Ionization and fragmentation of DNA-RNA bases induced by proton impact

"Experiments and calculations on doubly charged bases"

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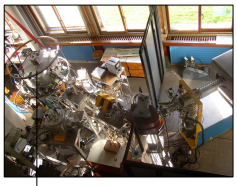
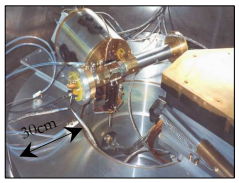
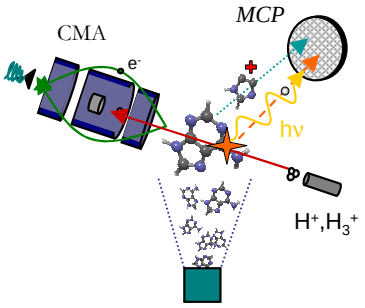
Experimental Setup



P = 10^{-8} T





Owen + powder (purity of 99%)
120°C : kt/2 =1.69 10^{-2} eV
(3N-6) degrees of freedom..

Projectile

- 100 keV protons (H^+), corresponding to the maximum LET in water <–> proton therapy interaction with bio-molecules.
- H_3^+ (25keV) <=> 3x 8.33keV
  Are used to normalize the cross sections in an absolute scale by measuring the 90° scattered protons (low impact parameter) [1]

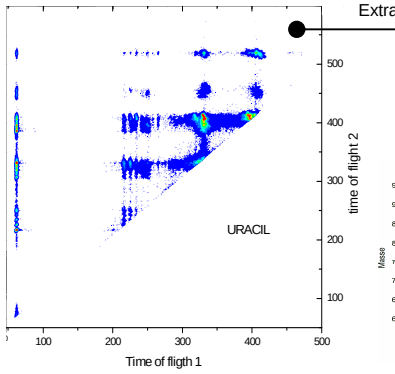
Detected particles

- Charged fragments by Time of Flight Mass Spectroscopy (multi-correlation) [2]
- 90° scattered protons
- *Emitted electrons – not detailed in this presentation –*

Not detected : Neutral and Anions

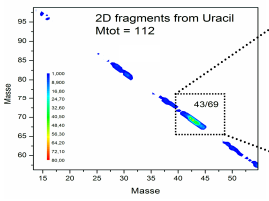
Results on Doubly Charged Bases : M + H^+ –> M^{2+*} –> (M_0) + M_1^+ + M_2^+

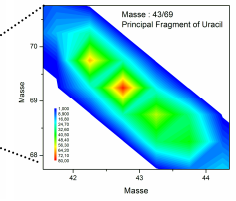
Uracil²⁺ : Fundamental State

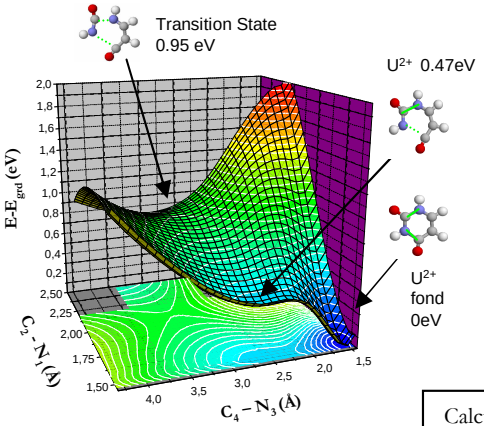


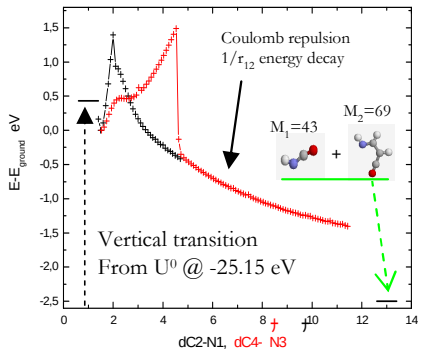
Extracted from TOF

M=43



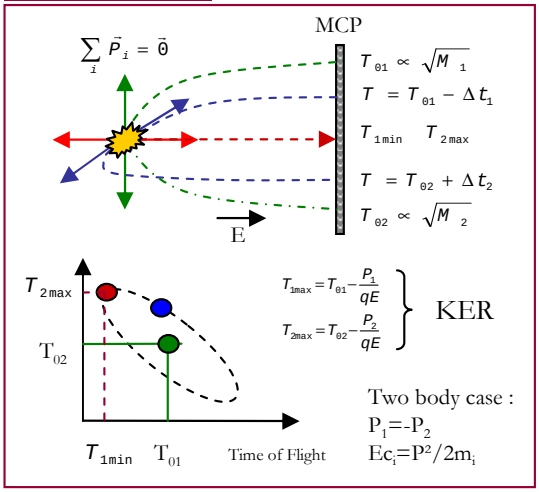






Calculated KER=0.95-(-2.5eV)≈**3.5eV**
Measured KER = **3.5 ± 0.5 eV !**

KER measurements



Calculations

- Mopac 2006-2007 (Semi-Empirical) [3]

  PM3 / AM1 : Neglected Differential Diatomic overlap integ. Approx and gaussians bases functions
  UHF : Unrestricted Hartree Fock method

  http://openmopac.net/

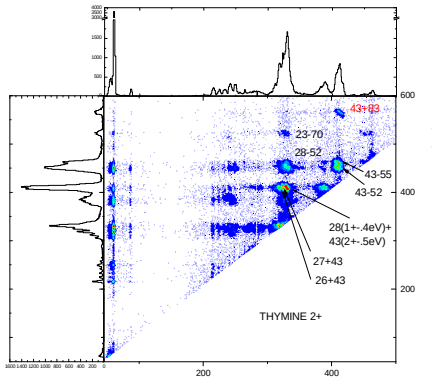
- Gamess – ab initio quantum chemistry calculation

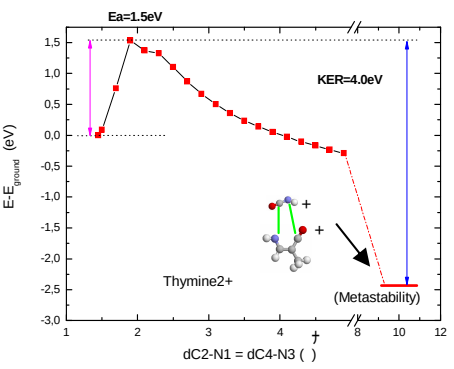
  http://www.msg.chem.iastate.edu/gamess/

References

[1] P. Moretto-Capelle et al., Phys. Rev. A, **74** (2006) 062705
[2] P.Moretto-Capelle et al, J.Chem.Phys.**127** (2007) 234311
[3] Stewart, J. J. P. *J. Comput. Chem. 10*, 209 (1989).
[4] M.W.Schmidt et al. J. Comput. Chem., 14, (1993) 1347-1363.

Thymine²⁺ - fundamental State

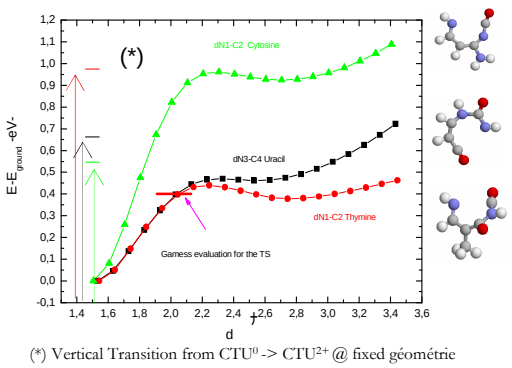




Calculated KER (43/83) = 4 eV
Measured KER = **3.9 ± 0.6eV !**

(*) Ker is overestimated in this calculation due to the dC2-N1=dC4-N3 (no rotation) conditions.

Comparison CTU²⁺ – Weak bond



(*) Vertical Transition from CTU^0 -> CTU^{2+} @ fixed géométrie

Uracil and Thymine N-C bonds breaks while doubly ionized from fundamental states. Cytosine N-C bond seems to be stronger but can be open anyway due to the oven heating (0.56 eV of internal energy @120°C)