

# Environmental effects on the excited state dynamics of DNA constituents : a quantum mechanical approach

Roberto Improta<sup>1</sup>, Fabrizio Santoro<sup>2</sup>, Alessandro Lami<sup>2</sup> Vincenzo Barone<sup>2</sup>

<sup>1</sup> *Dipartimento di Chimica and INSTM-Village, Università Federico II, Complesso Monte S. Angelo, via Cintia, I-80126 Napoli, Italy*

<sup>2</sup> *Istituto per i Processi Chimico-Fisici - CNR, Area della Ricerca del CNR Via Moruzzi,1 I-56124 Pisa, Italy*  
e-mail:robimp@unina.it

**Abstract.** By integrating the latest advances in time-dependent density functional theory and in the continuum solvation models we show that it is possible to get an accurate description of the excited state behavior of sizeable systems in solution. A detailed atomistic picture of the UV absorption by DNA oligomers, and of the subsequent excited state decay and emission, is presented. Important steps towards a quantum dynamical treatment of the excited state decay, taking solvent effect into account, have been made.

We have studied the static<sup>1-7</sup> and dynamical behavior of the DNA and of its constituents in their excited states, with special focus on solvent effect and on the influence of base stacking and base pairing.

Quantum mechanical calculations, rooted in the density functional theory (DFT) and in its time-dependent extension (TD-DFT), have been used to study adenine stacked oligomers and the double strand tetramer formed by two thymine-adenine stacked pairs in aqueous solution, providing absorption and emission spectra in very good agreement with their experimental counterpart. The long living components of the excited state population of (dA).(dT) oligomers correspond to a dark excimer produced by inter-monomer charge transfer between two stacked adenine bases, whereas adenine-thymine proton transfer plays a minor role in the excited state decay.

Solvent effect on the excited state dynamics of uracil derivatives has been studied on models including the nucleobases and four water molecules of the first solvation shell, taking into account bulk solvent effect by means of the Polarizable Continuum Model. Excited state geometry optimizations in solution and extensive explorations of the excited-state surfaces (PES) in the Franck-Condon region, performed at the PCM/TD-DFT level, show that solvent can modulate the accessibility of an additional decay channel, involving a dark  $n/\pi^*$  excited state.

On the ground of the ab initio PES, fully quantum dynamical calculations have been performed for Uracil in acetonitrile and in water, which indicate that, within  $\sim 50$  fs,  $\sim 30$  % of the population of the bright state decays to the dark state. This estimate is fully consistent with the result of transient absorption experiments.

Finally, preliminary excited state Born-Oppenheimer classical trajectory calculations, performed by exploiting the PCM/TD-DFT energy and gradients, provide interesting indications on the statical and dynamical behavior of the first solvation shell, and on its dependence on the solute electronic state.

Our study provides the first unifying explanation for the experimental trend of pyrimidine excited-state lifetime in different solvents and give useful hints on the role played by solvent degrees of freedom in modulating the excited state decay in solution.

[1] T. Gustavsson, A. Banyasz, E. Lazzarotto, D. Markovitsi, G. Scalmani, M.J. Frisch, V. Barone and R. Improta *J. Am. Chem. Soc.* 128, 607 (2006)

[2] F. Santoro, V. Barone, T. Gustavsson and R. Improta *J. Am. Chem. Soc.* 128, 16312 (2006)

[3] Y. Mercier, F. Santoro, M. Reguero and R. Improta *J. Phys. Chem. B* in press

[4] F. Santoro, V. Barone and R. Improta *Proc. Nat. Acac. Sci. U.S.A.* 104, 9931 (2007)

[5] F. Santoro, V. Barone and R. Improta *J. Comput. Chem* 29, 957 (2008)

[6] R. Improta *Phys. Chem. Chem. Phys* 10, 2656 (2008)

[7] F. Santoro, V. Barone and R. Improta *Proc. Nat. Acac. Sci. U.S.A.* submitted