Excess electron localization and the associated strand breaks of DNA — a method survey

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1. Low energy electron (LEE) induced DNA Damages

$$H_2O \xrightarrow[Radiation]{Ionising} H_2O^+ + e^-$$

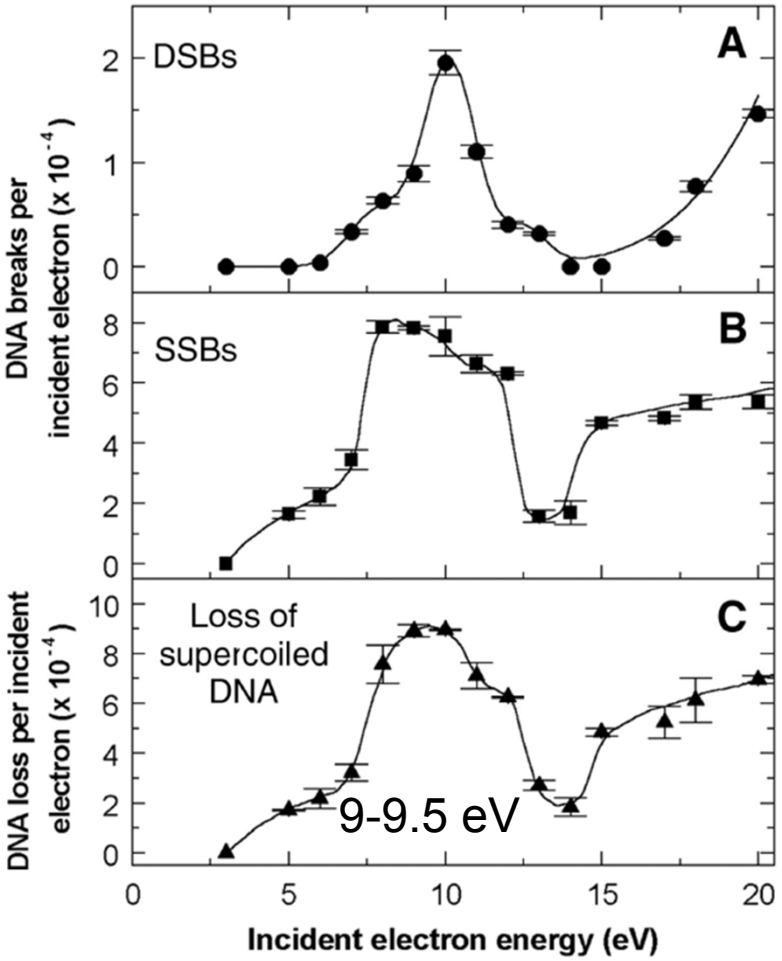
1Mev energy deposit: 5×10^4 secondary electron
LEE: the most abundant species produced by ionization of water

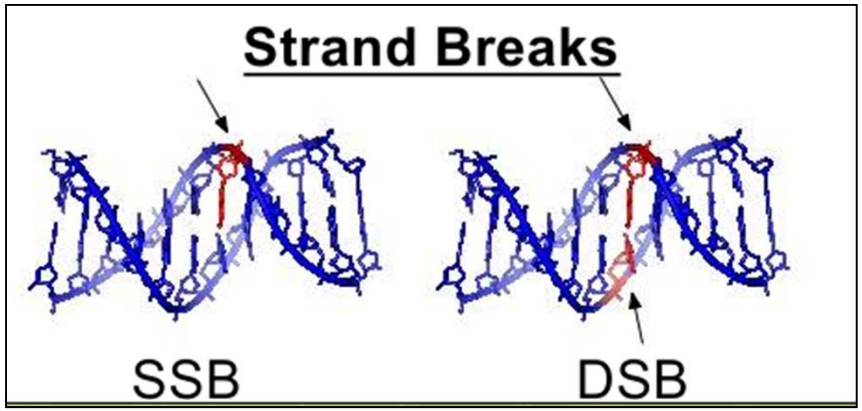
77 % of these electrons have energies below 20 eV,
56 % having energies below 8.76 eV (taken as the first ionisation potential in liquid water)
27 % of the secondary electrons and their daughters have energies between 0-1 eV.

V. Cobut Radiat. Phys. Chem., 51(3):229, 1998.
S. M. Pimblott Radiat. Phys. Chem., 76:1244, 2007.
E. Scifoni Phys. Rev. E, 81(2):021903, 2010.

LEE has been proved to be aggressive to DNA

-- at even lower energies down to zero kinetic energy





Boudaia et al, Science 287, 1659 (2000) and PRL

2. Methods (Self-interaction of excess electron)

- DFT
- SIC (a,b)
- Hybrid
  PBE0 (ADMM)
- Meta-GGA
  M06-2X
- UMP2

Criteria:

1. Electron structure

   spin density distribution: σ

2. Energy

a: vertical electron detachment energy:

$E_{VDE}=E(x)-E(X^-)$

b: Strand break:

Gas phases activation energy

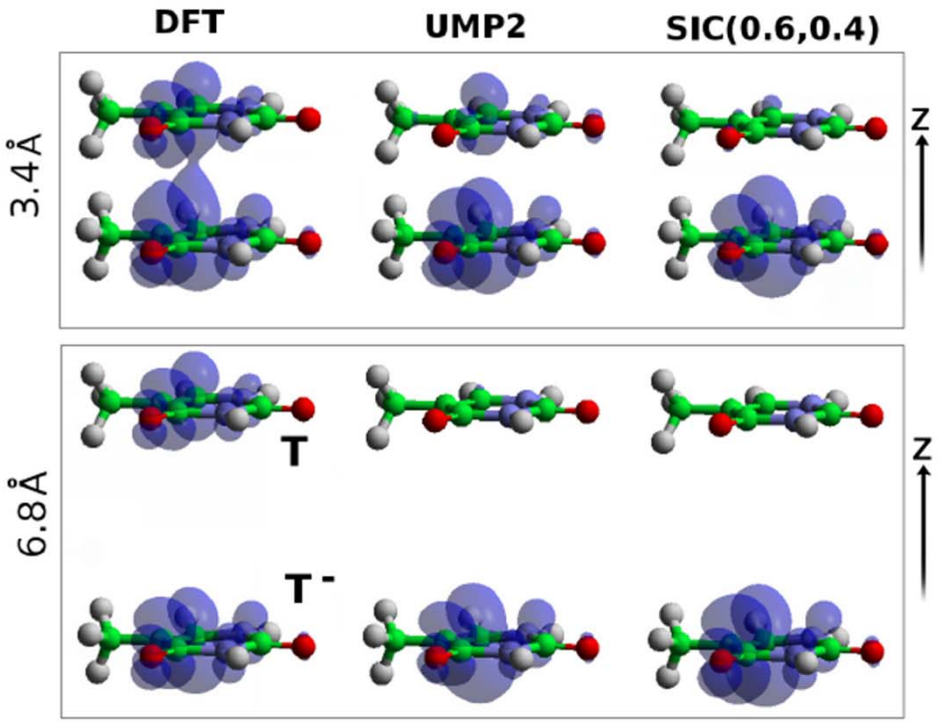
$E=E_{max}-E_{min}$

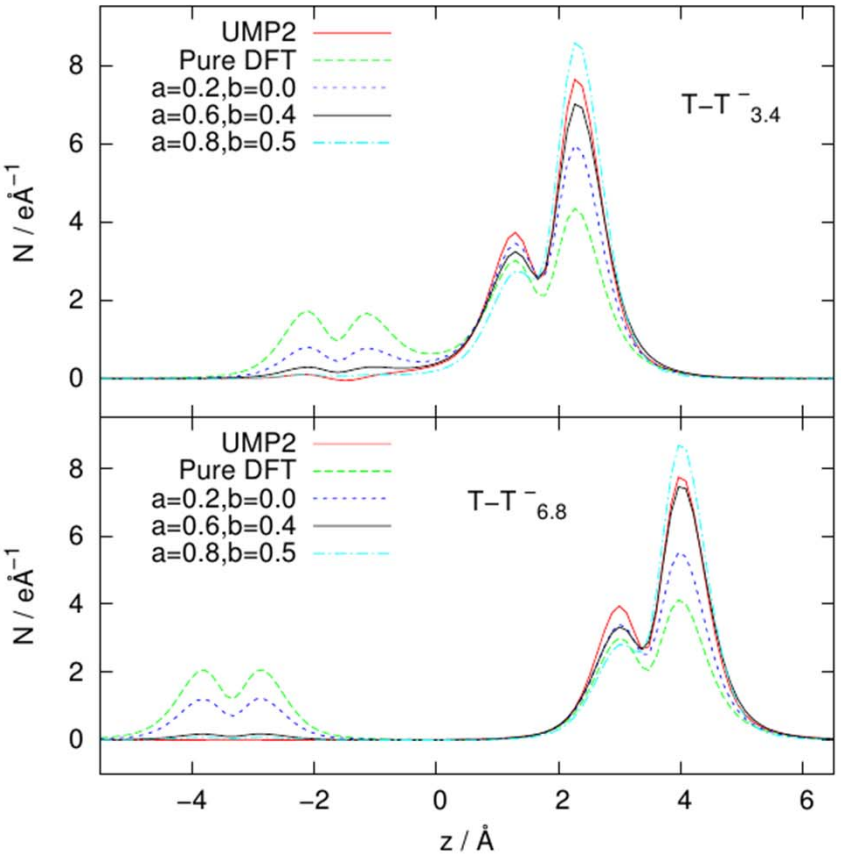
Free energy barrier

$$\Delta A(\xi_i) = -\int_{\xi_1}^{\xi_i} < \lambda(r') > dr'$$

3. Neutral and anionic Thymine base pair ($T\text{-}T^-$)

— results of the empirical SIC (Mauri-SPZ)



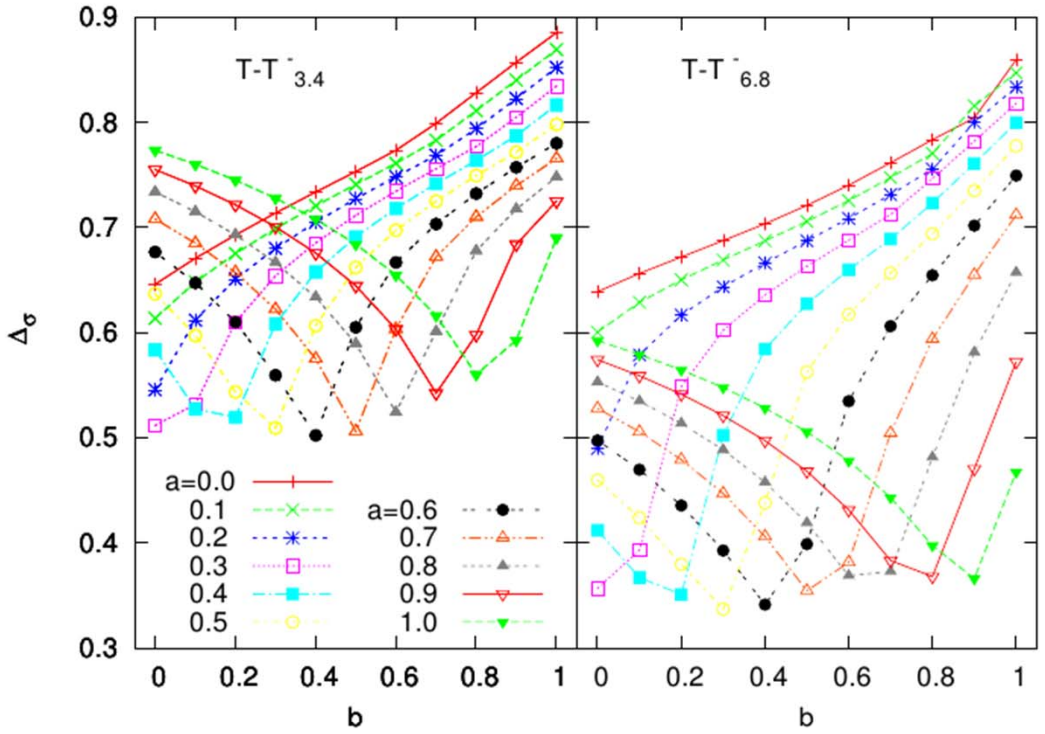


Joost Vande Vondele et al PCCP 2005 7 1363 OH radical (a=0.2,b=0.0)

Yves A Mantz et al JPCA 2007 111-1 105 stacked bases cation (0.8, 0.5)

3D Spin density difference:

$$\Delta_\sigma = \frac{\int |\sigma_{SIC} - \sigma_{UMP2}| dx dy dz}{\int |\sigma_{UMP2}| dx dy dz}$$



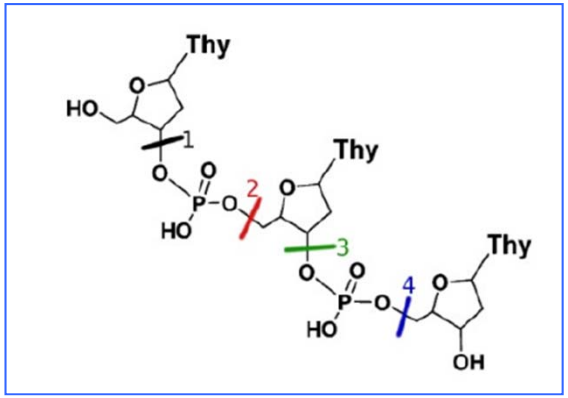
UMP2: NWChem
aug-cc-pvdz

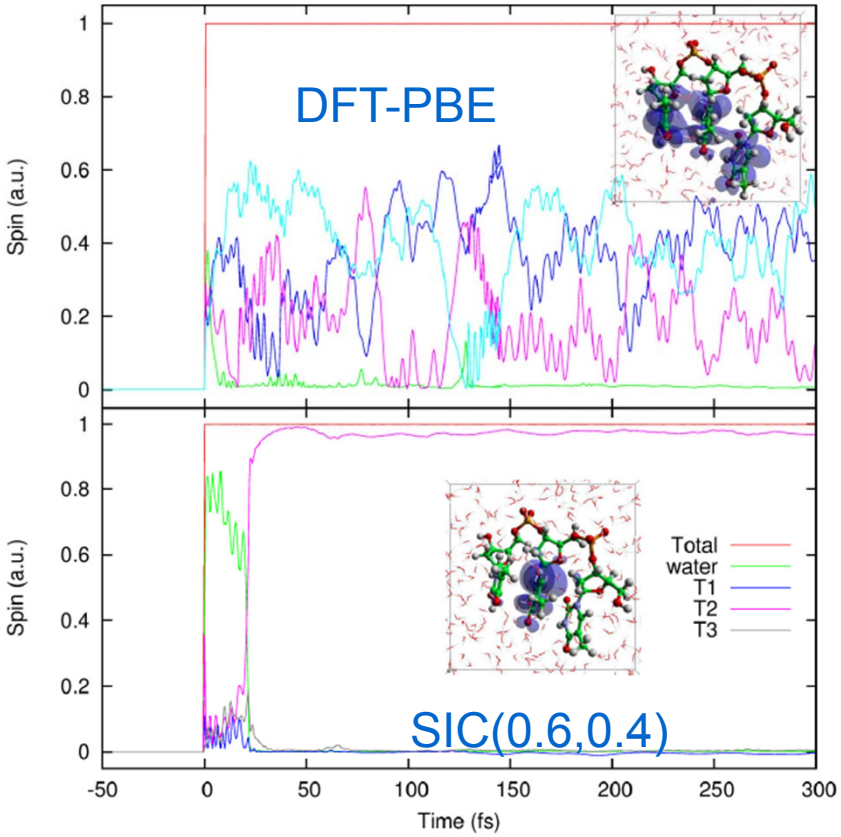
SIC(a,b): CP2K
aug-TZVP-GTH
GTH-PP
MT

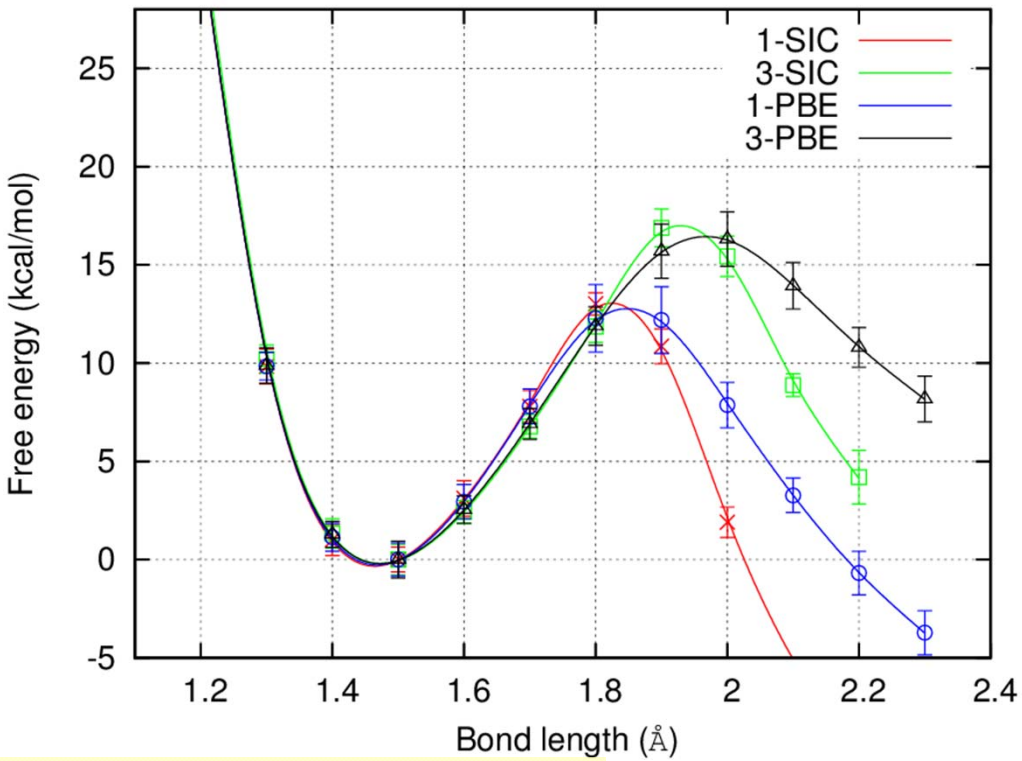
$$E_{VDE} = E(X) - E(X^-)$$

Configuration	UMP2	Pure DFT	(0.2,0.0)	(0.6,0.4)	(0.8,0.5)
$T\text{-}T^-_{3.4}$	0.53*	1.21	0.76	0.69	0.89
$T\text{-}T^-_{6.8}$	0.48*	1.14	0.64	0.75	0.78

DNA strand breaking Free energy:
aqueous solvent of $[dTdTdT]^-$

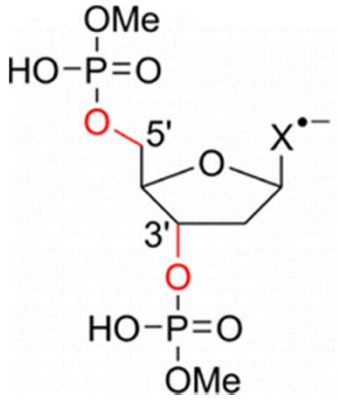






The SIC(a,b) --> localization,
but no change in Free energy barrier of bond breaking

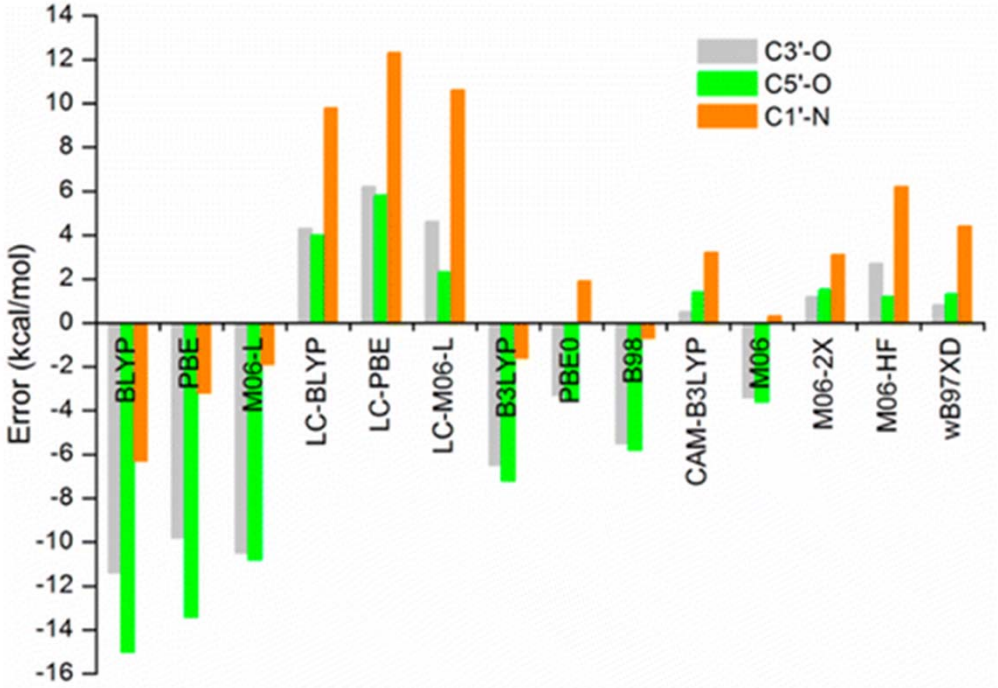
Hsing-Yin Chen et al JPCB 2014 118 11137



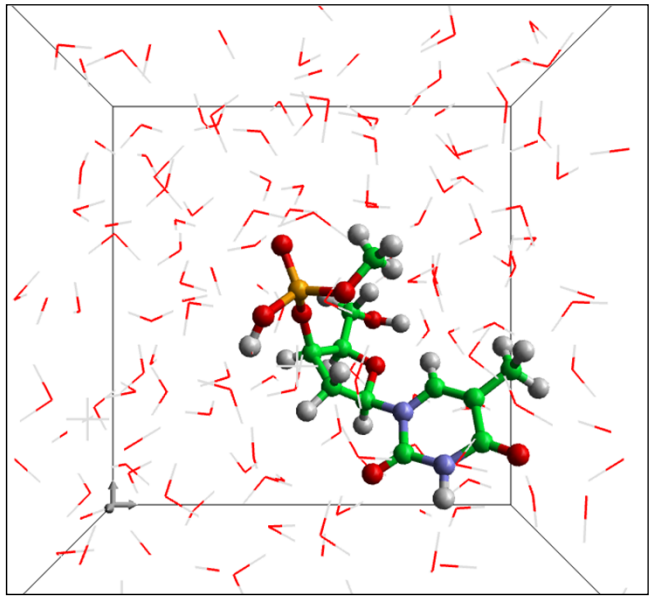
C–O bond-breaking barriers

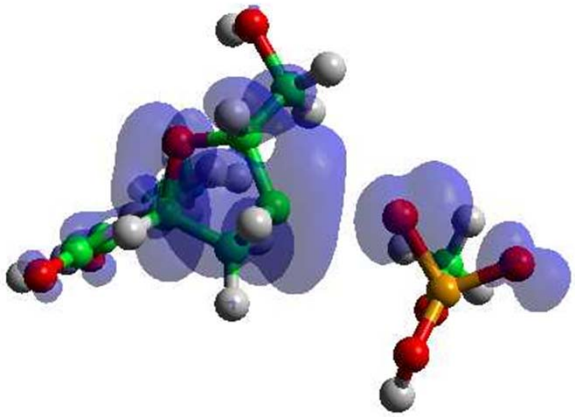
B3LYP: 6–14 kcal/mol

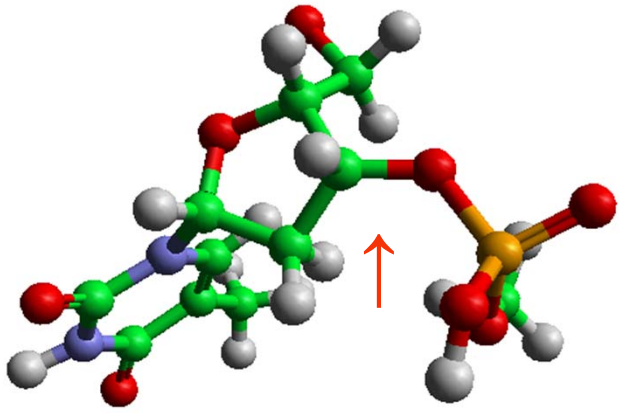
M06-2X: 17–24 kcal/mol



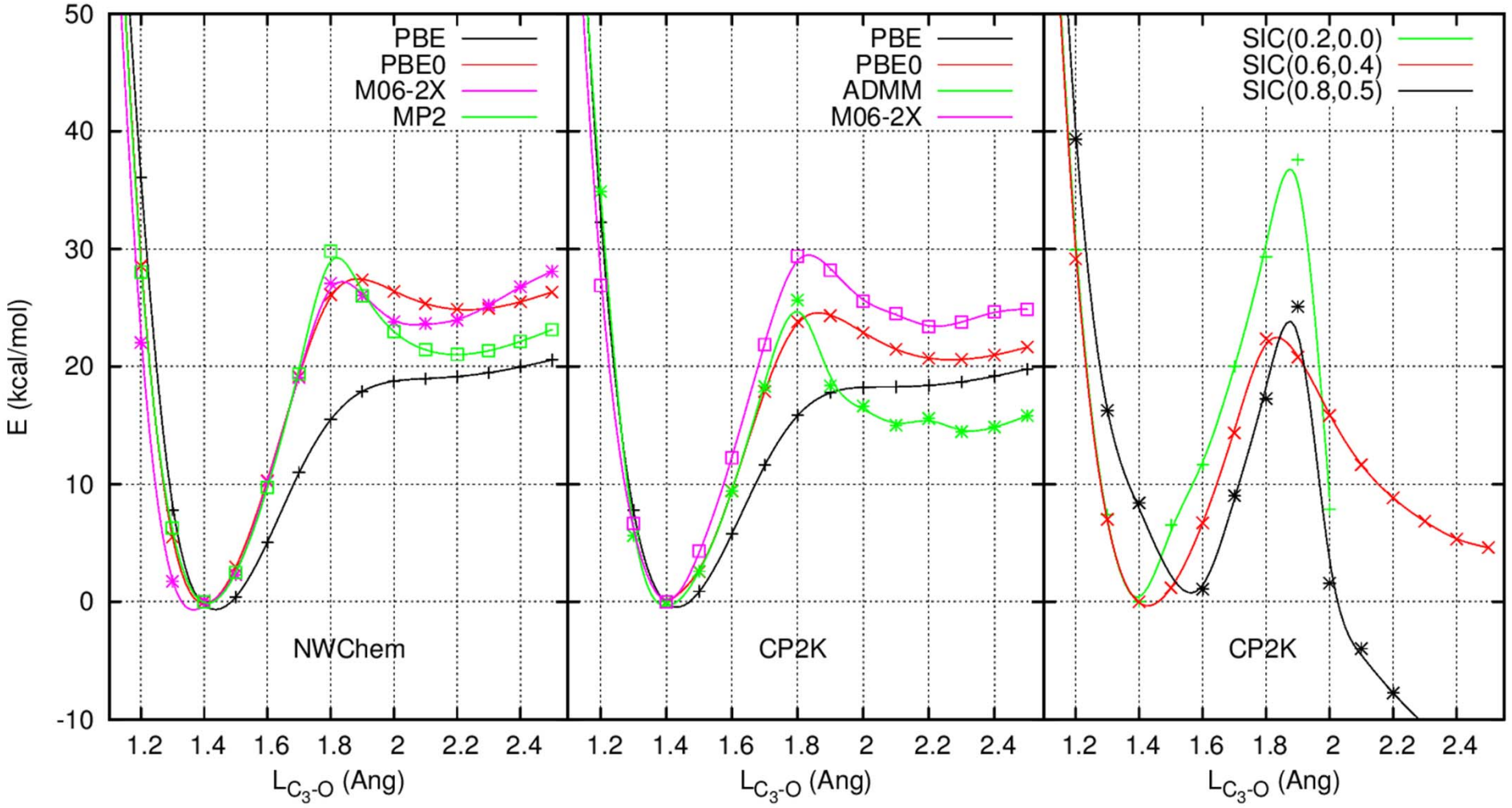
4. dTMP(m)$^-$ C_3-O bond dissociation barrier



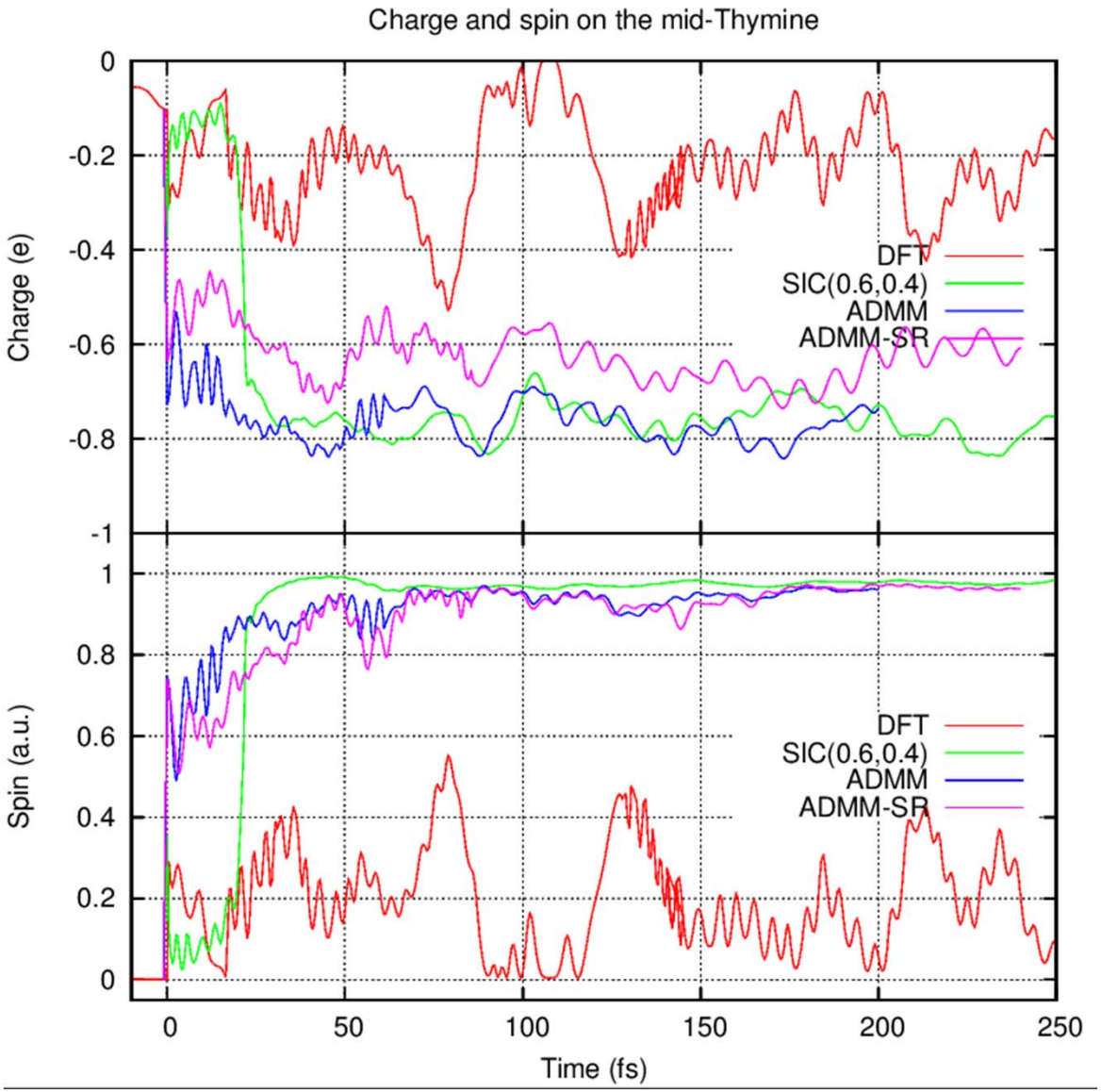


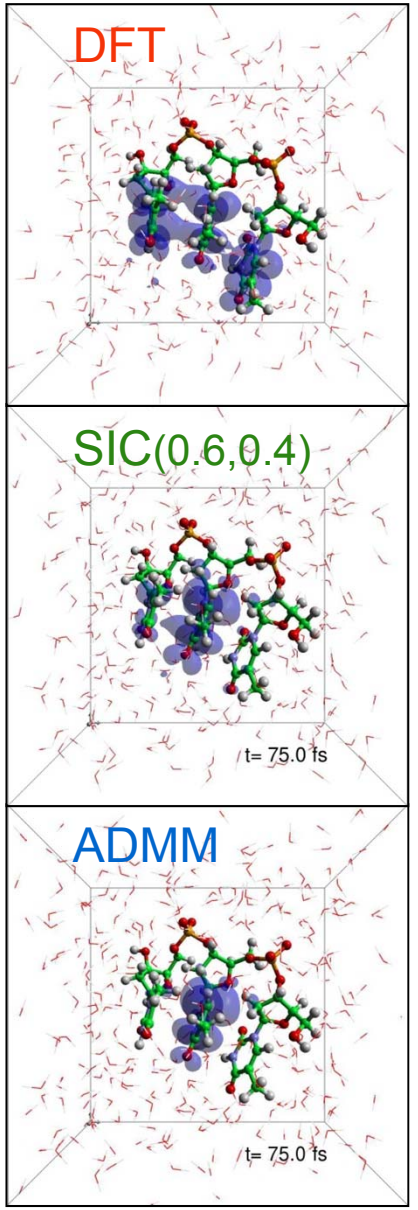


NWChem	CP2k	CP2k-SIC(a,b)
PBE aug-cc-pvdz	PBE all 6-311++G** | BASIS_SET aug-TZVP-GTH POTENTIAL GTH-PBE-qx HFX 0.2	BASIS_SET aug-TZVP-GTH POTENTIAL GTH-PBE-qx ROKS with OT SIC_METHOD MAURI_SPZ
PBE0 aug-cc-pvdz	PBE0 all 6-311++G** | BASIS_SET aug-TZVP-GTH POTENTIAL GTH-PBE-qx	
M06-2X aug-cc-pvdz	ADMM BASIS_SET TZV2P-MOLOPT-GTH AUX_FIT_BASIS_SET aug-pFIT3 POTENTIAL GTH-PBE-qx	
UMP2 aug-cc-pvdz	M06-2X FUNCTIONAL XC_MGGA_X_M06_2X XC_MGGA_C_M06_2X BASIS_SET aug-TZVP-GTH POTENTIAL GTH-PBE-qx HFX 0.54	


E (kcal/mol)
50
40
30
20
10
0
-10
1.2
1.4
1.6
1.8
2
2.2
2.4
$L_{C_3\text{-}O}$ (Ang)
PBE
PBE0
M06-2X
MP2
NWChem
PBE
PBE0
ADMM
M06-2X
CP2K
SIC(0.2,0.0)
SIC(0.6,0.4)
SIC(0.8,0.5)
CP2K

5. Condensed phases MD: $[dTdTdT]^-$





6. Conclusions and perspectives

a. Pure DFT: Not sufficient for DNA with excess electrons.
delocalization, bond stretching barrier

b. Gas phase
Hybrid (PBE0, ADMM), SIC(0.6,0.4), M06-2X: comparable with MP2 calculation.

c. Condensed phase
SIC(0.6,0.4) and ADMM: same electron structure
Free energy ? (in progress)

d. ADMM hybrid: promising in both efficiency and accuracy for condensed DNA systems with excess electron.

(not published)

Collaborators:

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- ✓ Gareth Tribello
- ✓ Maeve Smyth
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