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Ł. Walewski[1,2], **P. Bała**[3], **and B. Lesyng**[1]

[1] Department of Biophysics, Faculty of Physics, University of Warsaw,
Żwirki i Wigury 93, 02-089 Warszawa, Poland
E-mail: lesyng@icm.edu.pl

[2] Interdisciplinary Centre for Mathematical and Computational Modelling,
Pawińskiego 5a, 02-106 Warszawa, Poland
E-mail: ljw@icm.edu.pl

[3] Department of Mathematics and Computer Science, N. Copernicus University,
Chopina 12/18, 87-100 Toruń, Poland
E-mail: bala@mat.uni.torun.pl

MD simulations of many body quantum-classical systems is of big importance for the description of functioning of many (bio)molecular and nanosystems. Porphycene containing two strongly coupled quantum protons in a classical molecular scaffold is a model system which is used by us to develop novel methodological QCMD approaches. The system is also of practical importance for molecular nanotechnologies. Energy profiles for the proton motions in porhycene have already been studied by us using an SCC-DFTB approach[1], however, classical MD simulations were not sufficiently precise to determine effective barriers for the proton transfer. Since the quantum dynamical motions of the protons have considerable impact on the motions of the classical atoms and vice versa, in the current approach the whole system is simulated using a steered Path Integral Molecular Dynamics (PIMD) method with an on the fly Car-Parrinello DFT propagation scheme for all nuclei, and with the adiabatic QD of the electrons[2]. Such approach together with thermodynamic sampling of the conformational space provides realistic energy profiles along the reaction pathways for the protons motions. The method requires massively parallel computer systems to carry out simulations for real systems.

1 Introduction

In previous studies proton transfer reaction pathways in porphycene were determined[3]. The pathways *trans → ts-A → cis-A* and *trans → ss-A → trans* are low energy pathways. They contain barriers of 5 kcal/mol and 7.5 kcal/mol, respectively. The former participates in the stepwise mechanism of the double proton transfer reaction that requires two consecutive transitions of this type. The latter describes the concerted reaction mechanism. They are both accessible for the system in 300 K. The high energy pathways – *trans → ts-B → cis-B* and *trans → ss-B → cis-B* contain barriers of 43 and 64 kcal/mol, respectively, and are statistically irrelevant at 300 K. The aim of the computations carried out at NIC was to get mean-field energy profiles for selected proton-transfer pathways and to compare results of the standard Car-Parrinello Molecular Dynamics (CPMD) method with the Path Integral Molecular Dynamics (PIMD) approach. This comparison can reveal the influence of nuclear quantum effects, such as tunneling, on the reaction energy barriers.

Table 1. Relative energies between stationary points on the porphycene potential energy surface (PES) computed with different DFT functionals. Plane wave expansion cutoff (E_{cut}) is in Ry, energy in kcal/mol. Calculations with 120 and 70 Ry cutoffs where carried out using the Trouiller-Martins normconserving pseudopotentials, while those with 40 and 25 Ry cutoffs with the Vanderbilt ultrasoft ones. Structure names follow ref.[3], scheme 2 and 3.

Functional	E_{cut}	Structure						
		trans	*cis-A*	*ts-A*	*ss-A*	*cis-B*	*ts-B*	*ss-B*
B3LYP/TZ2P[a]	–	0.0	2.4	4.9	7.6	28.8	43.0	64.4
PZB	70	0.0	2.5	4.9	7.5	26.9	40.9	29.5
BLYP	120	0.0	2.1	3.9	5.9	28.5	40.7	30.7
	40	0.0	2.0	3.7	5.4	28.2	40.3	30.6
	25	0.0	2.4	3.5	5.1	27.9	39.9	30.4
PBE	120	0.0	1.5	2.4	3.5	30.3	39.5	32.2
	40	0.0	1.6	2.3	3.1	30.3	39.3	32.2
	25	0.0	1.5	1.9	2.5	30.2	39.0	32.2
BP	120	0.0	1.6	2.5	3.6	30.4	39.7	32.3
	40	0.0	1.6	2.4	3.3	30.2	39.6	32.1
	25	0.0	1.8	2.2	2.3	29.7	39.0	31.6

[a] Values cited from ref.[3] for comparison.

2   Selection of the Exchange-Correlation Potential

Locations of known stationary points on the potential energy surface (PES) of porphycene were optimized using a number of Density Functional Theory (DFT) approximations. Since Perdew, Zunger, Becke[4,5] gradient corrected exchange-correlation functional (PZB) was already successfully applied for the proton transfer reaction in malonaldehyde by other group[6] it was treated as the most trustworthy one. Other widely used functionals (BLYP, PBE and BP) were also tested. All results were compared with reference values of Kozlowski[3] *et al*. Plane wave expansion of valence orbitals and atomic pseudopotentials for the core electrons were used with different cutoff values. For results see Table 1.

In most cases lowering the expansion cutoff results in lowering the relative energies of the transition states and local minima of the energy landscape. The energy values with higher cutoff are closer to the reference values. The PZB functional with 70 Ry cutoff gives nearly the same results as B3LYP with TZ2P basis set in the low energy region, i.e. for the "A" pathways. In high energy region (the "B" pathways) the differences of 2 kcal/mol occur for *cis-B* and *ts-B* states, which is acceptable, however for *ss-B* a large difference of 35 kcal/mol appears. Although the discrepancy is large, the "B" pathway is not accessible for the system at room temperature, and we accept the PZB results with 70 Ry. The BLYP values with 120 Ry cutoff are also acceptable since the deviation from the reference energy is only 1.5 kcal/mol. It should be noted that reduction of the cutoff value causes significant gain in terms of the computing time. With this in mind one may consider the BLYP functional with 25 Ry cutoff as a promising choice for faster, although less accurate computations. The PBE and BP functionals significantly underestimate the energy barrier values for the "A" pathways (more than 50%), and are quite accurate in high energy region, which is however less interesting for our studies.

The PZB functional appeared to be the most accurate in describing the characteristic

points on the potential energy surface in comparison to previous *ab initio* studies. Therefore it was chosen for further calculations.

3 Free Energy Profiles

The calculation of the free energy profiles was carried out *via* thermodynamic integration in the "blue moon ensemble"[7]. In this approach the reaction pathway is divided into steps covering relevant values of the reaction coordinate. Then for each reaction step a constrained molecular dynamics run is carried out with the reaction coordinate being fixed at certain value by molecular constraints. Free energy derivatives are averaged over each run and integrated to give a free energy profile. This procedure was applied twice: with all atomic nuclei treated classically with CPMD, and with all atomic nuclei treated quantum-dynamically with PIMD. In the latter case the nuclei were quantized using 16 imaginary time-slices (see Figure 1 for visualization). The NVT constrained dynamics simulations were carried out in a 17 Å cubic box.

Two low energy reaction pathways in porphycene were studied. Calculations for *trans* → *ts-A* → *cis-A* and *trans* → *ss-A* → *trans* pathways were carried out using the CPMD and PIMD approaches. The former pathway was divided into 17 and 9 reaction steps, applying CPMD and PIMD, respectively. For the latter case, 10 reaction steps were used for only one half of the pathway, because the *trans* → *ss-A* transition is symmetrical to the *ss-A* → *trans* one. The total of number of 4000 steps of the constrained dynamics simulation was carried out for each reaction step, in each case. The time-step was 3 a.u. Fictitious electron mass was set to 350 a.u. for CPMD, and 300 a.u. for PIMD. Temperature of the Nose-Hoover thermostat was set to 300 K.

Figure 1. Path integral configuration of *trans* porphycene. Each nucleus is represented by cyclic polymer of 16 *beads*.

Figure 2 shows free energy profiles for the two pathways in porphycene computed from the averaged constraint forces. Averaging was carried out over the converged parts of the trajectories in order to avoid nonequilibrium regions.

The static calculations of the barrier height for the double proton transfer in porphycene on the *trans* → *ts-A* → *cis-A* pathway is 4.9 kcal/mol (see Table 1). Inclusion of classical thermal vibrations at 300 K increases the barrier by 1.4 kcal/mol to 6.3 kcal/mol. This is rather unexpected since the thermal vibrations should rather reduce the barrier. This may be the evidence of larger error of the method originating from poor equilibration of the system on one hand and small data set for the statistical averaging on the other. Taking this into account one would assume the error bar to be around 1 kcal/mol. Taking into account the quantum nature of the nuclei within the PIMD model reduces the barrier height to 1.8 kcal/mol (Fig. 2(a)). This can be treated as an expected result.

Interestingly the *cis-A* configuration turns out to be much more stable in the PIMD model than in the CPMD one. The free energy difference is about 3 kcal/mol, which is
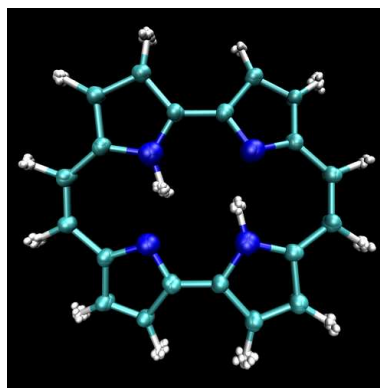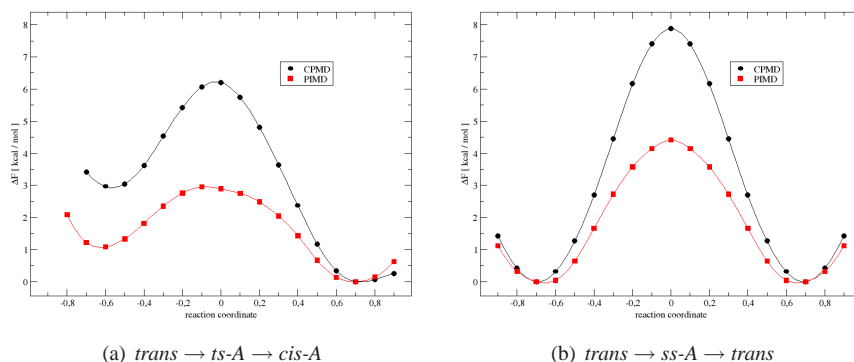
(a) *trans → ts-A → cis-A*

(b) *trans → ss-A → trans*

Figure 2. CPMD and PIMD free energy profiles for two reaction pathways in porphycene.

a significant effect even assumed a 1 kcal/mol error. This results in equal barrier heights for the transitions in both directions: the *trans → cis-A* barrier is approximately equal to the *cis-A → trans* barrier which yields 1.8 kcal/mol. This makes the *trans* and *cis-A* states practically indistinguishable, which is not the case for the CPMD model where the 'forward' barrier is 6.3 kcal/mol while the 'reverse' one yields 3.0 kcal/mol.

The *trans → ss-A → trans* pathway leads through the classical barrier of 7.5 kcal/mol. Applying the CPMD integration the barrier height is slightly higher and equals 7.9 kcal/mol which is consistent with the tendency observed previously. The PIMD computations show the low barrier of 4.4 kcal/mol.

4   Conclusions

The obtained so far results show that inclusion of nuclear quantum effects reduces the free energy barrier for the proton transfer reaction in porphycene. The *trans → ts-A → cis-A* pathway showed a 4.5 kcal/mol reduction of the barrier height. Qualitatively, it is expected, however, exact values of the free energy barriers require further refinement, carrying out longer simulations. Some difficulties in averaging the free energy derivatives in the process of thermodynamic integration result mostly from not fully equilibrated constrained dynamics trajectories.

The goal of comparing the free energy profiles of the two low-energy proton-transfer reactions in porphycene, i.e. concerted vs stepwise one between two symmetrical *trans* isomers, could not be completed yet, since we were not able to carry out the PIMD calculations of the *trans → ss-A → trans* pathway based on the NIC granted resources. Computations are being carried out.

The presented results may also suggest that a more precise description of the double proton transfer mechanism would require even a more sophisticated approach. This could account for a two-particle quantum state, which is the two-proton wave function defined on a spatial grid. The dynamics of such system should be governed by the time-dependent Schrödinger equation. The Hamiltonian should then contain terms describing the interactions between the two-particle, proton wave function and the classical ionic environment forming the molecular skeleton.

Acknowledgments

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