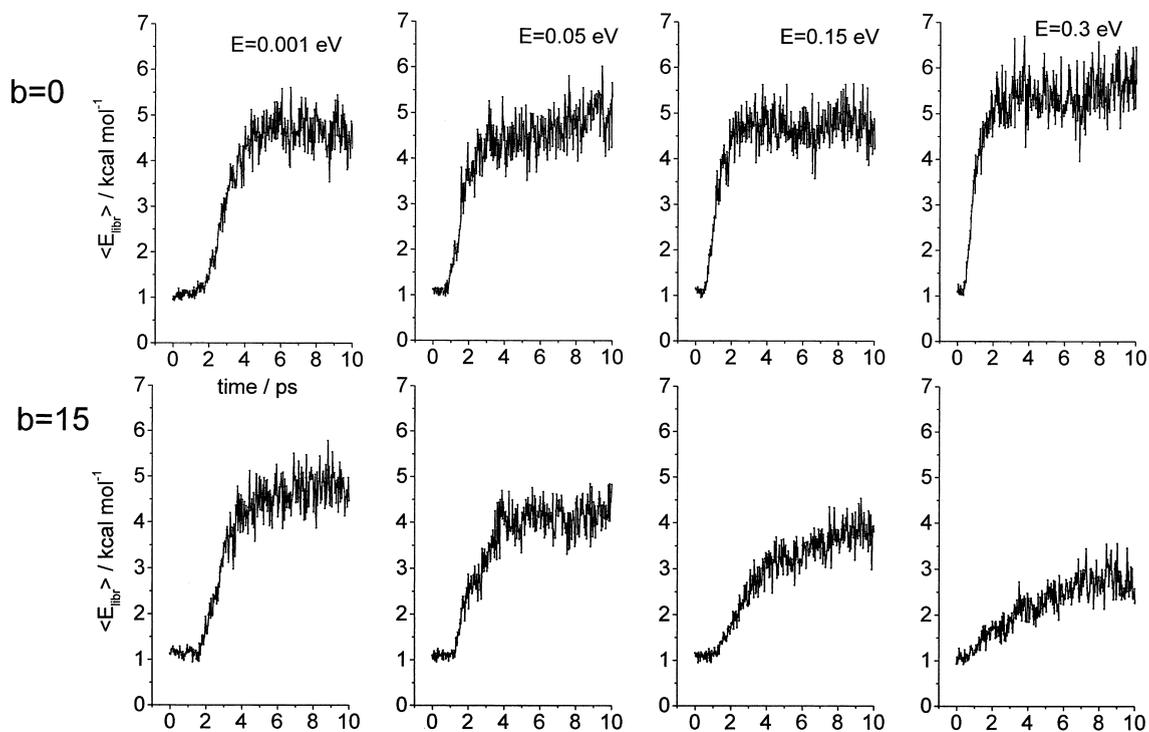


Fig. 7. The time evolution of the ensemble-averaged librational energy (Eq. (3)) for initially cold tetramers at two impact parameters and several initial collision energies.

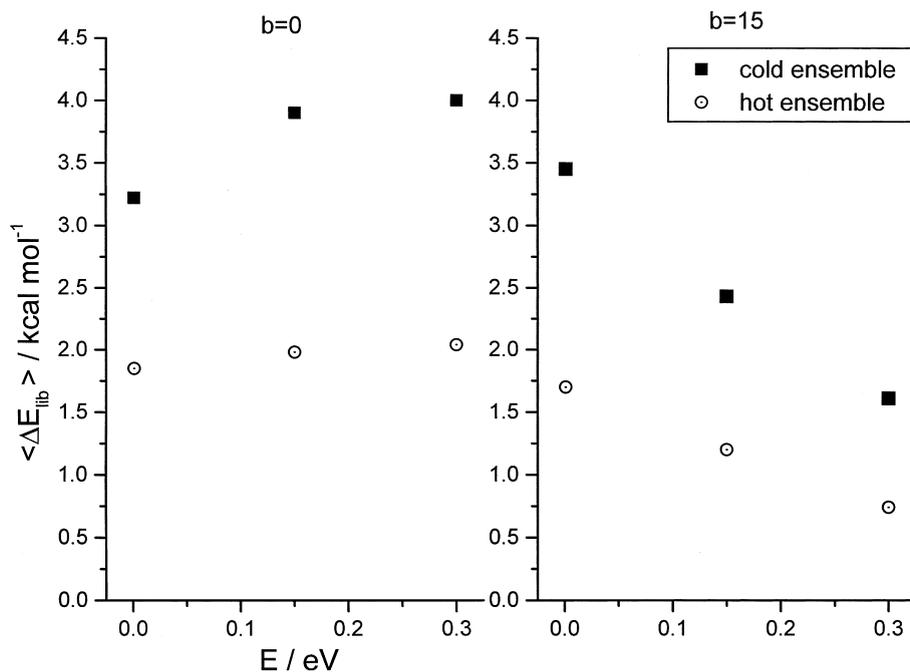


Fig. 8. Time- and ensemble-averaged librational energy transfer are shown for cold and hot initial tetramers at two different impact parameters as a function of the initial collision energy.

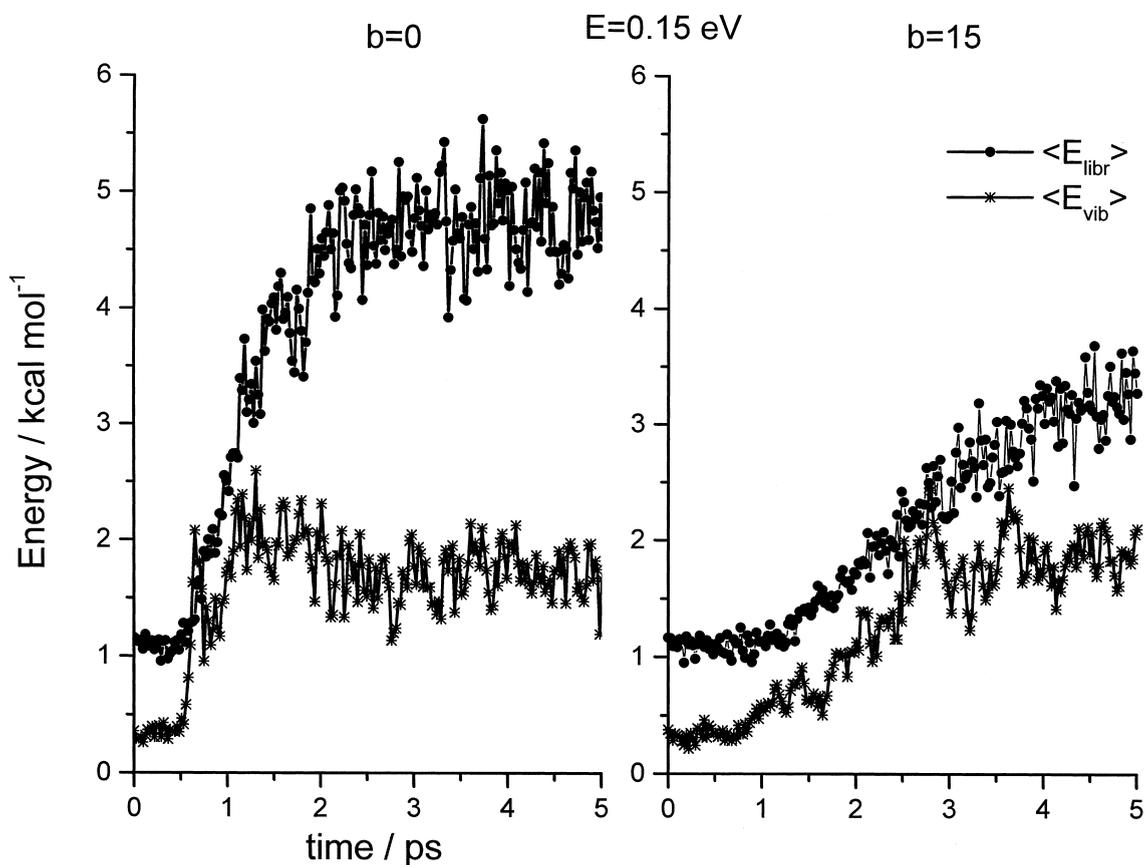


Fig. 9. The ensemble-averaged time evolution of the vibrational–rotational energy (Eq. (4)) at the collision energy of $E = 0.15$ eV.

vibrational–rotational kinetic energy, $E_{\text{vib-rot}}^1 + E_{\text{vib-rot}}^2$ (Eq. (4)), as well as the librational energy, E_{lib} (Eq. (3)), are plotted, vibrational motions are excited first and reach a plateau before librations are fully excited. For example, at $b = 0$ the vibrational–rotational kinetic energy reaches the plateau at 1 ps whereas the E_{lib} at 2 ps. This is also an indication that the square frames of the tetramers are not seriously perturbed.

4. Conclusions

The conditions and mechanisms for the formation of cubic octamers in collisions of two square water tetramers have been examined with classical molecular dynamics calculations and using an empirical potential function. Monitoring

the collisions with the impact parameter, the collision energy and the internal energies of the tetramers we find that a direct complex formation is favored by small impact parameters and collision energies. The cubic isomers of the octamer are formed mainly with cold, low internal energy, tetramers.

The main mechanism for reaching a cubic minimum of the octamer is via the initial formation of a single hydrogen bond followed by proper rotations in order to have face to face arrangements of the two tetramers. Apparently, slow motions allow better these transformations to take place. On the contrary, at large impact parameters orbiting cluster dimers have been observed.

A quantitative description of the collision output of the two water tetramers is provided by plotting distributions of the translational, libra-

tional and vibrational–rotational energies. Small impact parameters lead to a librational energy increase with the collision energy whereas for large impact parameters the librational energy transfer decreases with the collision energy. The distributions of the translational energies can distinguish trajectories driving to complex formation from those which result in scattering or orbiting events.

Acknowledgements

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