A CLASSICAL MECHANICAL STUDY OF *CIS–TRANS* ISOMERIZATION REACTION OF $(H_2O)_4$ CLUSTER: AN EXAMPLE OF NON-ERGODIC BEHAVIOUR

S. Kapetanakis and S. C. Farantos

Institute of Electronic Structure and Laser, FORTH, and
Department of Chemistry, University of Crete,
Iraklion, Crete 711 10, Greece.

ABSTRACT

The isomerization process between the most stable structures of water tetramer which have the free hydrogen atoms in *trans* (absolute minimum) and *cis* (relative minimum) orientation is studied with classical mechanical methods and an empirical potential function. The density of vibrational states is computed with Nosé-Hoover dynamics as a function of total energy. For a substantial energy range above the barrier of isomerization a non-ergodic behaviour is found in the dynamics of the cluster. This results in smaller densities of states for the anharmonic model than the corresponding harmonic model. The detailed mechanism of the *cis–trans* isomerization process is examined and rate constants are calculated in the frame of the transition state theory.

1. INTRODUCTION

Recent spectroscopic results on small water clusters have launched new interest on these prototype hydrogen bonding systems. Particularly, we refer to the *Far Infrared Vibrational Rotational-Tunneling Spectroscopy (FIR-VRT)* of Saykally and coworkers.[1–3] Accurate ab initio calculations for the water-water interactions have been presented,[4–6] and quantum Monte Carlo calculations[7] have produced results which are favorably compared with the experimental findings.

Among the small water clusters the tetramer has drawn special attention. The reason is that the square geometry of oxygen atoms with the hydrogen bonds oriented in the same direction exhibits an extra stability. Empirical potentials[8,9] and ab initio calculations[10–14] predict that the absolute minimum has a geometry with the non-bonded hydrogens to be alternatively in *up (u)* and *down (d)* positions; that is the four hydrogen atoms which do not participate in the hydrogen bonds are arranged in *(udud)* or *(dudu)* positions (symmetric equivalent minima). We have named such structures in previous publications[15,16] as *trans* (Fig. 1c).

The first relative minimum is also cyclic in geometry but with the free hydrogens in *(uudd)* orientation (Fig. 1a).

Figure 1: The optimum geometries of the *cis* isomer of water tetramer (1a), *trans* isomer (1c) (absolute minimum) and a low energy transition state that separates the two minima (1b). The saddle point has one hydrogen atom which is not involved in hydrogen bonding to be in a parallel position with respect to the plane of the four oxygens.

This structure has four symmetric equivalent minima. A low energy transition state that connects the *cis*–*trans* minima has a geometry which could be characterized as *(uudp)*. This means that one free hydrogen comes into an almost parallel *(p)* position with the plane of the oxygens (Fig. 1b). At higher energies we have found more relative minima with tetrahedral geometries.[15] Wales and Walsh[17] have recently presented a systematic study of the rearrangement mechanisms of water tetramer using Hartree-Fock, density functional theory (BLYP, Becke-Lee-Yang-Parr) and an empirical rigid-body intermolecular potential, that of Millot and Stone (ASP-W2).[18] They have located a significant number of transition states of first and higher order as well as new minimum energy structures.

Our early Molecular Dynamics (MD) calculations[15] showed a fast isomerization between the *cis–trans* isomers. By running trajectories at constant energy we found that the flipping of the free hydrogen atoms which leads to the *cis* or *trans* isomers persists for hundreds of picoseconds even at relatively high vibrational states. An example is presented in Fig. 2 where we show the results of quenching the energy of the cluster at equal time intervals during the run of a trajectory. What is shown in Fig. 2 is the potential energies of the minima which are visited at each time. We can see that the most frequently visited minima are the *trans* and *cis*. We must underline the fact that the total energy (-15 kcal/mol) for the selected trajectory is enough to allow the cluster to visit other non cyclic minima which exist at higher energies. However, this happens rather rarely and the trajectory is not trapped in their region as can be seen in Fig. 2.

Figure 2: Minimization plot for a trajectory run at -15 kcal/mol total energy (see text). The plot is produced by quenching the kinetic energy of the cluster at equal time steps, 0.0242 ps, during the run of a trajectory. For most of the times the cluster is quenched in the *trans* and *cis* minima. Only rarely higher energy minima are visited and the trajectory stays in their region for sort time intervals.

The persistence in the torsional type motion indicates a kind of adiabatic decoupling of the torsional degrees of freedom which are related to the motion of the free hydrogens from the stretch and angle bend motions of the oxygens and hydrogens which are involved in hydrogen bonding. This behaviour contrasts what we found for the water trimer and pentamer[15] which show an early coupling among all the degrees of freedom. As a matter of fact this stability and dynamical behaviour of the tetramer has led some investigators to use the $(H_2O)_4$ as a building block for the structure of liquid water in an effort to explain some of the unique thermodynamical properties of liquid water.[19]

The far infrared vibrational-rotational tunneling spectroscopy of Saykally and coworkers[2,3] supports the cyclic geometry of the water tetramer. Furthermore, they observed double peaks separated by 5.6 MHz in the spectral lines. They attributed this spectroscopic feature to the splitting of doubly degenerate vibrational levels which result from the two symmetric equivalent *trans* structures rather, than excitations from the *cis* and *trans* minima. This is an interesting conclusion if we take into account that the *cis–trans* transition states lie at lower energies than the transition states among symmetric equivalent minima.

This work has motivated us to study the *cis-trans* isomerization dynamics of water tetramer. To accomplish such a task we apply Molecular Dynamics to study the flipping of the free hydrogens. We compute density of states (DOS) using Nosé-Hoover[20–22] techniques and rate constants at several excitation energies for both reactions, from *cis* to *trans* ($C \rightarrow T$) and its reverse ($T \rightarrow C$).

2. METHODS

In the present work we use the potential function of Cieplak, Kollman, and Lybrand (CKL)[8] as in our previous studies.[15,16,23,24] This potential is written as the sum of pairwise potentials which include, the electrostatic interactions based on a model with charges placed on the two hydrogens and on the bisector of the HOH angle, oxygen-oxygen repulsions, Morse-type attractions among hydrogens and oxygens, and dispersion interactions, plus polarization terms. The latter are formed by dipole-dipole interactions. In the previous studies of small water clusters an extensive comparison was made among the CKL potential and other potential functions. At least for the tetramer and cubic conformations we do find agreement which reveals the structural stability of these types of geometries. The energy of the *trans* isomer is -22.316 kcal/mol, of *cis* -21.757 kcal/mol and the energy of transition state shown in Fig. 2b is -21.601 kcal/mol for the potential function with no polarization terms. For the polarizable potential the corresponding values are: -25.66, -25.02 and -24.84 kcal/mol respectively.

In ref. [15] we have examined the role of many body polarization forces in the structure of minima and dynamics. It was found that the polarization terms make a contribution of about 14% in the total energy and do not affect the geometry of the minimum, although the variations of the absolute energies may cause changes in the order of some relative minima. In the following we present results using both the additive and the polarizable potential functions.

The time evolution of water tetramer is followed by solving Hamilton equations. The water molecules are treated as rigid bodies and their rotations are described by four quaternions, whereas translational motions are described by the three cartesian coordinates of the center of mass of each molecule. The system is of 18 degrees of freedom. Trajectories are integrated for 1 ns at several energies and allowing the system to equilibrate its energy after a variation of the total energy. The total angular momentum is always zero. During the evolution of the trajectory we examine at every time step (0.0242 ps) the criterion which determines if the trajectory explores the *cis* or *trans* region of the configuration space. Such a criterion involves the calculations of the angles of the free hydrogens with respect to the plane of the oxygen atoms. The cluster is characterized as being in the *cis* region if the pairs of the diagonal free hydrogen atoms are alternatively above and bellow the plane of the oxygens and *trans* if the diagonal free hydrogens are on the same side, one pair above and the other below.

The isomerization rate constants are computed with microcanonical MD using the histogram method or from the average times which the cluster spends in the regions of the two isomers. We have examined the energy range from -20 kcal/mol to -12 kcal/mol. The equilibrium constants of the isomerization reaction are calculated as the ratio of the two rate constants; $\mathrm{K}_{C\to T}$ and its reverse $\mathrm{K}_{T\to C}$. These values are then compared to the equilibrium constants obtained as the ratio of DOS of the *trans* and *cis* isomers.

For the calculation of the exact microcanonical density of states, we discretize the total energy probability distributions using for sampling canonical ensembles.[20–22] The probability distributions of the total energy E is defined at constant temperature as

$$P_T(E) = \frac{\omega(E)\Delta E\, e^{-\beta E}}{Z(\beta)}, \tag{1}$$

where $Z(\beta)$ is the canonical partition function, and $\beta = 1/kT$ (k is the Boltzmann constant). This relationship can be over a grid of energies E_i and temperatures T_j. Thus, at a given temperature β_j the probability to obtain the total energy E_i can then be expressed as :

$$P_{ij} = \frac{\rho_i\, e^{-\beta_j E_i}}{Z_j}, \tag{2}$$

where $\rho_i = \omega_i \Delta E$.

It follows that if canonical simulations are run for M different temperatures in order to obtain a set of M normalized probability curves, the multiple histogram method as described by Weerasinghe and Amar,[25] can be used for the extraction of the exact anharmonic microcanonical density of states. Such canonical simulations were carried out by running Nosé-Hoover dynamics[20–22] with zero total angular momentum. Fig. 3 presents energy probability distributions for several temperatures. The overlapping of these distributions is necessary for the smoothness of the DOS curves. The scaling of the $\omega(E)$ function was then adjusted by fitting it at low internal energies to the harmonic curve, which is completely defined by the knowledge of the harmonic frequencies at the equilibrium configuration. The canonical partition function can then be deduced by :

$$Z(\beta) = \int_0^\infty \omega(E) e^{-\beta E} dE. \tag{3}$$

From the total density of states, the mean energy at temperature T, $U(T)$, can also be calculated[26] :

$$U(T) = \int_0^\infty \frac{E\, \omega(E) e^{-\beta E} dE}{Z(\beta)}. \tag{4}$$

The heat capacity is evaluated by the equation

$$C_v(T) = \frac{\partial U(T)}{\partial T}. \tag{5}$$

Figure 3: Distributions of the total energy obtained by running trajectories at constant temperature (Nosé-Hoover). Distributions which cover larger energy ranges have been computed.

3. RESULTS AND DISCUSSION

We have computed the vibrational DOS starting very close to the absolute minimum (*trans*). Calculations have been performed using both the pair additive and the polarizable model for the water-water interactions. The results are presented in Fig. 4 and are compared with the harmonic calculations (solid lines).

The characteristic of these curves is that the DOS curves obtained from the anharmonic potential (both non-polarizable and polarizable) lie below the DOS of the harmonic model even after putting 10 kcal/mol energy in the cluster. At this energy the cluster could be dissociated. In such events to prevent overestimation of the DOS we have applied the method of Wales[27] which adds a modified Lennard-Jones type potential to reflect the trajectory back to the region of strong interaction. This potential is

$$V(r_i) = \left\{ \begin{array}{ll} 4\epsilon \left[\left(\frac{\sigma}{R-r_i} \right)^{12} - \left(\frac{\sigma}{R-r_i} \right)^{6} \right] + \epsilon, & R - r_i < 2^{1/6}\sigma \\ 0, & R - r_i \geq 2^{1/6}\sigma \end{array} \right\} \tag{6}$$

For the present work, we have taken $\epsilon = 3$ kcal/mol, $\sigma = 1.2a_o$, and $R = 25a_o + \sigma$. The above modification of the potential is compatible with the conservation of the total energy and angular momentum in the strong interaction region.

Usually, the anharmonicity of the potential results in larger density of states especially at high excitation energies. Therefore, the smaller values of DOS are attributed to the fact that the flipping degrees of freedom are not strongly coupled to the other degrees of freedom, and thus the energy is trapped in the flipping modes of the free hydrogen atoms. The quality of the calculations can be estimated by comparing the caloric curves obtained from the density of states (Eq. 4) and microcanonical molecular dynamics calculations by averaging the kinetic energy during the time evolution of the cluster. This is shown in Fig. 5.

Figure 4: The logarithm of the density of vibrational states multiplied by the energy increment ΔE. Calculations with the polarizable (POL) and non-polarizable (NON-POL) potential function have been performed. The computed DOS is adjusted to the values of the harmonic model at energies close to the bottom of the well (solid lines).

Figure 5: Caloric curves calculated with the canonical ensemble and constant energy Molecular Dynamics averaging methods. A “phase transition” is predicted to occur at about 225 K.

The two curves coincide up to about 200 K and start to deviate after the phase transition point. The change of the slope in the caloric curve starts when the trajectory visits regions in configuration space with non planar geometries which of course is the result of the strong coupling of all degrees of freedom. However, we find that even at these energies the cluster spends substantial time in the regions of *cis* and *trans* minima. This is clearly shown in Fig. 2 where we have run a trajectory for 1 ns and at -15 kcal/mol total energy. The DOS calculated separately for the *trans* and *cis* isomers are presented in Fig. 6. Here, the calculations have been done with the non-polarizable model. They have been obtained by integrating the trajectories for a long time and checking at short time steps whether they have crossed the transition states. Points which are found in the *trans* region are used to construct the energy probability distributions for the *trans* isomer and points which correspond to *cis* are used to construct the *cis* energy distributions respectively. Comparisons with the harmonic approximation (dash lines) are also shown. Above -18 kcal/mol the two anharmonic DOS for the two isomers move parallelly whereas the harmonic curves cross at a higher energy. We use these results to compute the equilibrium constants for the isomerization reaction.

Figure 6: The logarithm of the density of vibrational states multiplied by the energy increment ΔE for the *trans* and *cis* isomers. The dash lines are the predictions of the harmonic model given by using the harmonic frequencies of each isomer.

Table 1 summarizes the rate and equilibrium constants for the two isomerization reactions (C $\rightarrow$ T) and its reverse (T $\rightarrow$ C). $\mathbf{K_h}$ are the rate constants obtained by fitting the distributions of isomerization events with the time to an exponential function $\exp(-\mathbf{K_h}t)$. $\mathbf{K_t}$ are the rate constants obtained from the average lifetime of the cluster in *trans* or *cis* region. $\mathbf{K^N_{eq}}$ is the equilibrium constant calculated as the ratio of the density of states obtained with the multiple histogram method, $\mathbf{K^h_{eq}}$ is the ratio of the rate constants for the C$\rightarrow$T and T$\rightarrow$C isomerization reactions, and finally, $\mathbf{K^t_{eq}}$ are the values obtained using the time average rate constants. All calculations have been done with the pair additive potential. The isomerization events used to obtain the values in Table 1 range from 3500 at energy -20 kcal/mol up to 65000 at the energy of -12 kcal/mol. The main remark we can make from the values of Table 1 is the stabilization of the rate constants and consequently of equilibrium constants, for energies above -18 kcal/mol. The equilibrium constants obtained from the DOS are lower than those obtained from the rate constants.

Table 1: Rate and equilibrium constants at several energies E (see text). The rate constants are measured in ps^{-1}.

	C → T		**T → C**				
E	$\mathbf{K_h}$	$\mathbf{K_t}$	$\mathbf{K_h}$	$\mathbf{K_t}$	$\mathbf{K^N_{eq}}$	$\mathbf{K^h_{eq}}$	$\mathbf{K^t_{eq}}$
-20.0	1.57	1.47	0.12	0.15	2.23	13.08	9.80
-19.0	2.42	2.13	0.70	0.84	0.76	3.45	2.53
-18.0	2.76	2.44	1.50	1.66	0.60	1.84	1.46
-17.0	2.86	3.56	3.14	3.86	0.61	0.91	0.92
-16.0	3.63	4.74	3.75	4.78	0.64	0.96	0.99
-15.0	4.25	5.25	3.81	5.23	0.64	1.11	1.00
-14.0	4.44	5.48	4.46	5.37	0.64	0.99	1.02
-13.0	4.80	5.73	4.92	5.77	0.64	0.97	0.99
-12.0	5.24	5.68	4.92	5.55	0.66	1.06	1.02

We have followed several trajectories in time and we have plotted snapshots of the cluster during its time evolution. Up to energies of -15 kcal/mol the sequence *trans-cis-trans-* ... or *cis-trans-cis-*... always found. Even in cases where we thought that we have transitions *cis* to *cis* (Fig. 7) examination of the cluster for shorter time steps and quenching the energy to reach the nearby minimum, revealed that the cluster visits successively the regions of *trans* and *cis*. We were not able to find any transition from *trans* to *trans* or from *cis* to *cis*.

Figure 7: Snapshots of the water tetramer from a trajectory at -17 kcal/mol. $\mathbf{C}_i$ denotes a *cis* isomer and **T** the *trans*. The black oxygens show the molecules on which a change in the orientation of the free hydrogens will happen.

This is understood since the barriers between non equivalent minima are lower than the barriers between symmetric minima. The equilibrium constants above -18 kcal/mol approach the value of one which means that now the cluster spends equivalent amounts of time in both areas, *cis* and *trans*. There is a lot of activity in the motion of the free hydrogens which we describe as irregular. Indeed, we have computed the Maximum Lyapunov Characteristic Number (MLCN) at several energies and they converge to positive numbers. These are shown in Fig. 8. The inverse of the MLCN has the dimension of time and represents the time needed for the system to forget its initial conditions. We have conjectured[28,29] that the MLCN is an upper bound of the RRKM rate constant, since for a statistical theory like RRKM it is necessary to have complete randomization of the energy among all the involved degrees of freedom. Our calculations confirm this conjecture as can be seen from Table 1 and Fig. 8.

Figure 8: The average rate of exponential divergence of two initially neighboring trajectories with time. The converged values for the Maximum Lyapunov Characteristic Numbers are: -20.0 (2.58), -19.0 (4.08), -18.0 (4.92), -17.0 (5.43), -16.0 (5.79), -15.0 (6.24), -14.0 (6.64), -13.0 (7.04), -12.0 (7.74), -11.0 (8.31). Units in ps^{-1}.

4. CONCLUSIONS

We have carried out a classical mechanical analysis of the dynamics of water tetramer using an empirical potential function (CKL) to describe the interactions of rigid molecules. The CKL potential has a pair additive part plus polarization terms.

The characteristic of the dynamics of water tetramer is the weak coupling of the torsional motions of the free hydrogens with the degrees of freedom of hydrogen bonds. The four free hydrogen atoms, one on each water molecule, rotate in an erratic way. The chaotic rotations of the hydrogen atoms is deduced from the positive Maximum Lyapunov Characteristic Numbers computed at several energies.

The densities of vibrational states obtained with the multiple histogram method and the Nosé-Hoover canonical dynamics are found to be smaller than the predictions of harmonic models which include all the degrees of freedom of the cluster (18 degrees of freedom for rigid molecules). We attribute this results to the weak coupling of the torsional degrees of freedom to the hydrogen bonds.

The MLCN have been interpreted as upper bounds of the RRKM rate constants. For the particular case of water tetramer we find good agreement of the isomerization rate constants with the MLCN which we attribute to an early ergodic behaviour of the trajectories in the subspace of the free hydrogens.

ACKNOWLEDGMENTS

This work was financially supported by the Greek secretariat for research and technology, PENED-1994 (15774/296).

References

[1] K. Liu, J. D. Cruzan, and R. J. Saykally. *Science*, 271:929, 1996.

[2] J. D. Cruzan, L. B. Braly, K. Liu, M. G. Brown, J. G. Loeser, and R. J. Saykally. *Science*, 271:59, 1996.

[3] J. D. Cruzan, M. G. Brown, K. Liu, L. B. Braly, and R. J. Saykally. *J. Chem. Phys.*, 105:6634, 1996.

[4] S. S. Xantheas, and T. H. Dunning, Jr. *J. Chem. Phys.*, 98:8037, 1993.

[5] S. S. Xantheas, and T. H. Dunning, Jr. *J. Chem. Phys.*, 99:8774, 1993.

[6] M. Schutz, W. Klopper, H-P. Luthi, and S. Leutwyler. *J. Chem. Phys.*, 103:6114, 1995.

[7] J. K. Gregory, and D. C. Clary. *J. Chem. Phys.*, 105:6626, 1996.

[8] P. Cieplak, P. Kollman, and T. Lybrand. *J. Chem. Phys.*, 92:6755, 1990.

[9] O. Matsuoka, E. Clementi, and M. Yoshimine. *J. Chem. Phys.*, 64:1351, 1976.

[10] K. S. Kim, M. Dupuis, G. C. Lie, and E. Clementi. *Chem. Phys. Letters*, 131:451, 1986.

[11] W. Klopper and M. Schutz. *Ber. Bunsenges. Phys. Chem.*, 99:469, 1995.

[12] Ch. Lee, H. Chen, and G. Fitzgerald. *J. Chem. Phys.*, 102:1266, 1995.

[13] C. J. Tsai, and K. D. Jordan. *J. Chem. Phys.*, 95:3850, 1991.

[14] C. J. Tsai, and K. D. Jordan. *J. Phys. Chem.*, 97:5208, 1993.

[15] A. Vegiri, and S. C. Farantos. *J. Chem. Phys.*, 98:4059, 1993.

[16] S. C. Farantos, S. Kapetanakis, and A. Vegiri. *J. Phys. Chem.*, 97:12158, 1993.

[17] D. J. Wales, and T. R. Walsh. *J. Chem. Phys.*, 106:7193, 1997.

[18] C. Millot, and A. J. Stone. *Mol. Phys.*, 77:439, 1992.

[19] S. W. Benson, and E. D. Siebert. *J. Am. Chem. Soc.*, 114:4269, 1992.

[20] S. Nosé. *Mol. Phys.*, 52:255, 1984.

[21] S. Nosé. *J. Chem. Phys.*, 81:511, 1984.

[22] W. G. Hoover. *Phys. Rev. A*, 31:1695, 1985.

[23] B. R. Eggen, A. J. Marks, J. N. Murrell, and S. C. Farantos. *Chem. Phys. Letters*, 219:247, 1994.

[24] S. C. Farantos. *Z. Phys. D*, 31:213, 1994.

[25] S. Weerasinghe, and F.G. Amar. *J. Chem. Phys.*, 98:4967, 1993.

[26] L. D. Landau, and E. M. Lifshitz. *Statistical Mechanics.* Pergamon Press, New York, 1970.

[27] D.J. Wales. *Mol. Phys.*, 78:151, 1993.

[28] S. C. Farantos. *Chem. Phys. Letters*, 92:379, 1982.

[29] S. C. Farantos. *J. Phys. Chem.*, 87:5061, 1983.