COST 06

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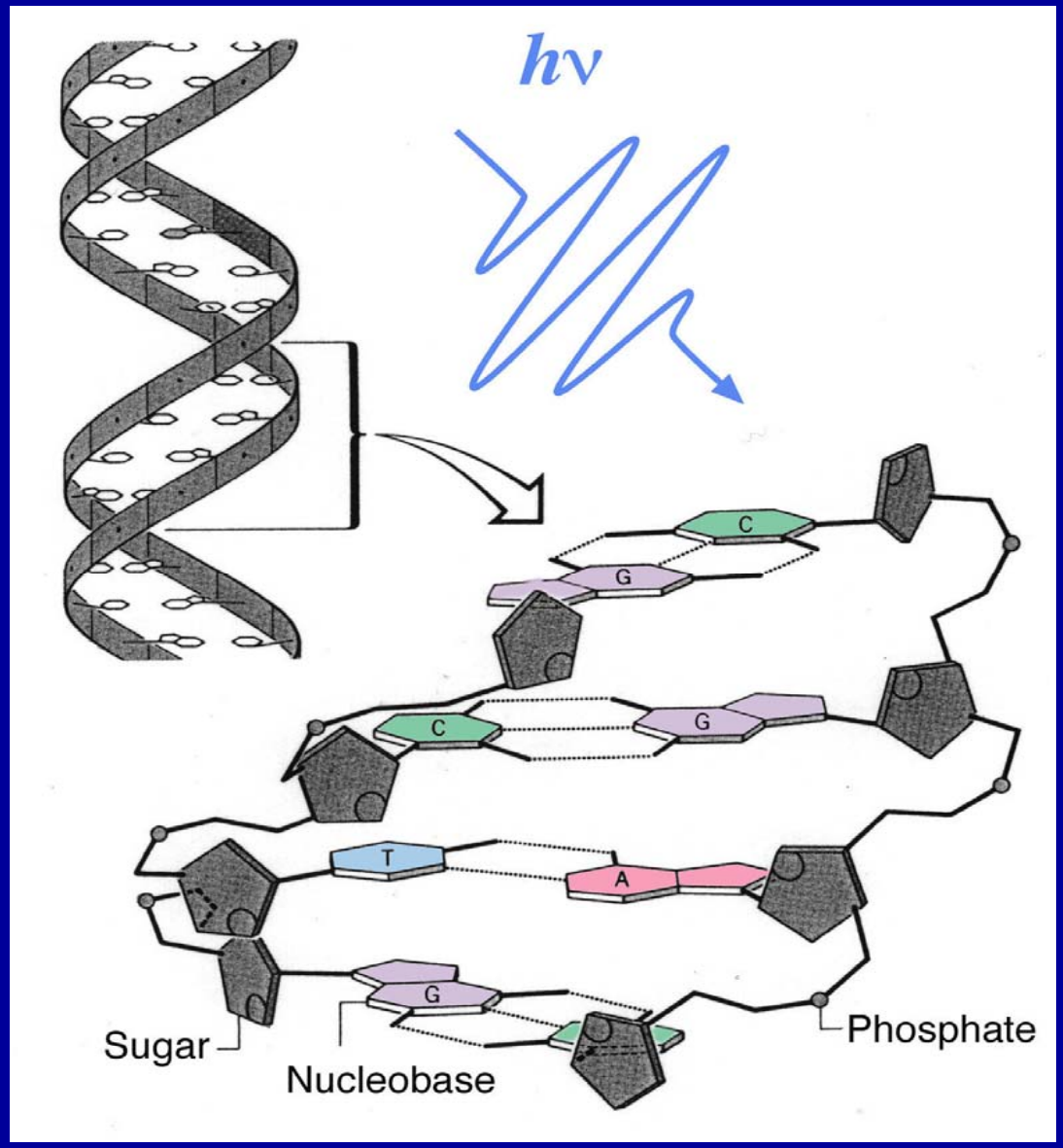
Electron driven reactions in biosystems

Eugen Illenberger

and coworkers

Institut fuer Chemie und Biochemie

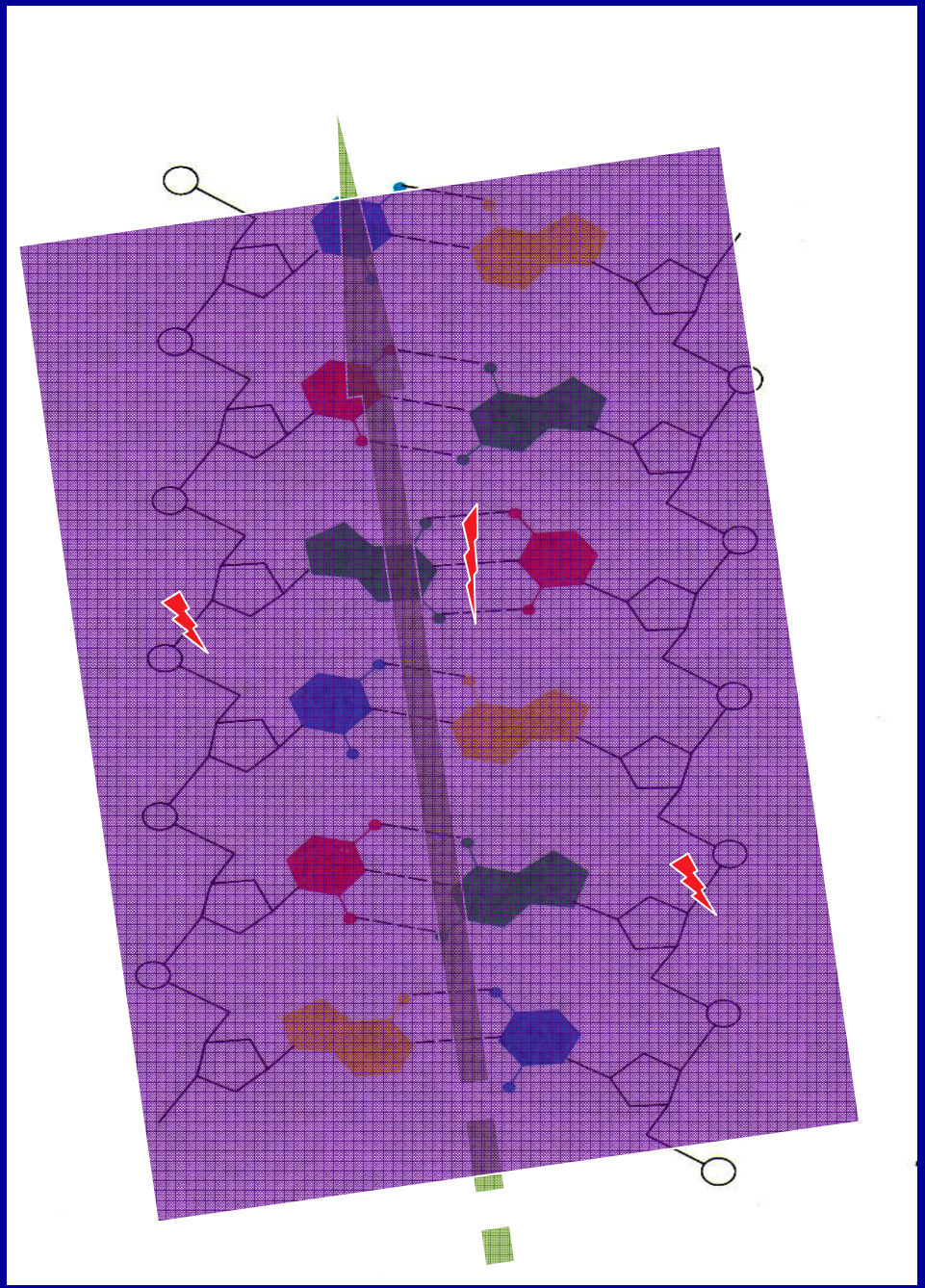
Physikalische und Theoretische Chemie



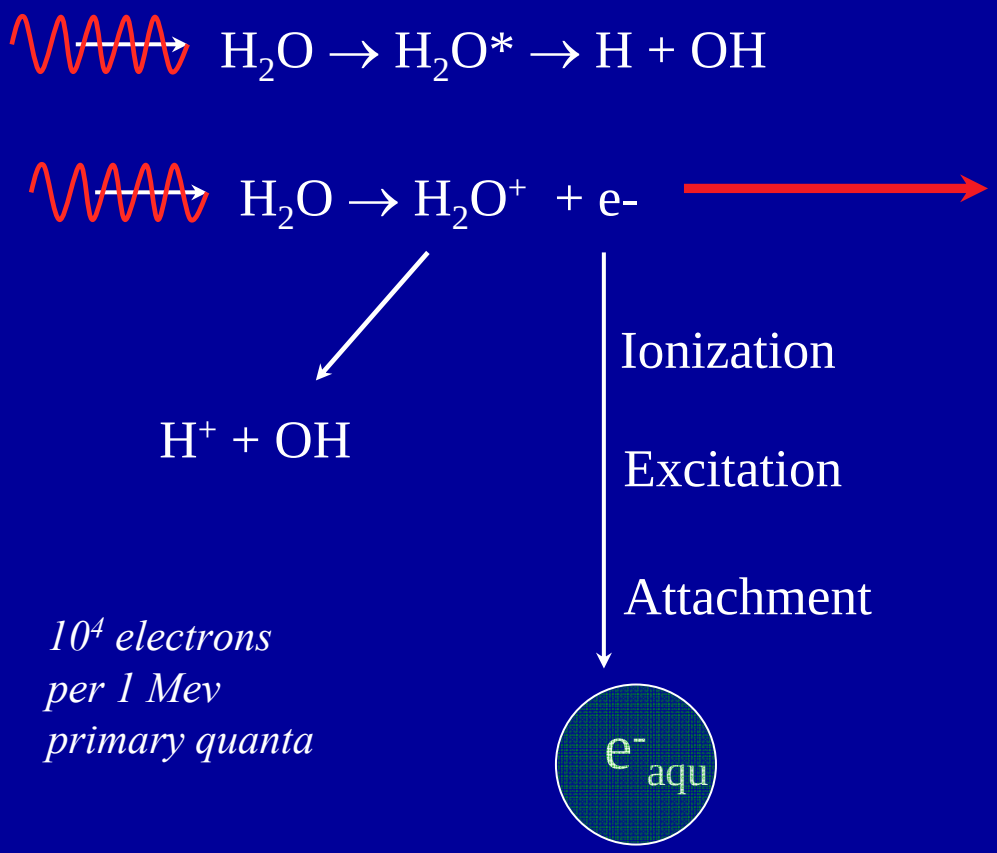
Radiation Damage

Cancer Therapy

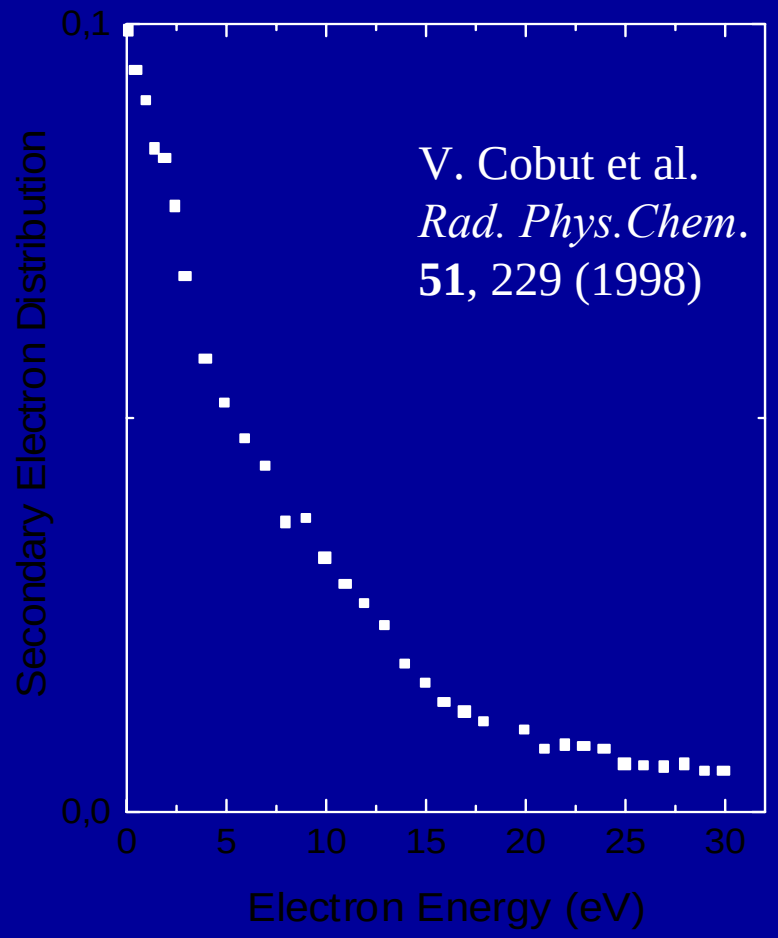
Electron driven rections



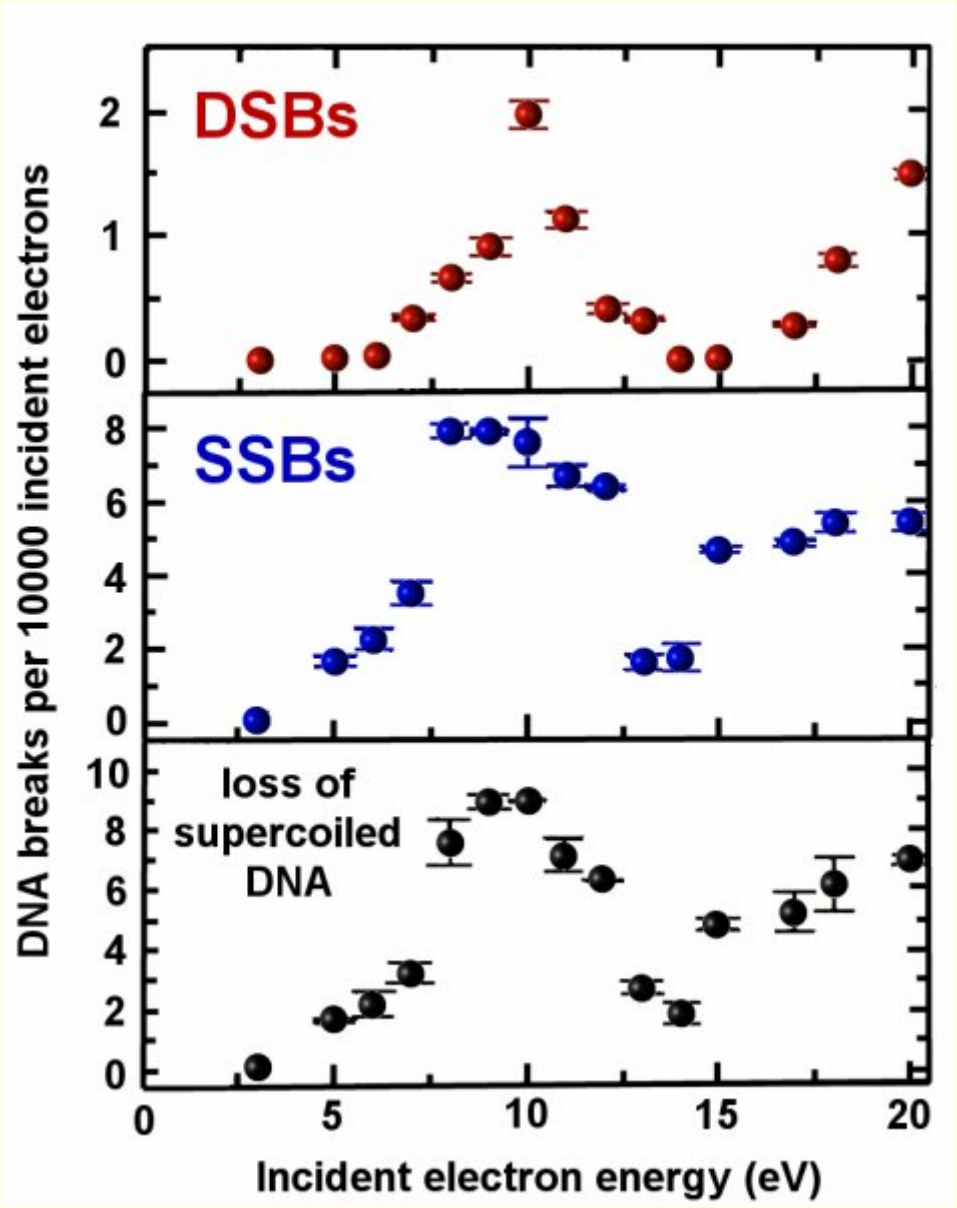
Interaction of Radiation with Biological Matter (Water)



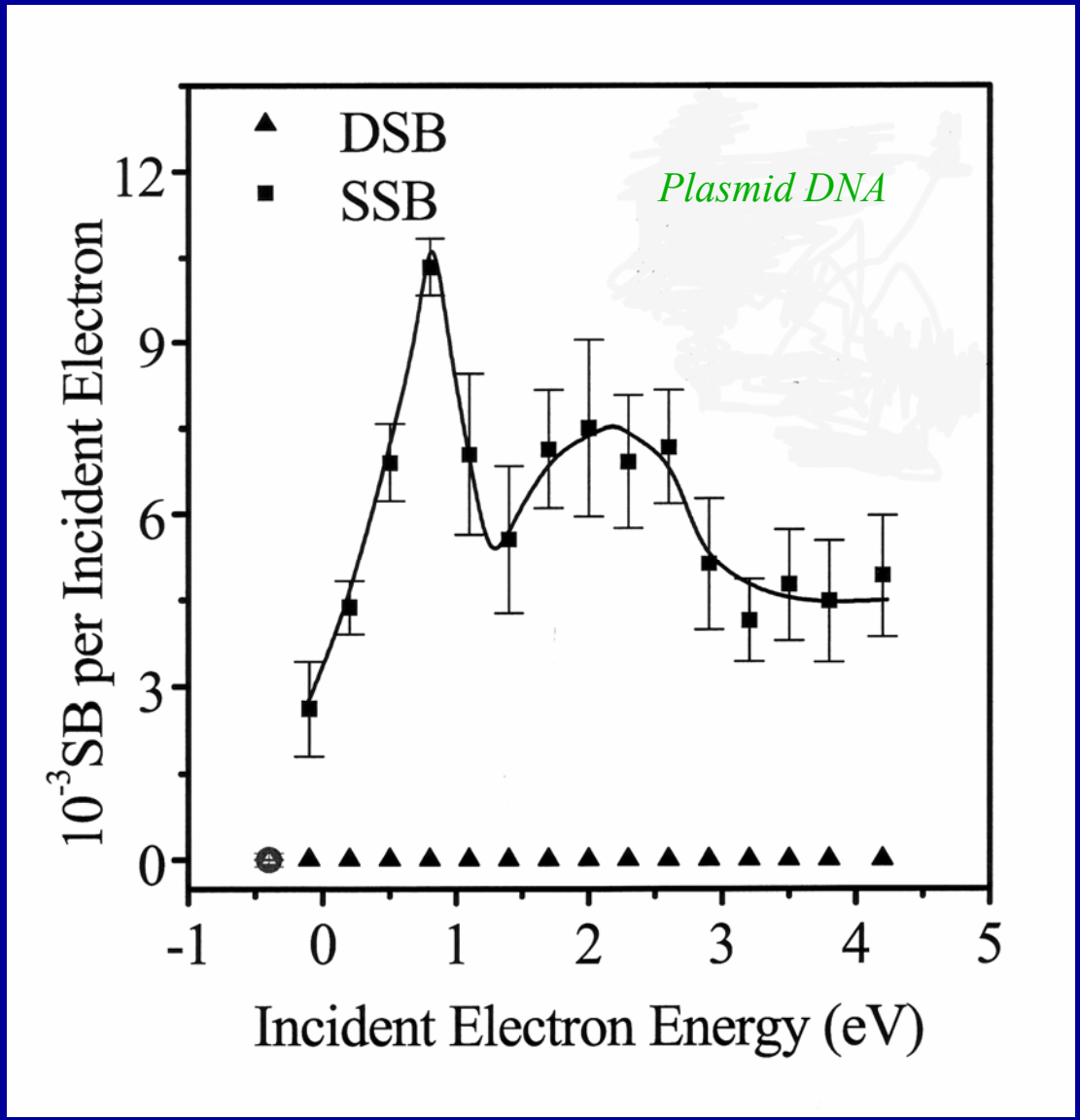
10^4 electrons per 1 Mev primary quanta



DNA-strand breaks

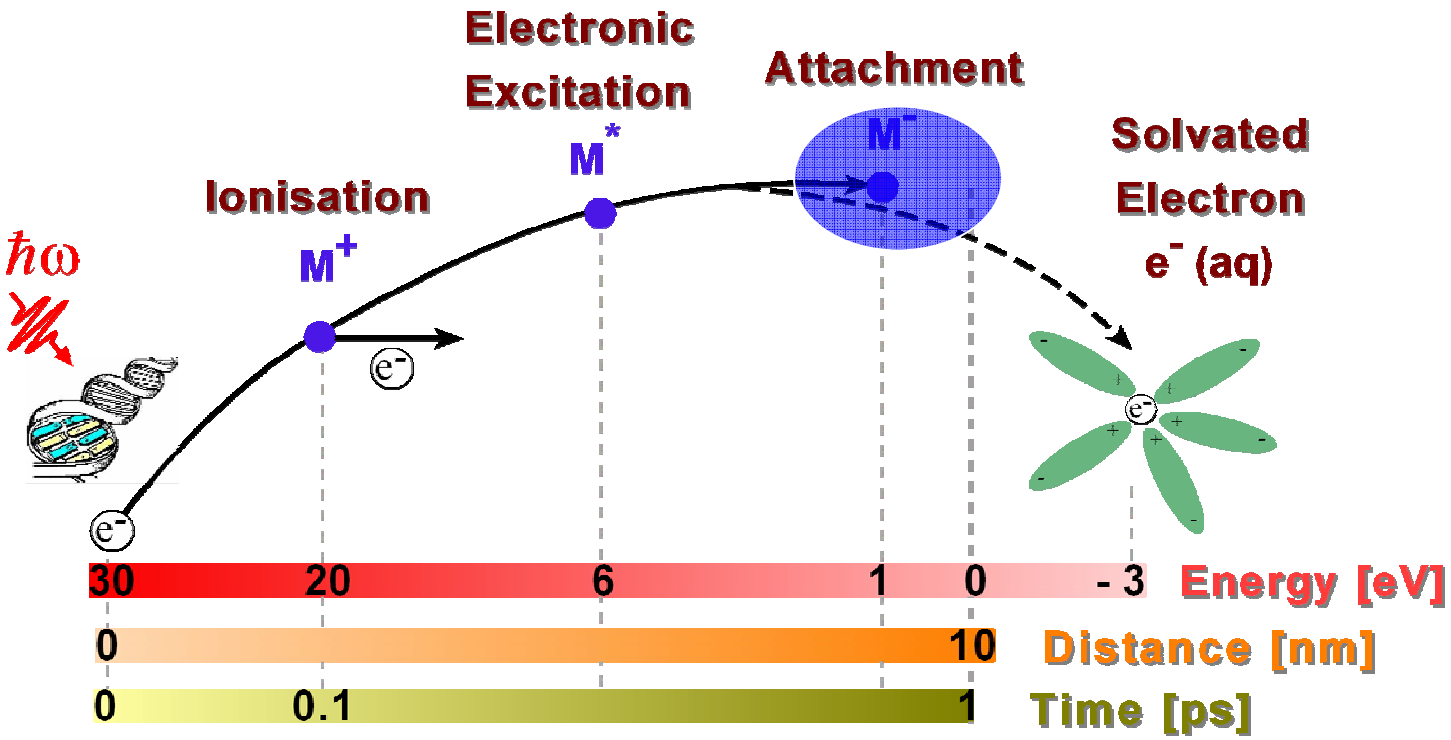


Sanche a.c. Science, 287 (2000) 1659



Léon Sanche et al., PRL 93 (2004) 068101

Energy - Time - Space



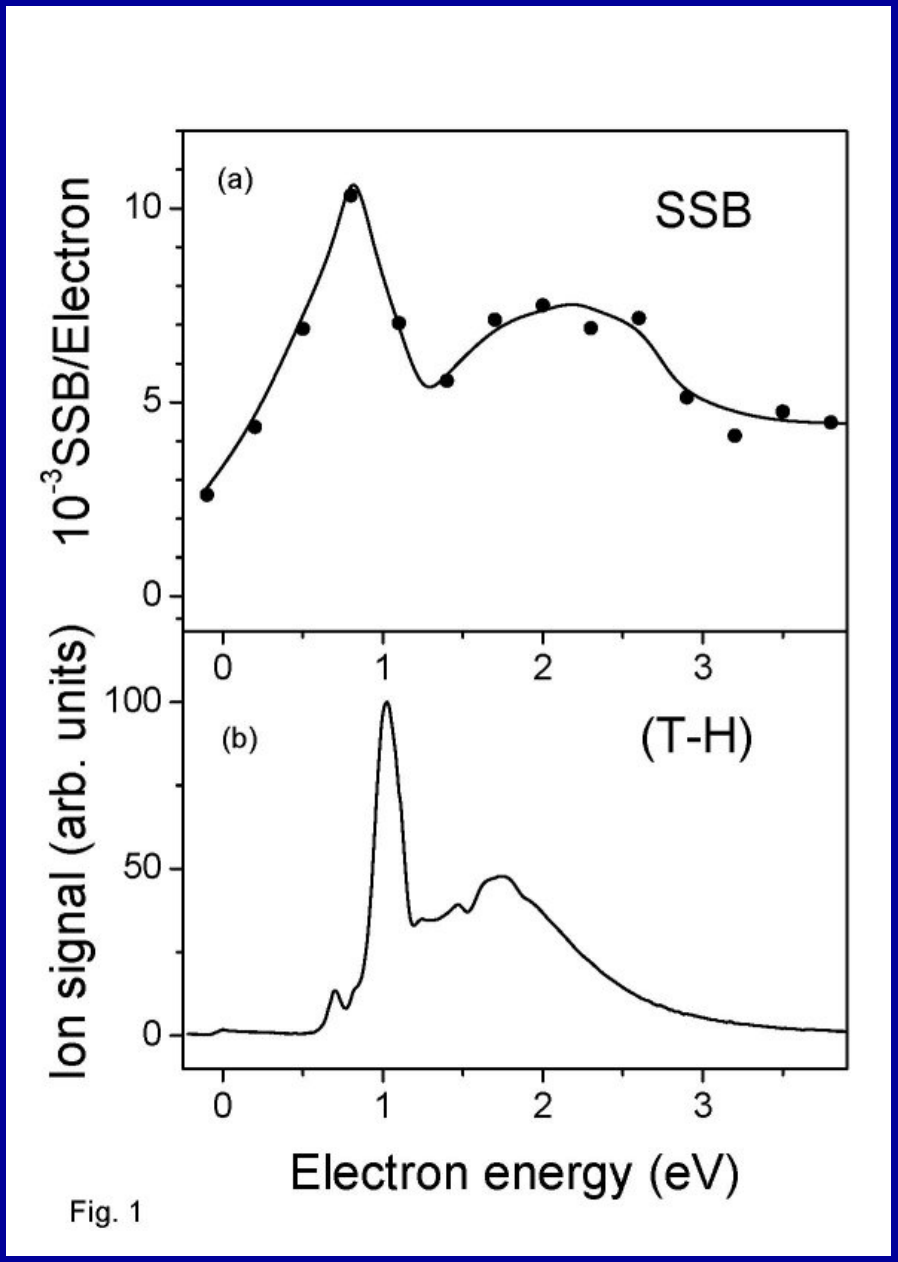


Fig. 1

Single strand breaks
Plasmid DNA

Léon Sanche et al.
PRL 93 (2004) 068101

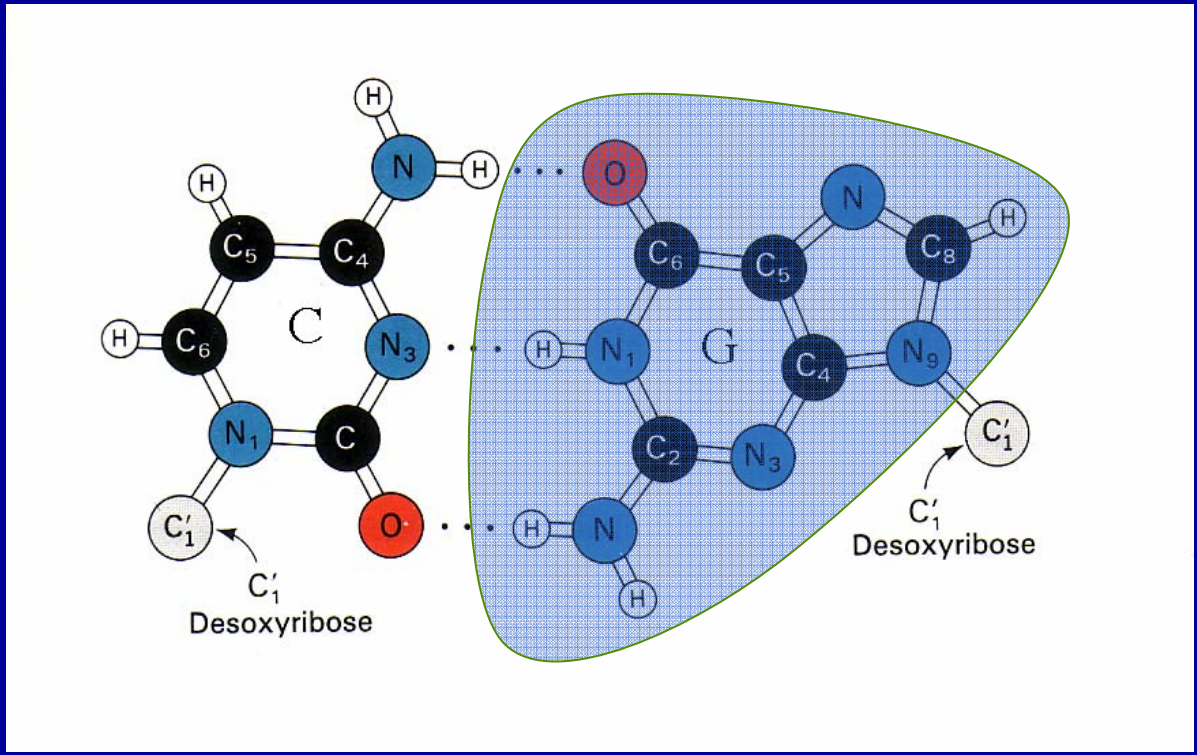
Hydrogen loss from gas phase T

Molecular mechanisms for direct damage of DNA by low energy electrons

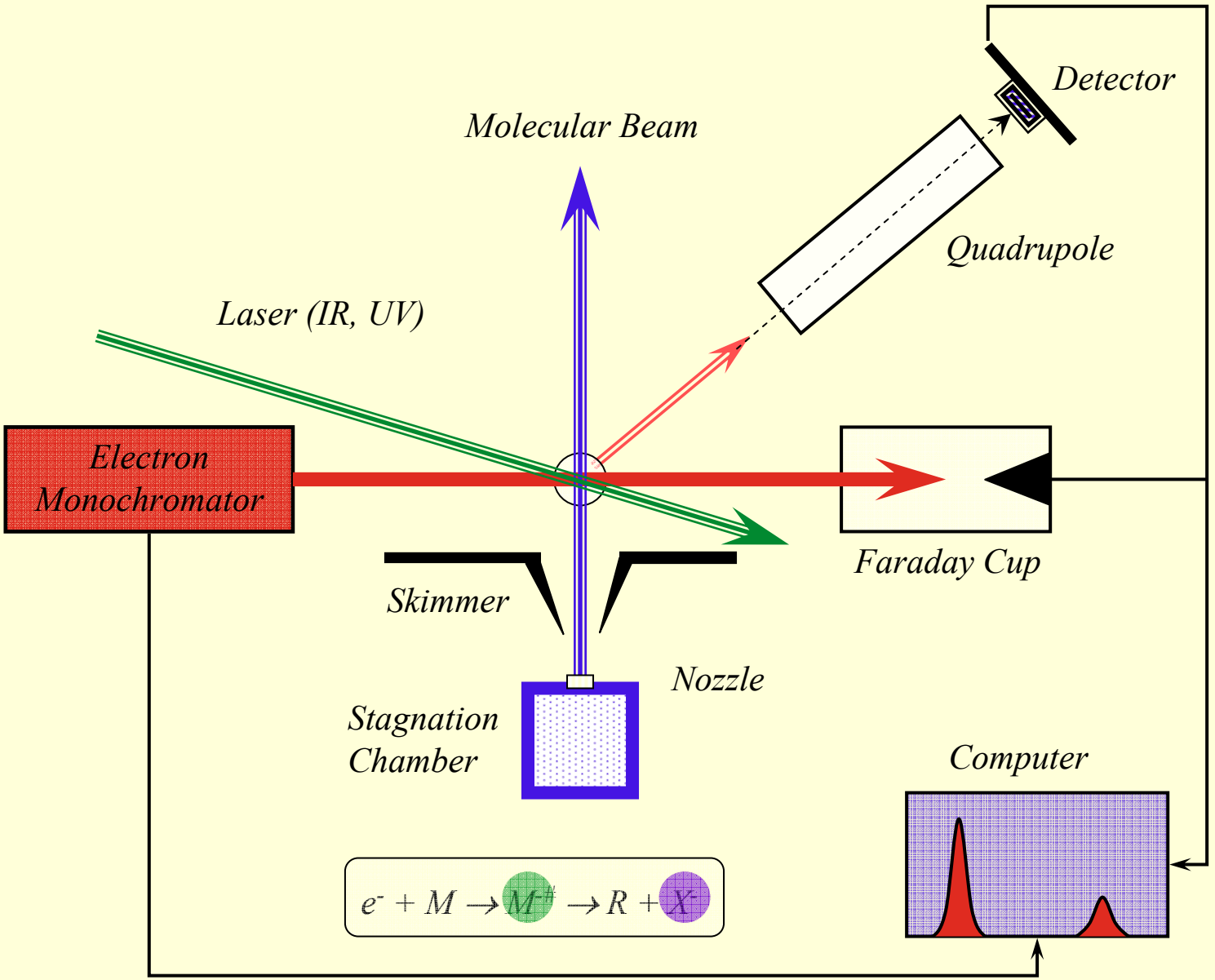
Operation of a radiosensitiser

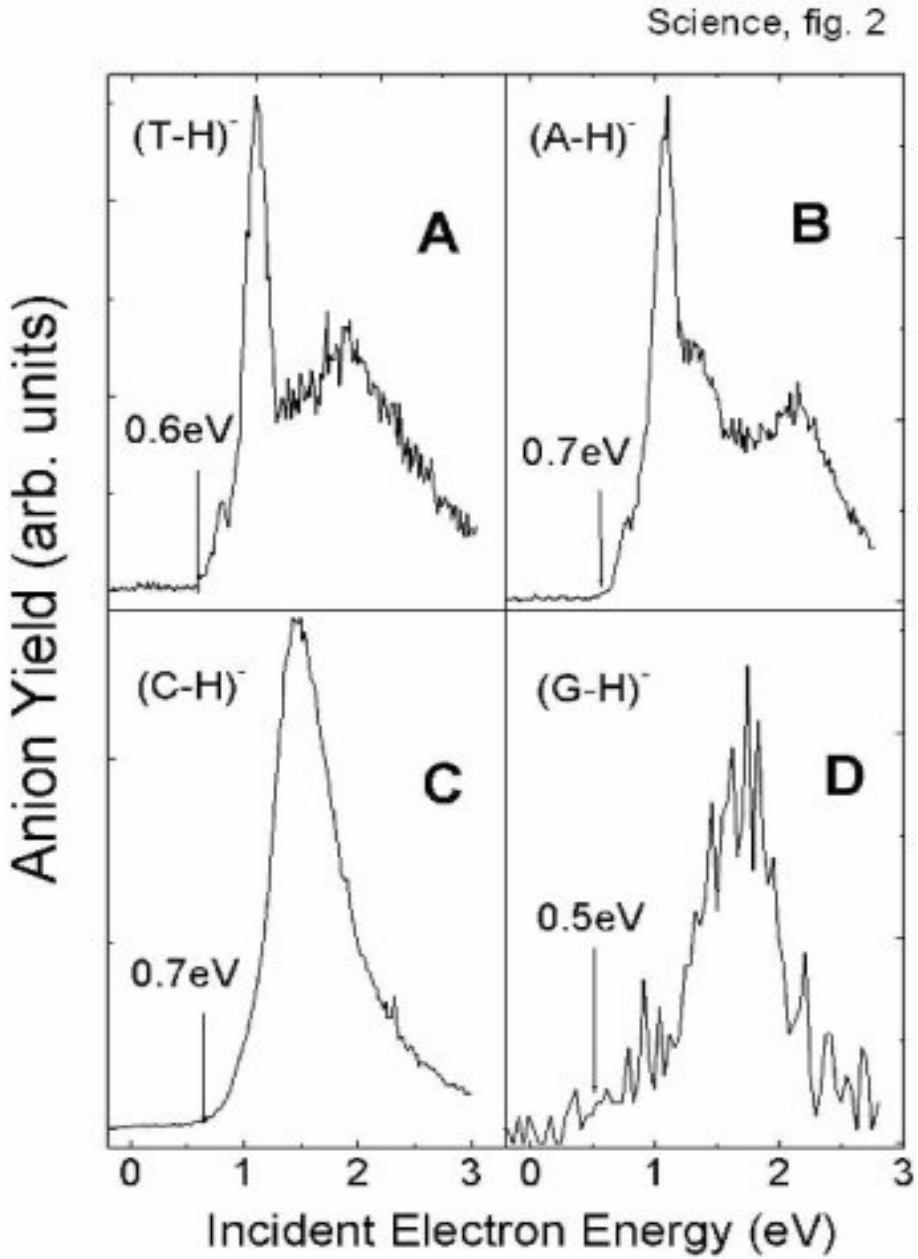
Subexcitation energies (< 3eV) SSBs

Higher Energies (< 5eV): DSBs and SSBs



Guanine $C_5N_5H_5O$: 78 electrons


Detector
Molecular Beam
Quadrupole
Laser (IR, UV)
Electron
Monochromator
Faraday Cup
Skimmer
Nozzle
Stagnation
Chamber
Computer
$e^- + M \rightarrow M^{\#} \rightarrow R + X^-$



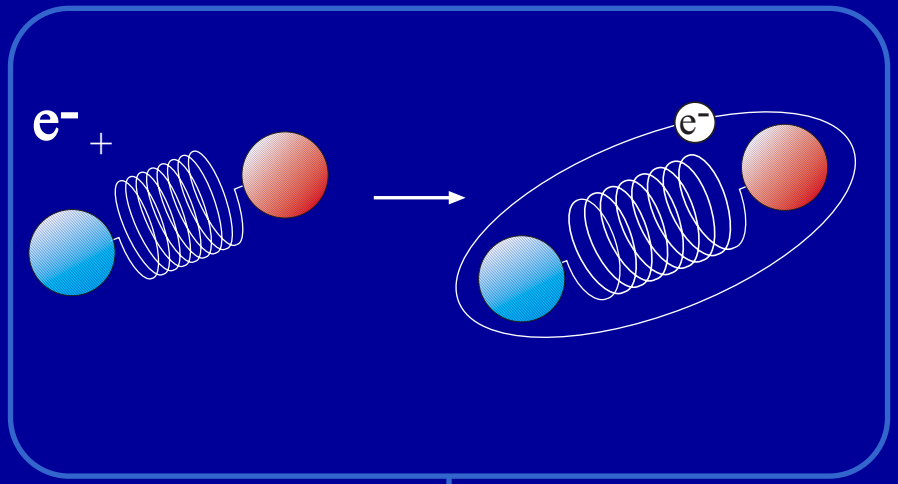
Thymine:

$e^- + T \rightarrow T^{-\#} \rightarrow (T\text{-}H)^- + H$

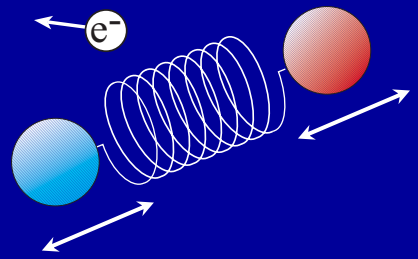
EA(T-H) ≈ 3 - 4 eV

Sascha Gohlke et al.
PRL 92 (2004) 168103

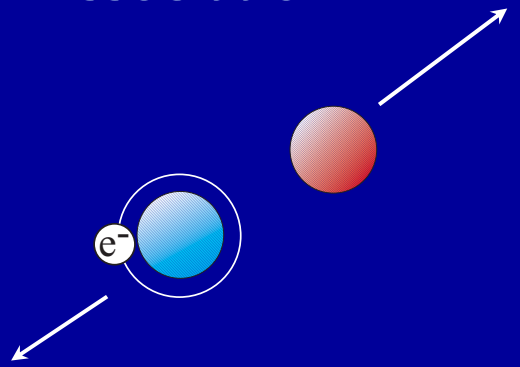
Resonant Capture



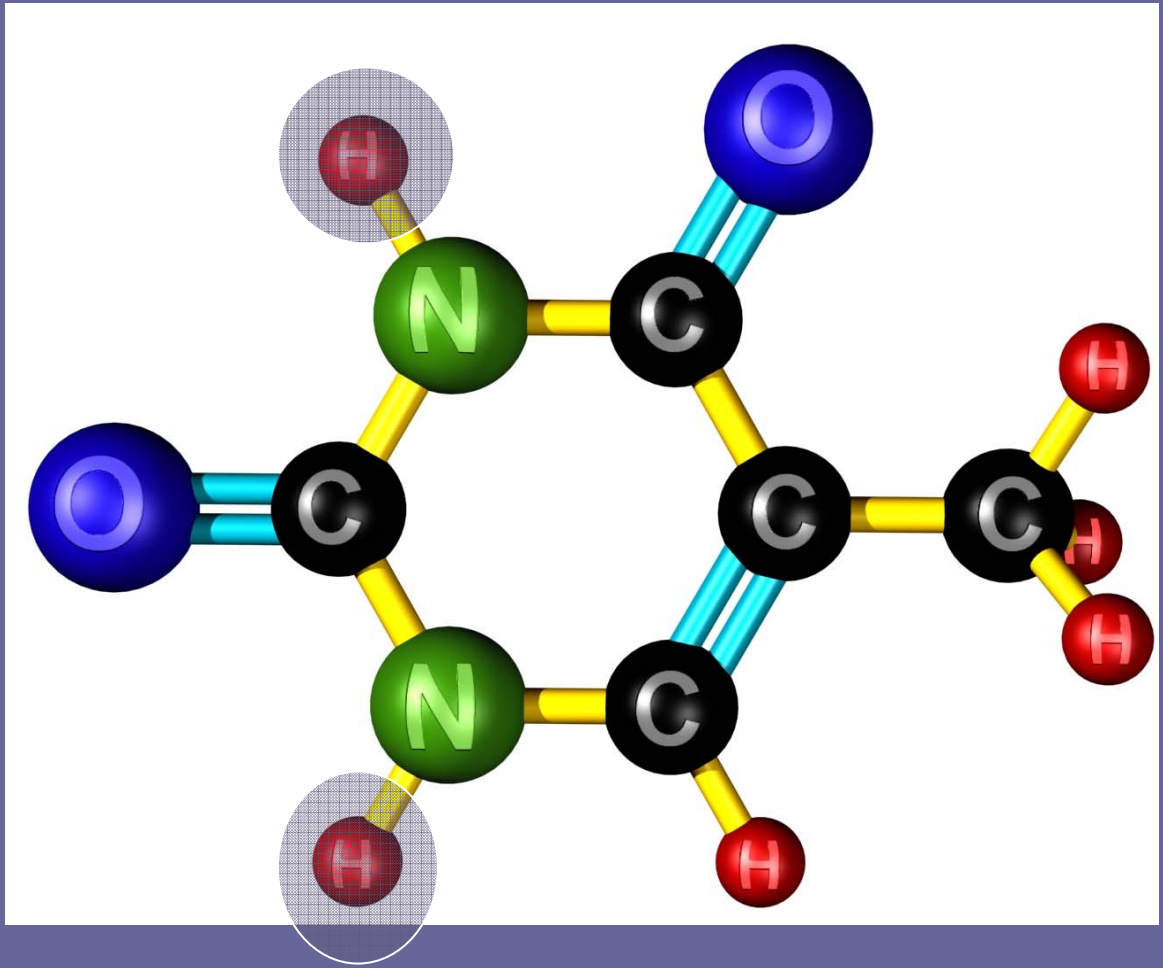
Autodetachment

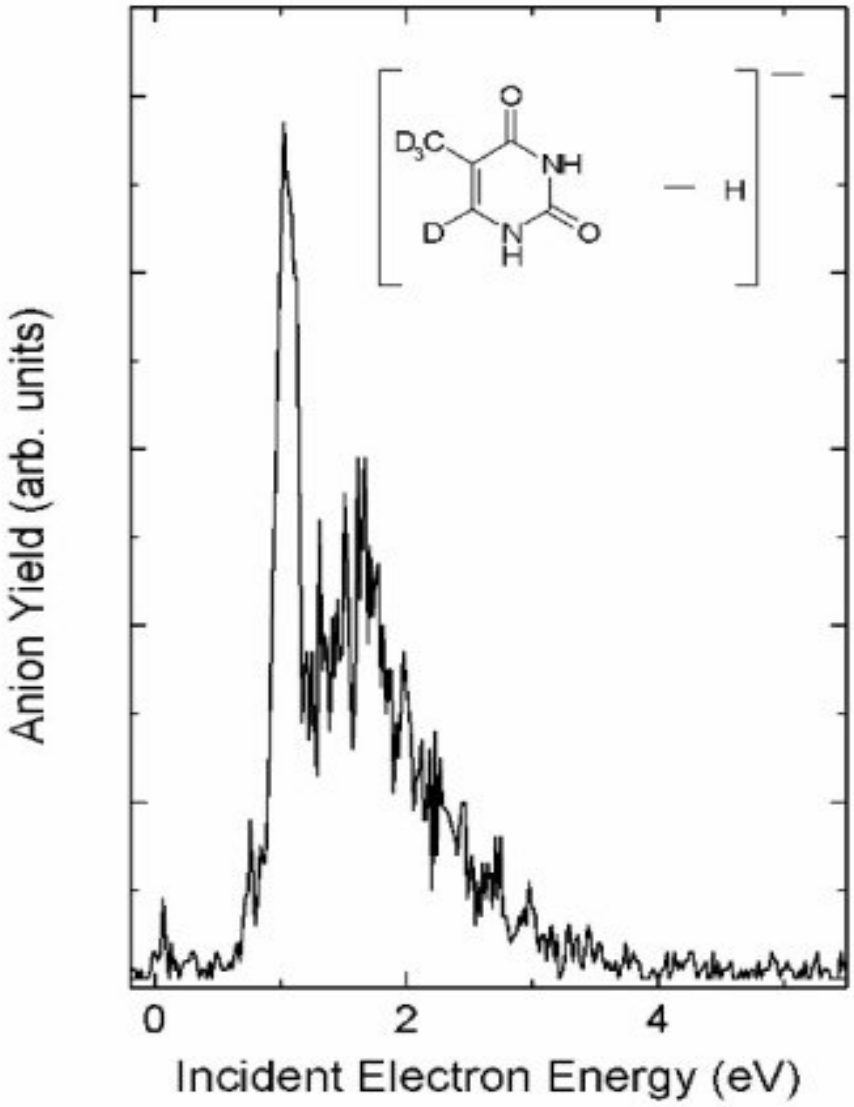


Dissociation



Thymine





Deuterated Thymine

$(M-H)^-$ but no $(M-D)^-$

$\Rightarrow$ *H loss from N sites*

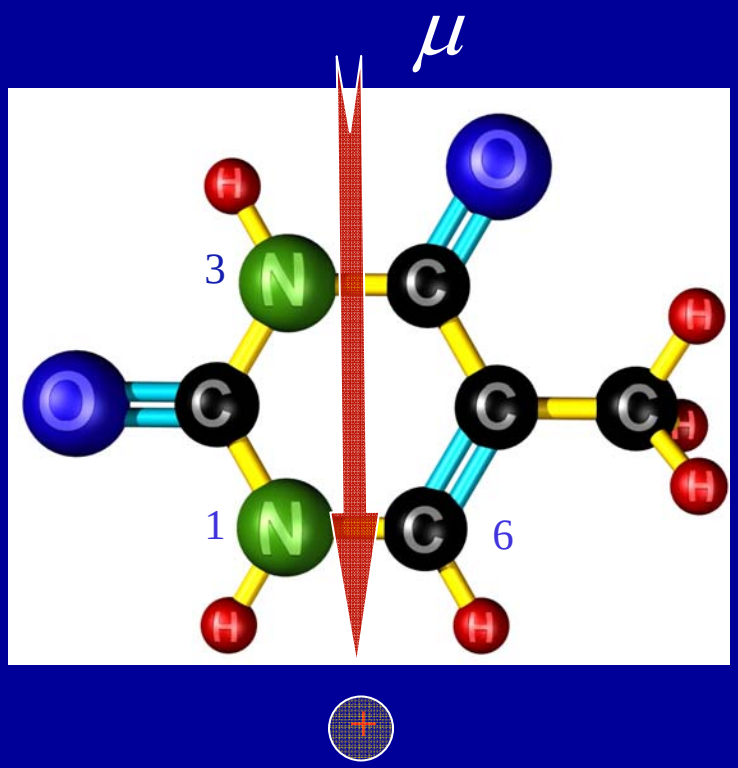
PRL 92 (2004) 168103

Capture of electrons at subexcitation energies

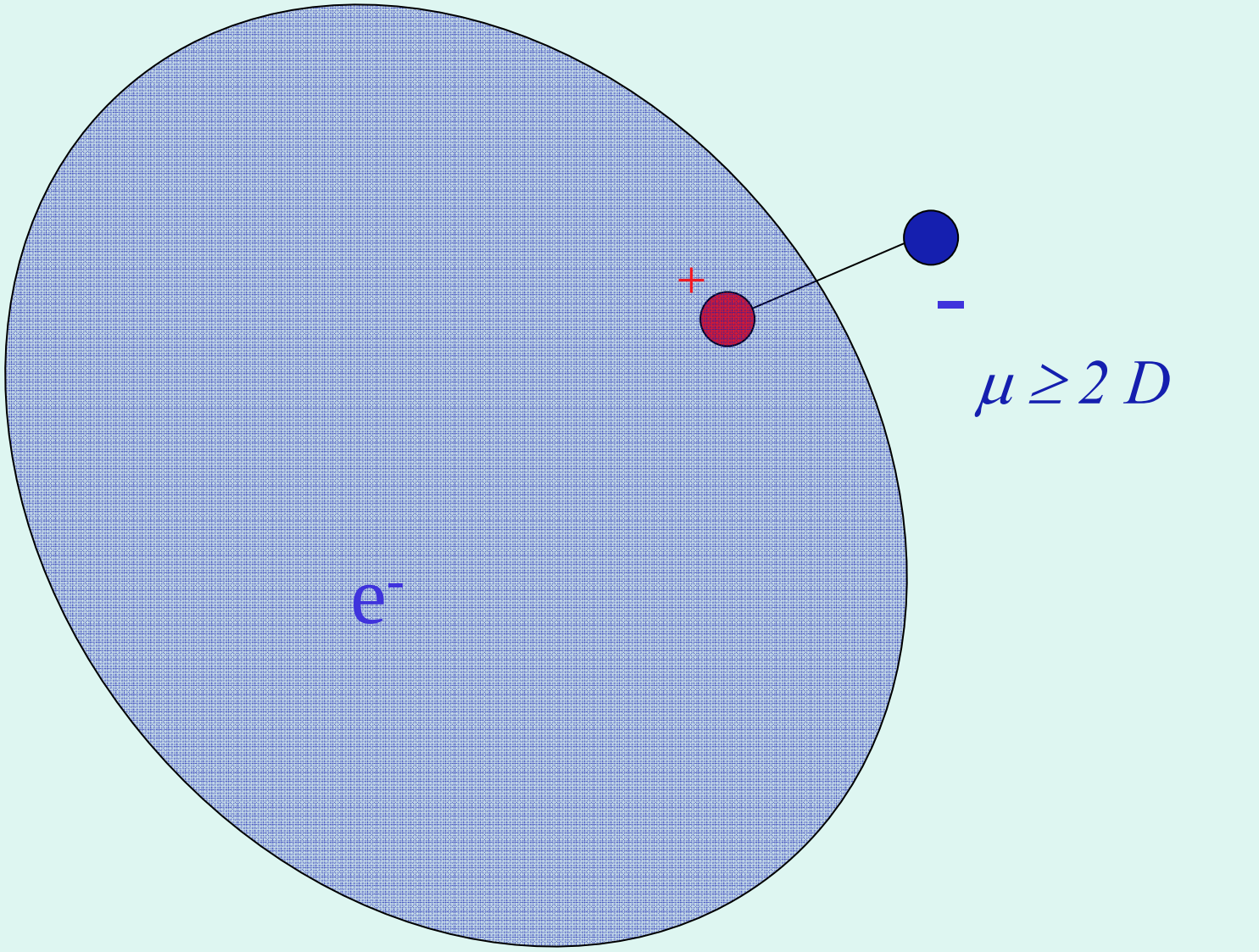
Bond selective decompositions: σ^*(C-I) MOs

Site selective decompositions

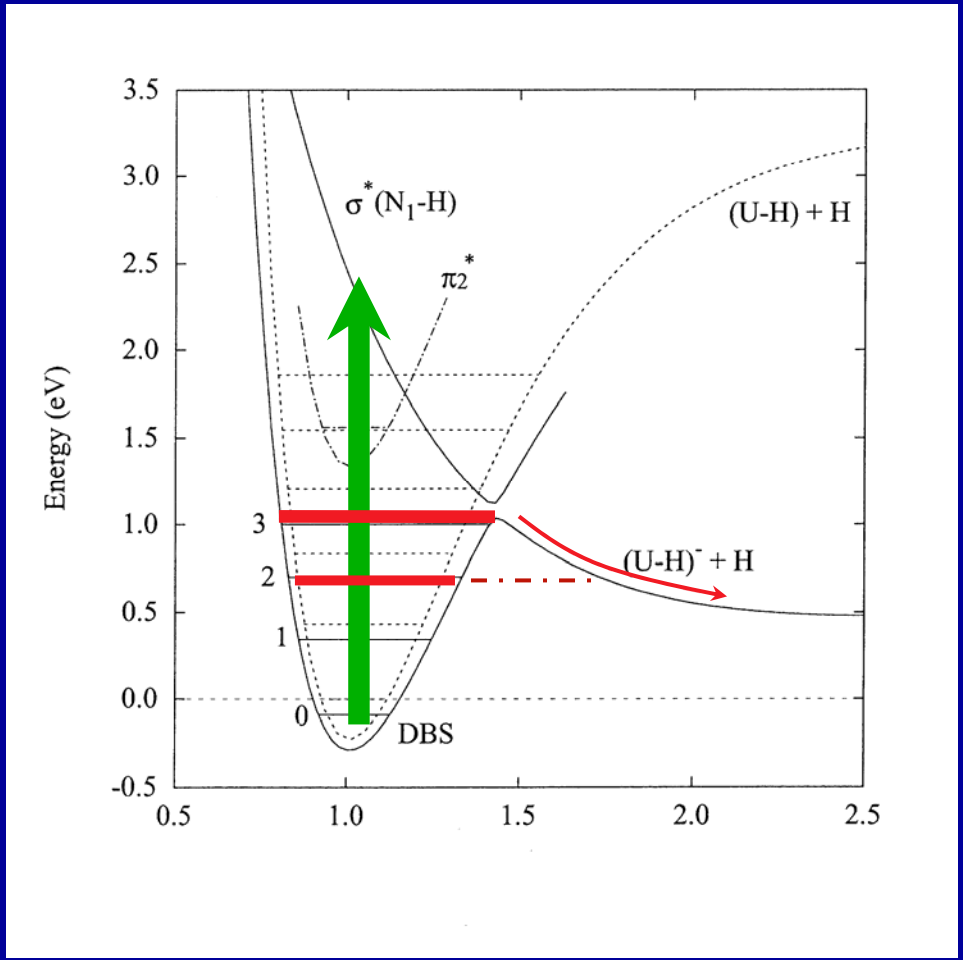
Gas Phase



Dipole moment: $\mu(T) \approx 4.5$ D



Dipole-bound state



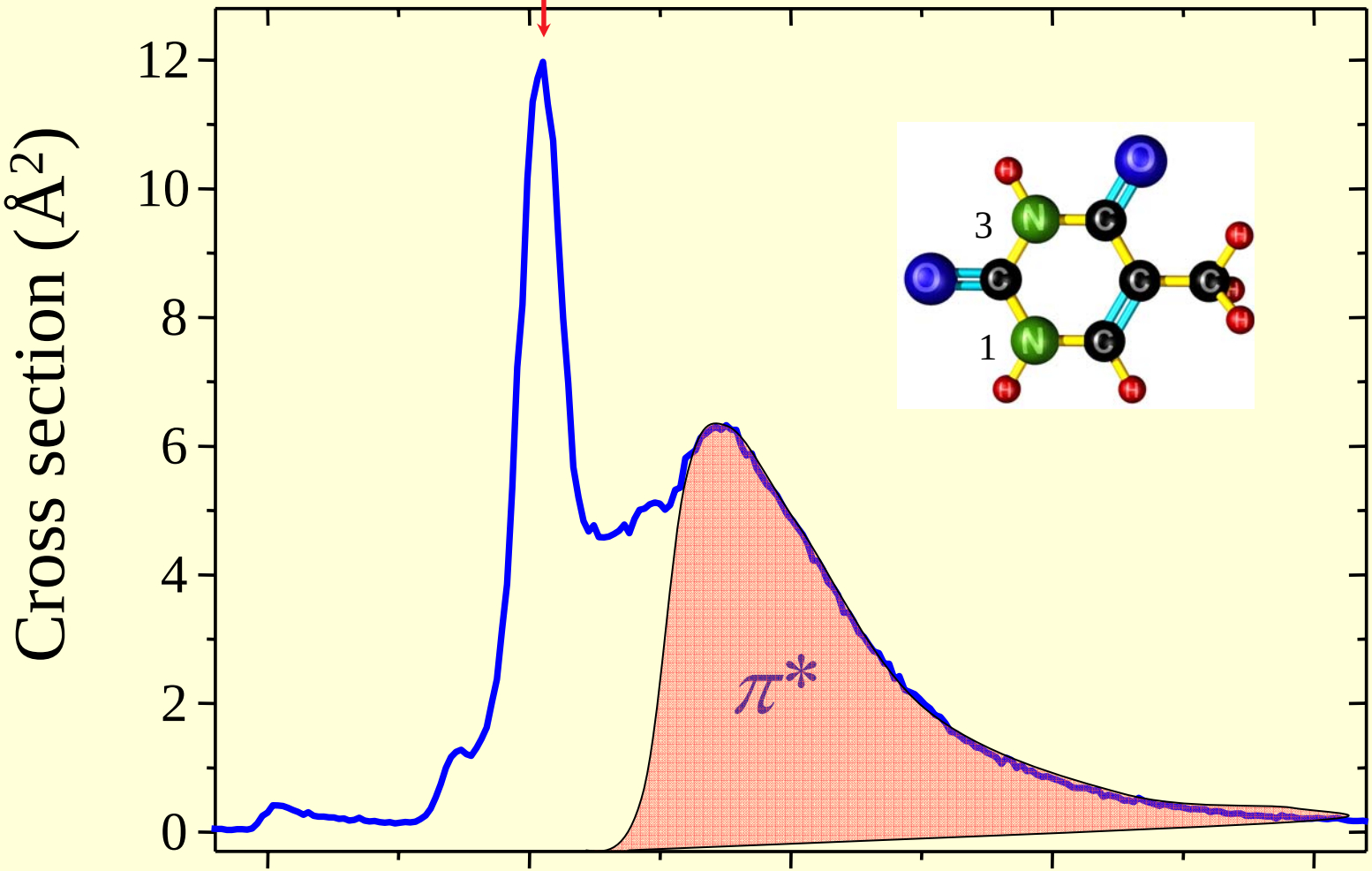
Paul Burrow et al. Phys. Rev. Letters 92 (2004) 068102

Dipole supported vibrational Feshbach resonance

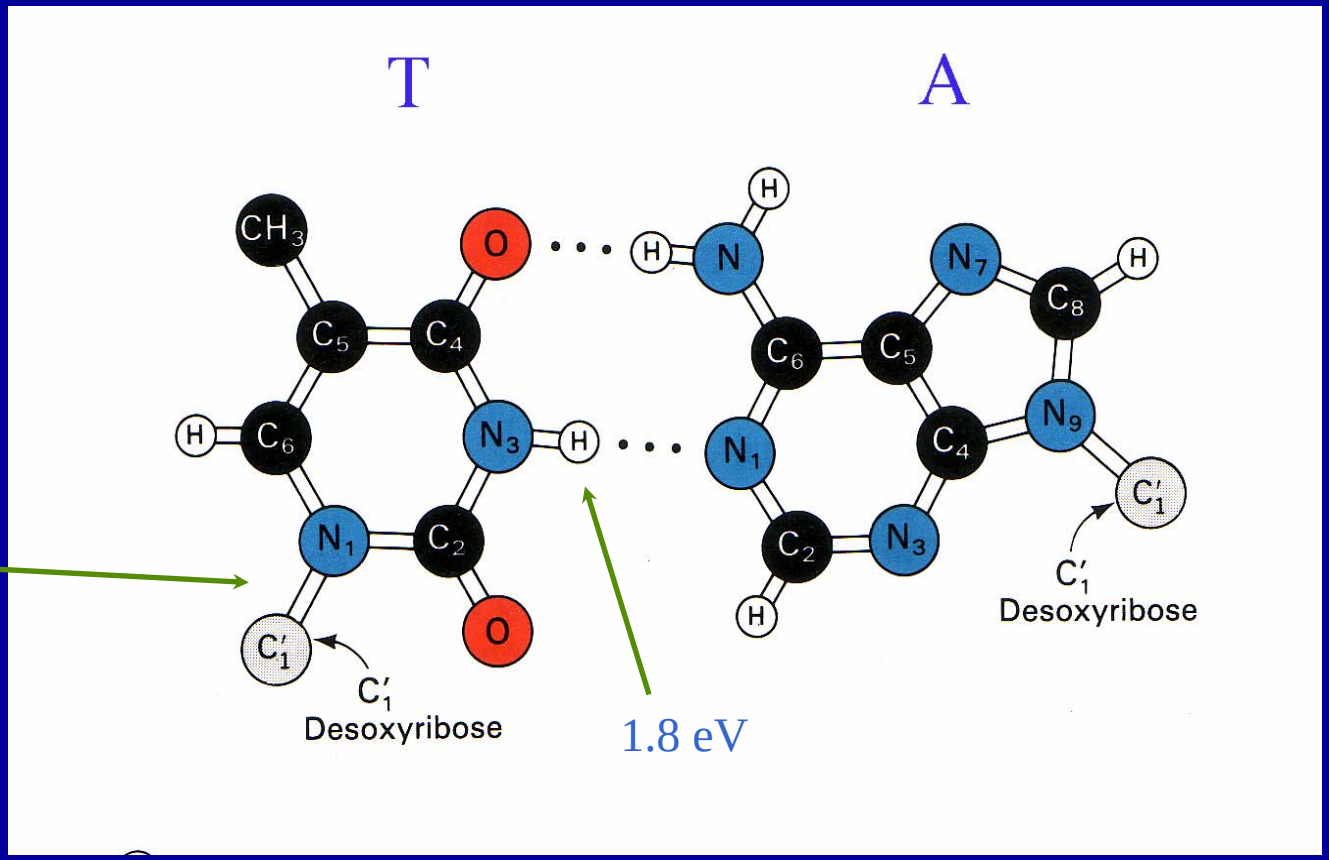
Thymine

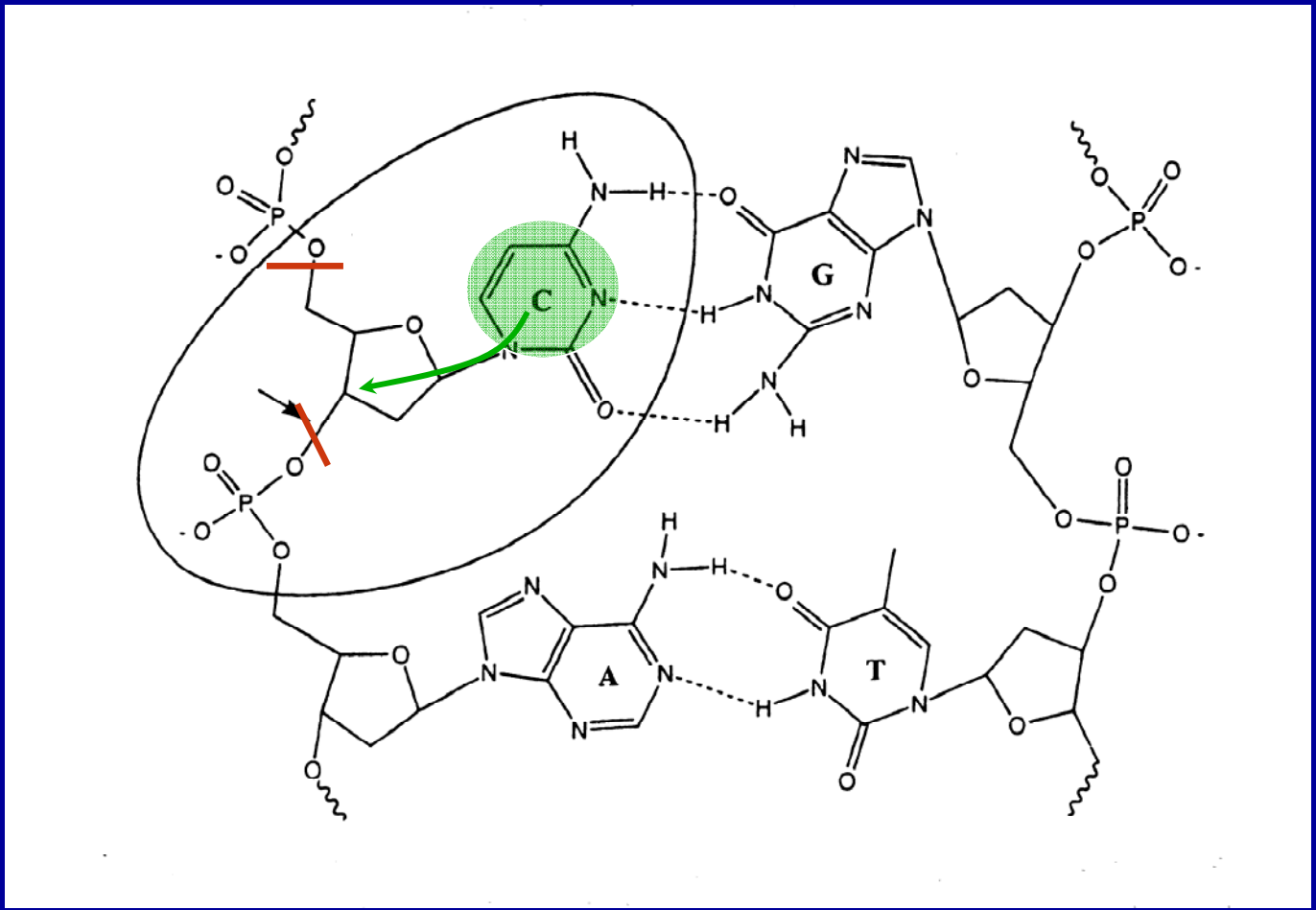
DB state

H-loss



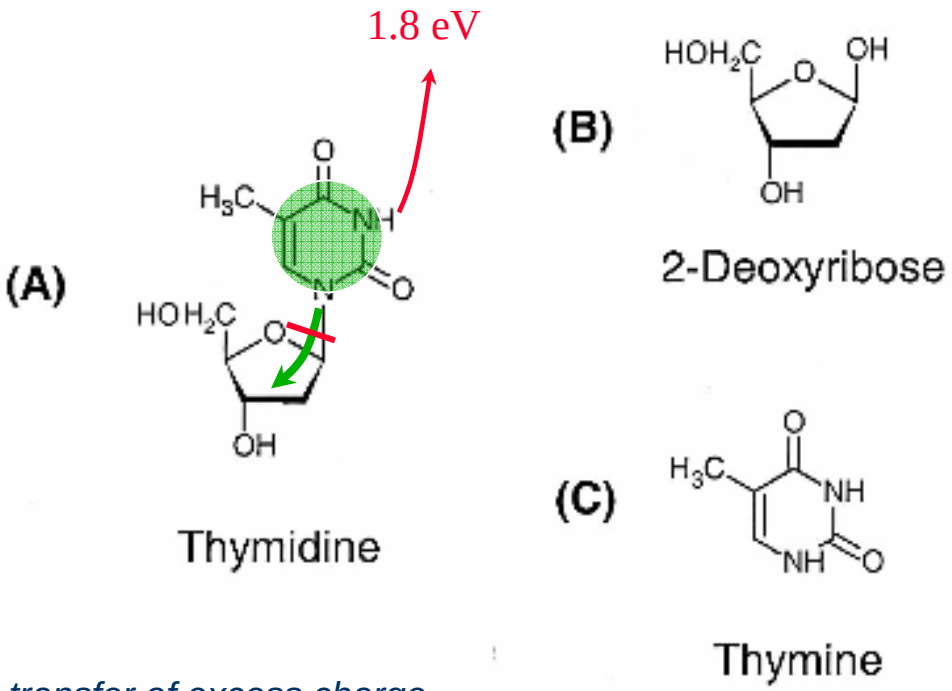
T-A Pairing





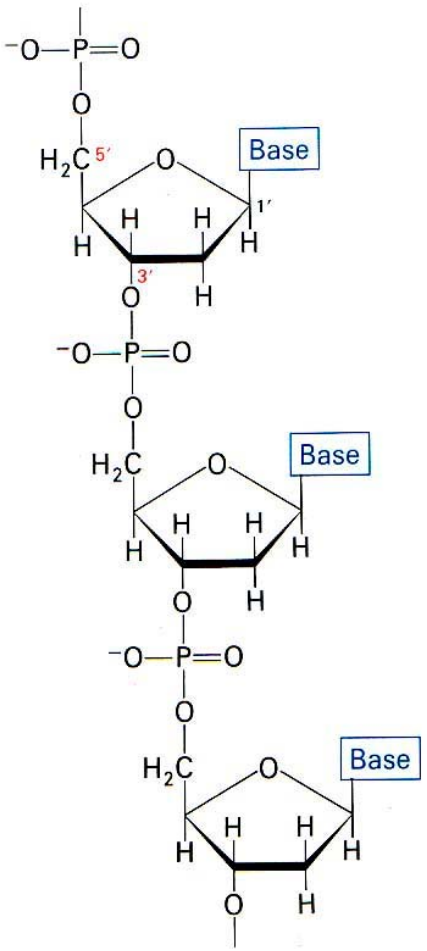
R. Barrios, P Skurski and J. Simons, JPC B 106 (2002) 7991

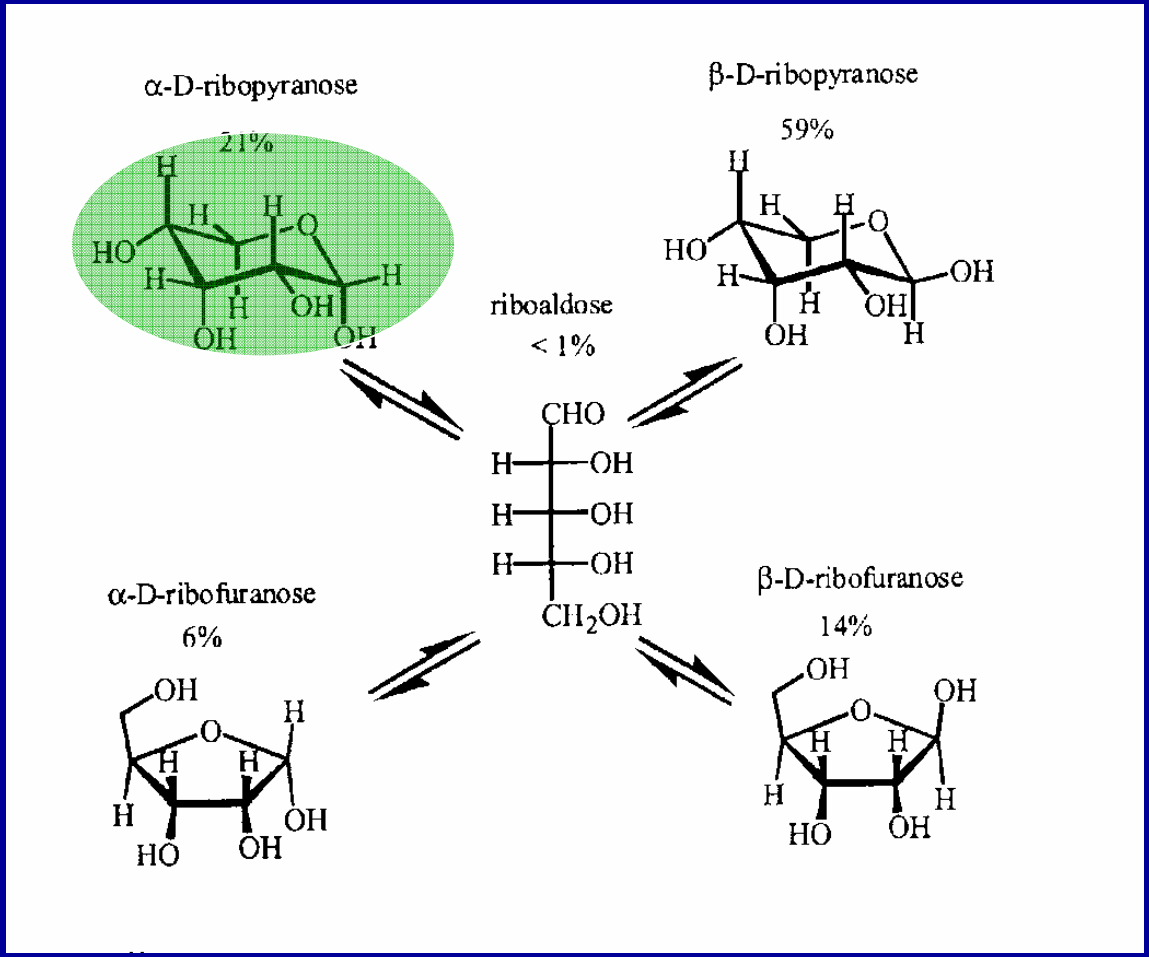
Simons et al. JACS 126 (2004) 6441.



No transfer of excess charge initially localised on T

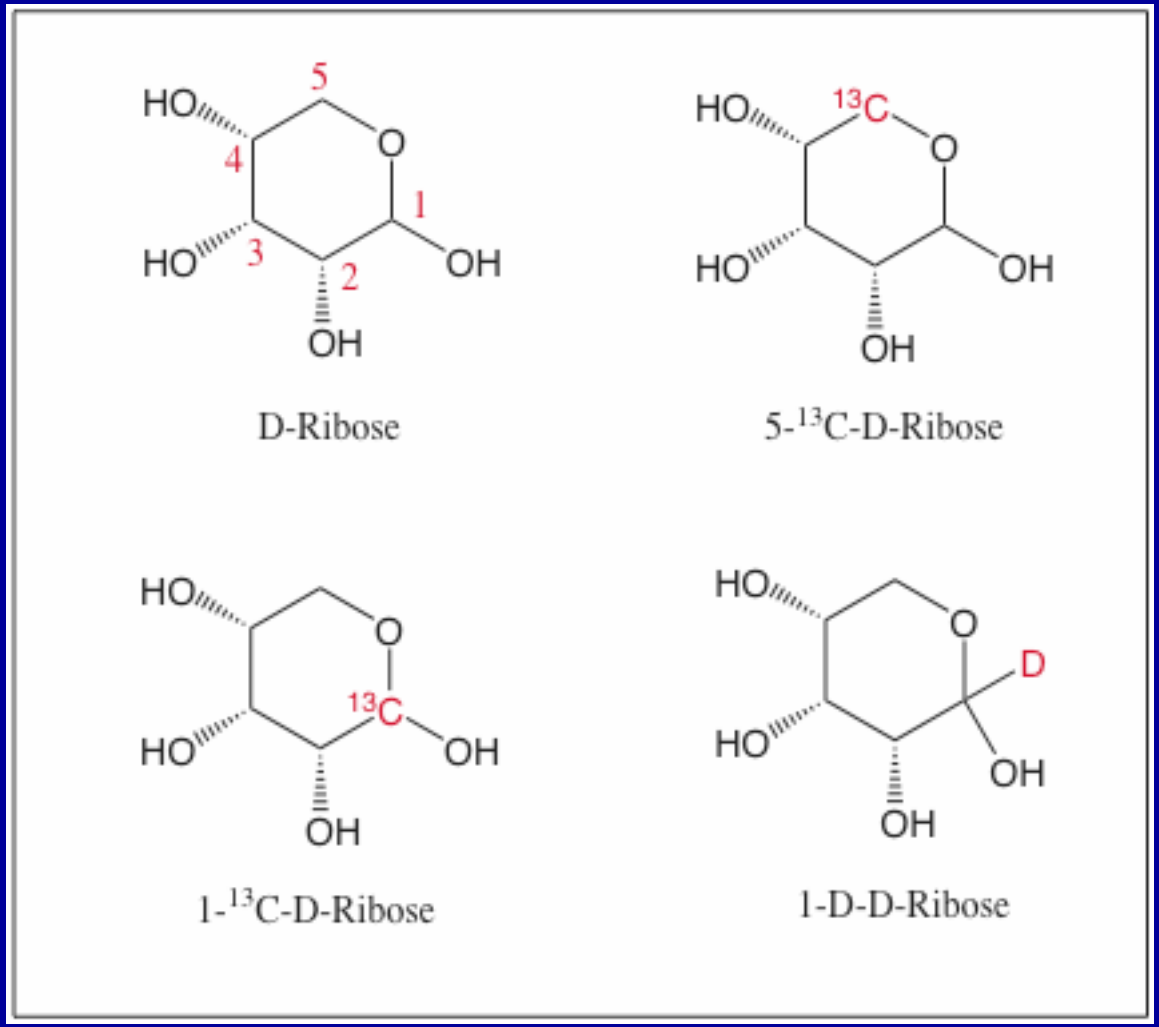
- *H. A.Carime et al., Chem. Phys. Letters 387 (2004) 267.*
- *S. Ptasinska et al., Angew. Chem. Int. Ed. (in print).*





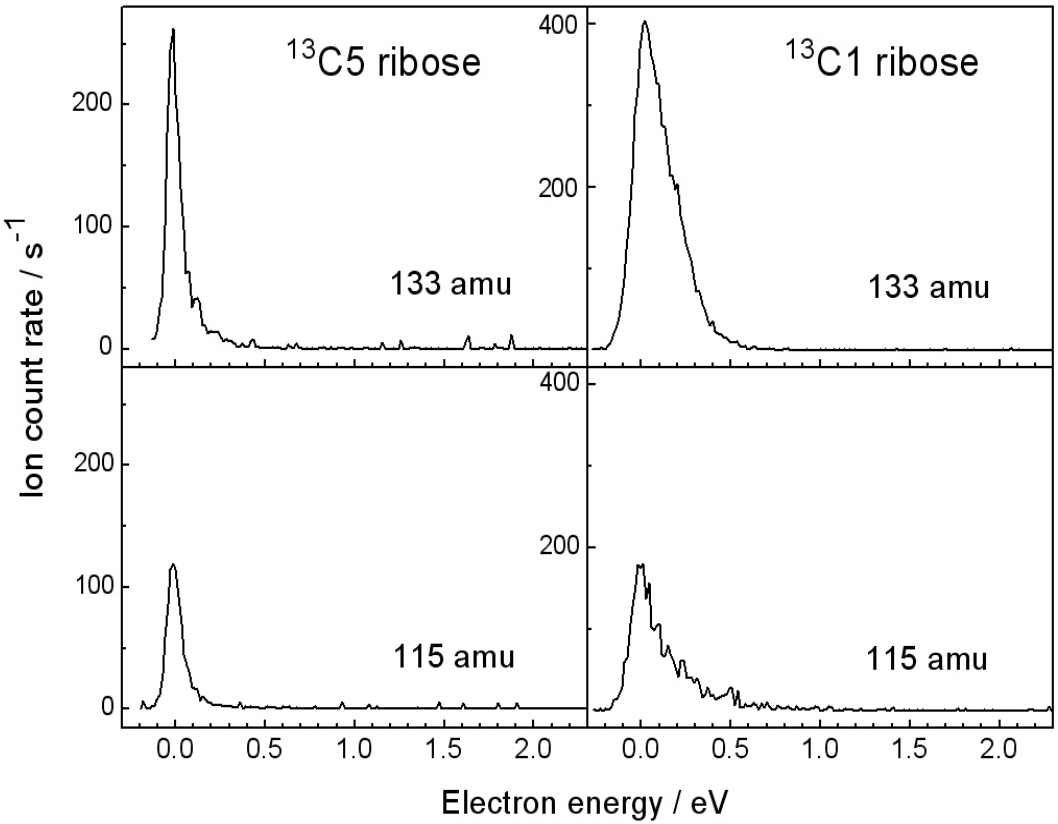
Ribose: equilibrium in liquid phase

Thermal evaporation: pyranosyl form in gas phase (Guler, Yu, Kentämaa, JPC 106 (2002) 6754)



Electron Interaction with Deoxyribose:

S. Ptasinska, S. Denifl, P. Scheier, T. D. Märk, J. Chem. Phys. 120 (2004) 8505



$(M\text{-}H_2O)^-$

$(M\text{-}2H_2O)^-$

M: Ribose 150 amu ($C_5H_{10}O_5$) ⇒ *132amu/114 amu*

^{13}C ribose 151 amu ⇒ *133amu/115 amu*

(C1-D) ribose 151 amu ⇒ *133amu/115 amu* ⇒ *no H_2O loss from C1*

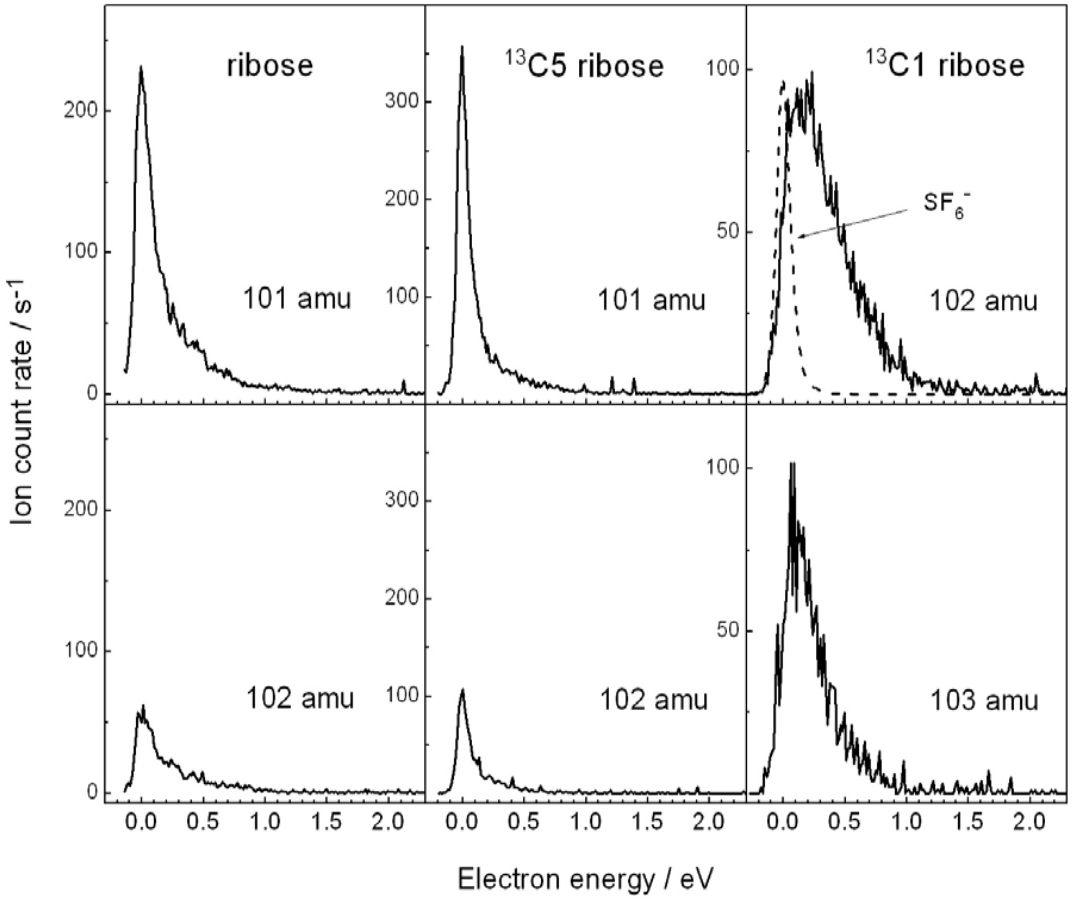


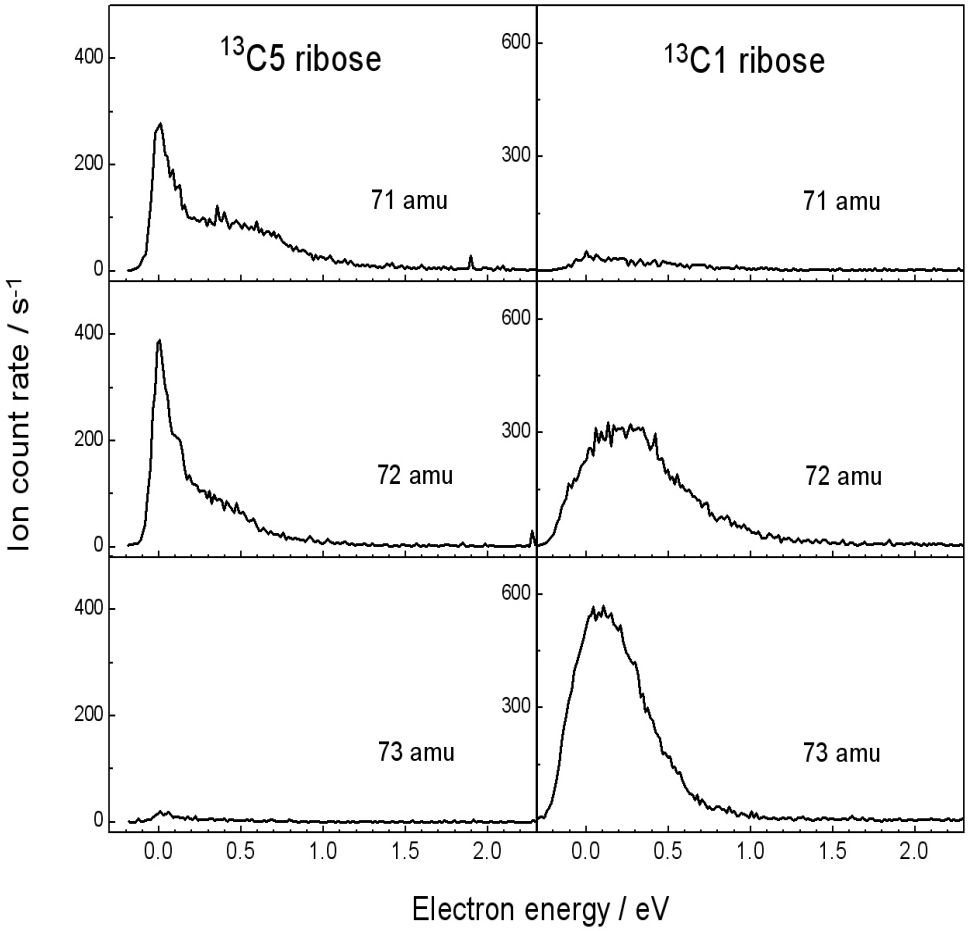
Fig. 2

$C_4H_5O_3^-$ + CO_2 + H_2 + H

$C_4H_6O_3^-$ + CO_2 + H_2

⇒ *selective excision of C5* ⇒ *C1 and D remain on negative ion*

Ilko Bald, Janina Kopyra, EI, submitted



$C_4H_4O_2^-$ + CO_2 + CH_3OH + H_2

Fig. 3

Excision of 2 C containing units ⇒ C5 and D remain on negative ion fragment

Ilko Bald, Janina Kopyra, EI, submitted

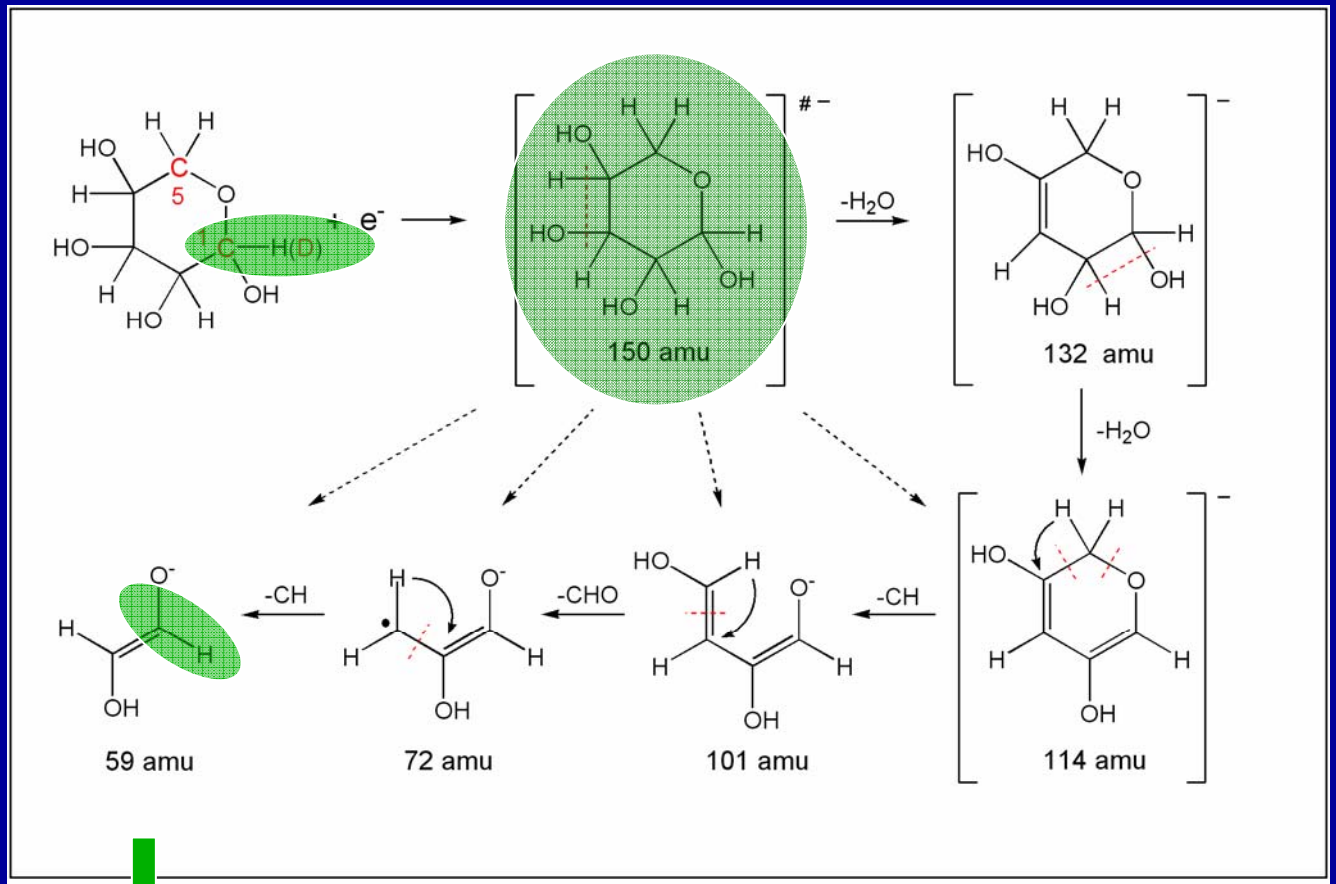
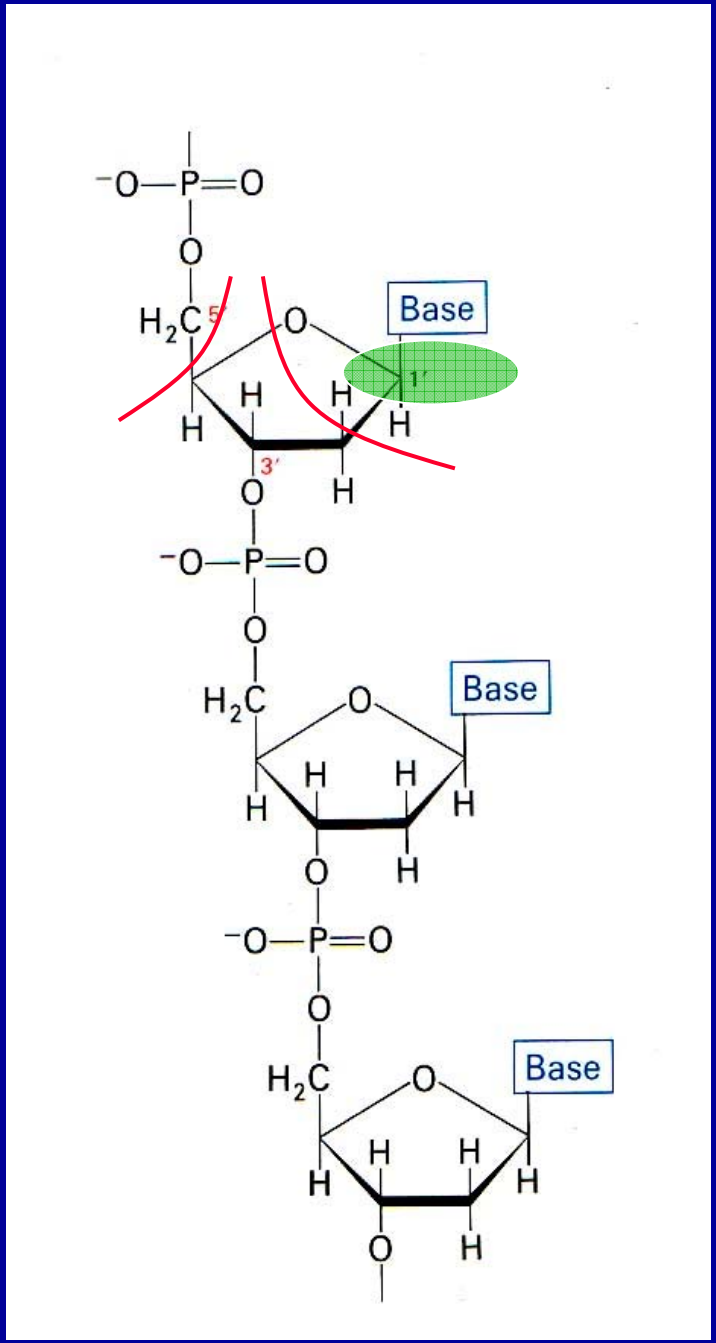


Fig. 4

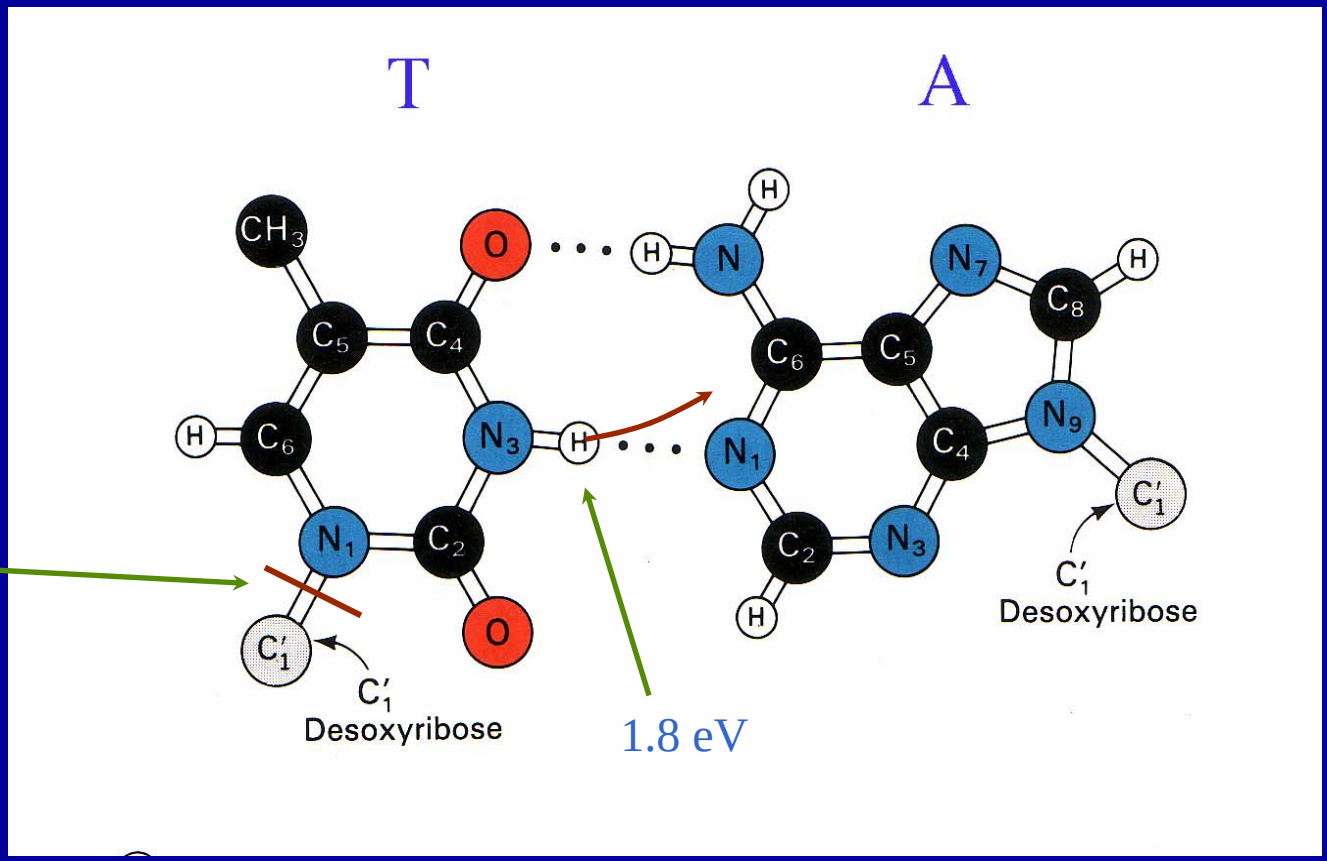
$HCOO^-$ appears as $DCOO^-$ or $H^{13}C1OO^-$



Excision of DNA Base

Strand break

- *No transfer of excess electrons from NBs to the backbone*
- *Sugar unit is very sensitive*
- *Phosphate group is sensitive*

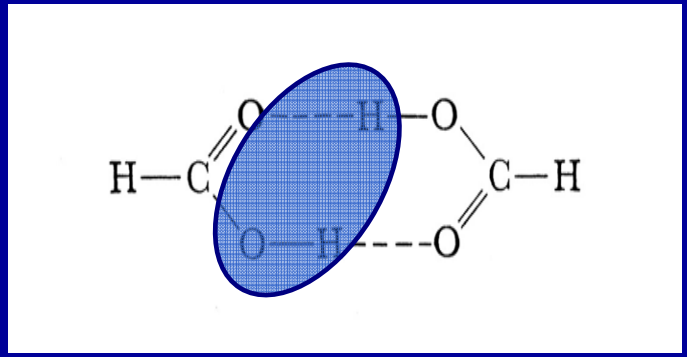


Respond of the Hydrogen Bridge?

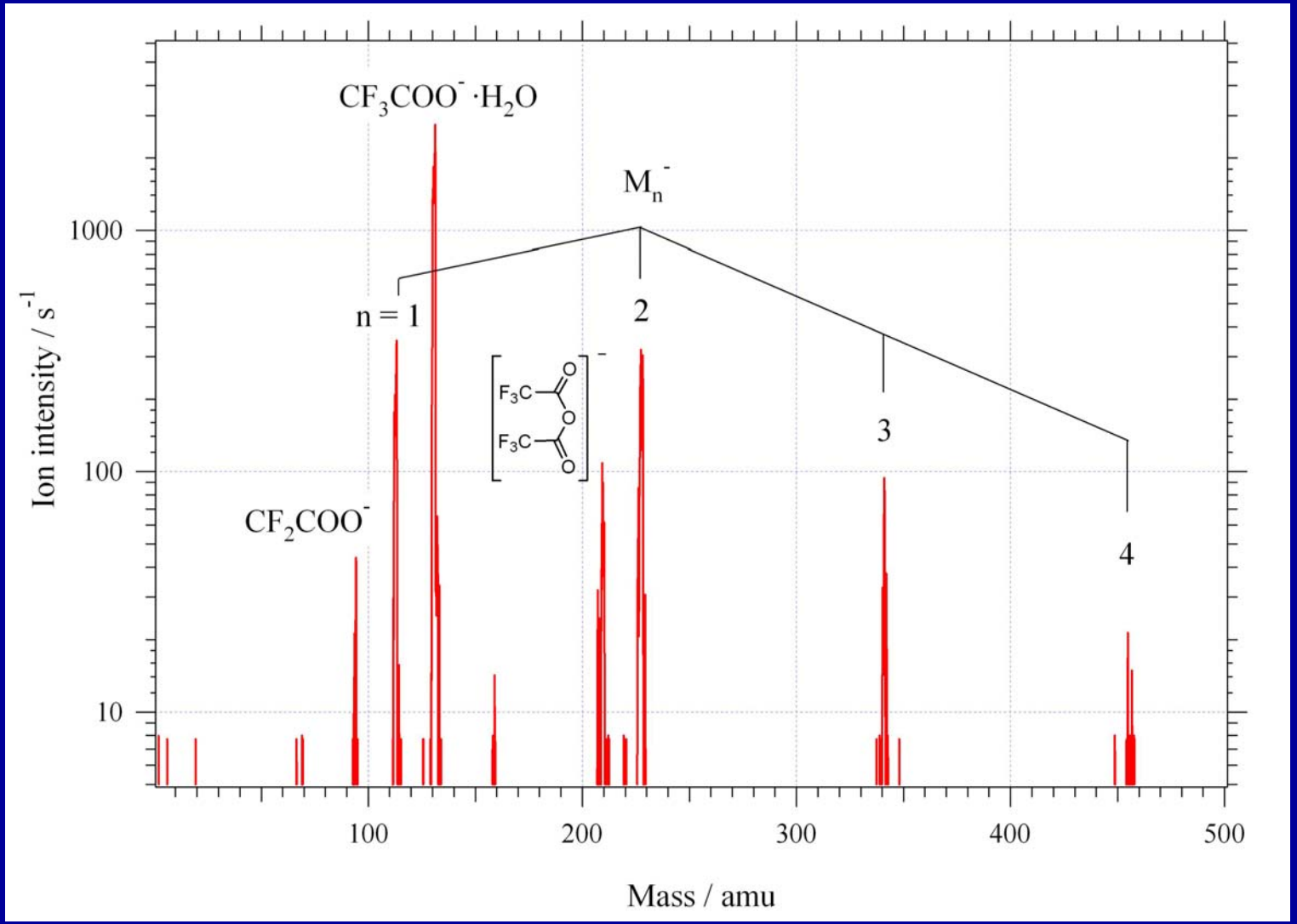
Cluster Experiments

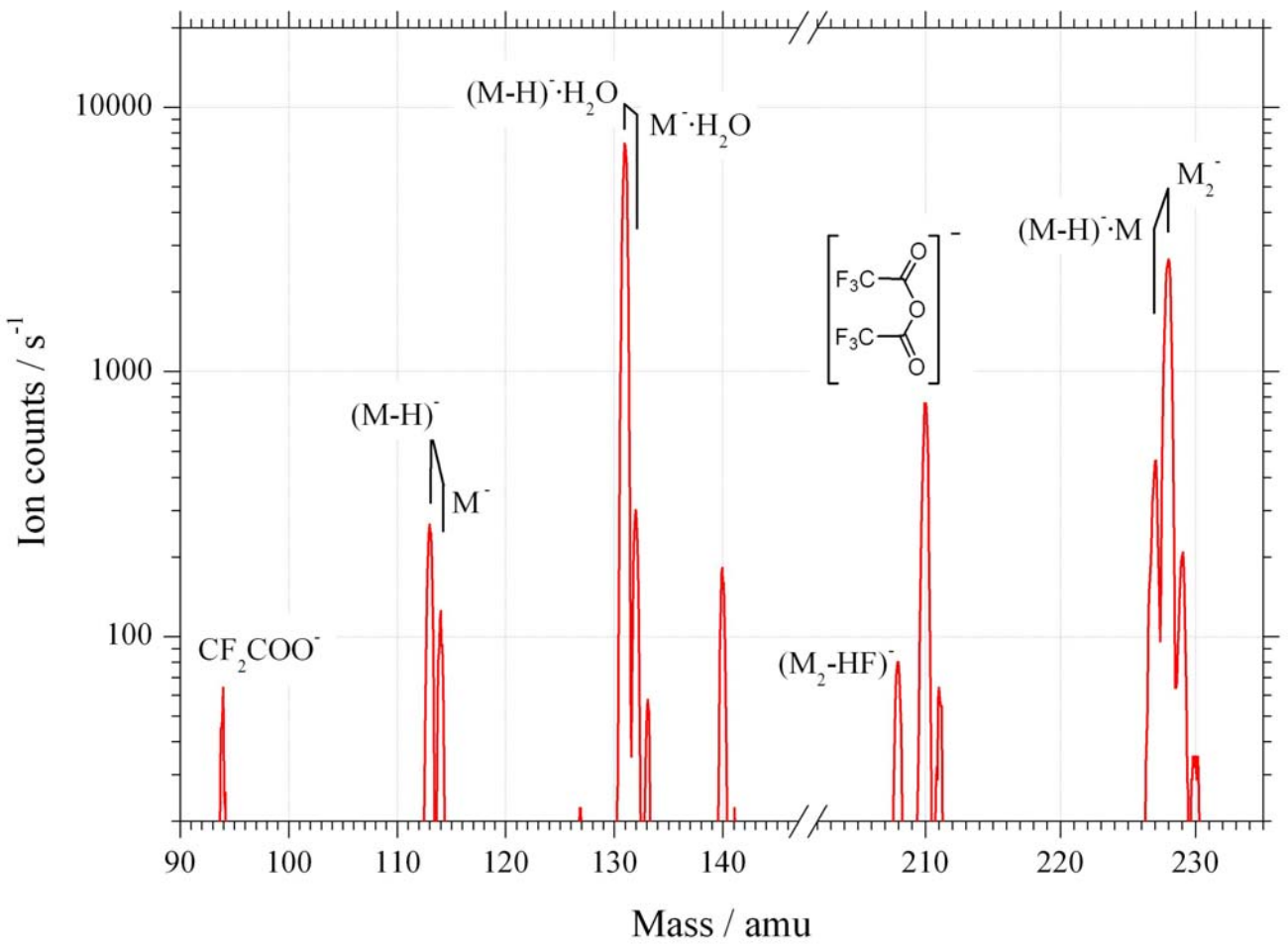
(Supersonic beam)

HCOOH *formic acid*

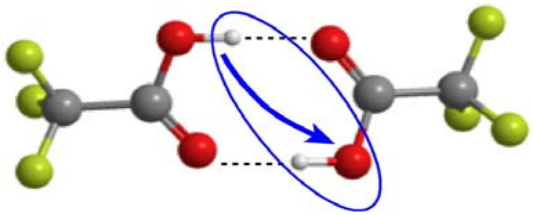


CF_3COOH / CF_3COOD


CF3COO- ·H2O
Mn-
1000
100
10
Ion intensity / s-1
n = 1
2
3
4
CF2COO-
F3C
F3C
O
O
O
O
-
100
200
300
400
500
Mass / amu

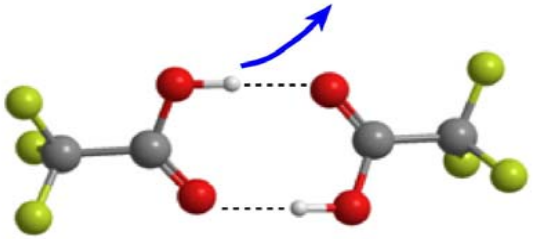

Ion counts / s-1
10000
1000
100
90
100
110
120
130
140
210
220
230
Mass / amu
(M-H)-·H2O
M-·H2O
(M-H)-
M-
CF2COO-
(M2-HF)-
(M-H)-·M
M2-
F3C
O
O
O
F3C
O
O
-

a)



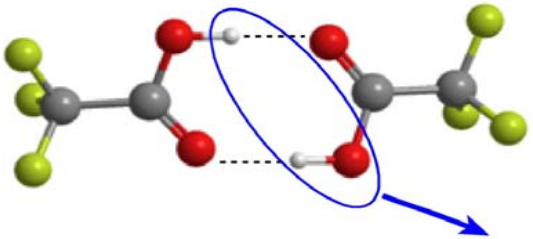
$(M–H)^{-}\cdot H_2O + C_2F_3O$

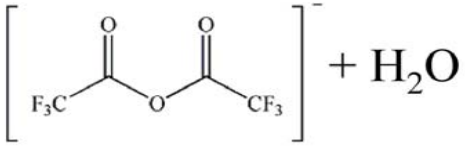
b)



$(M–H)^{-}\cdot M + H$

c)





$+ H_2O$

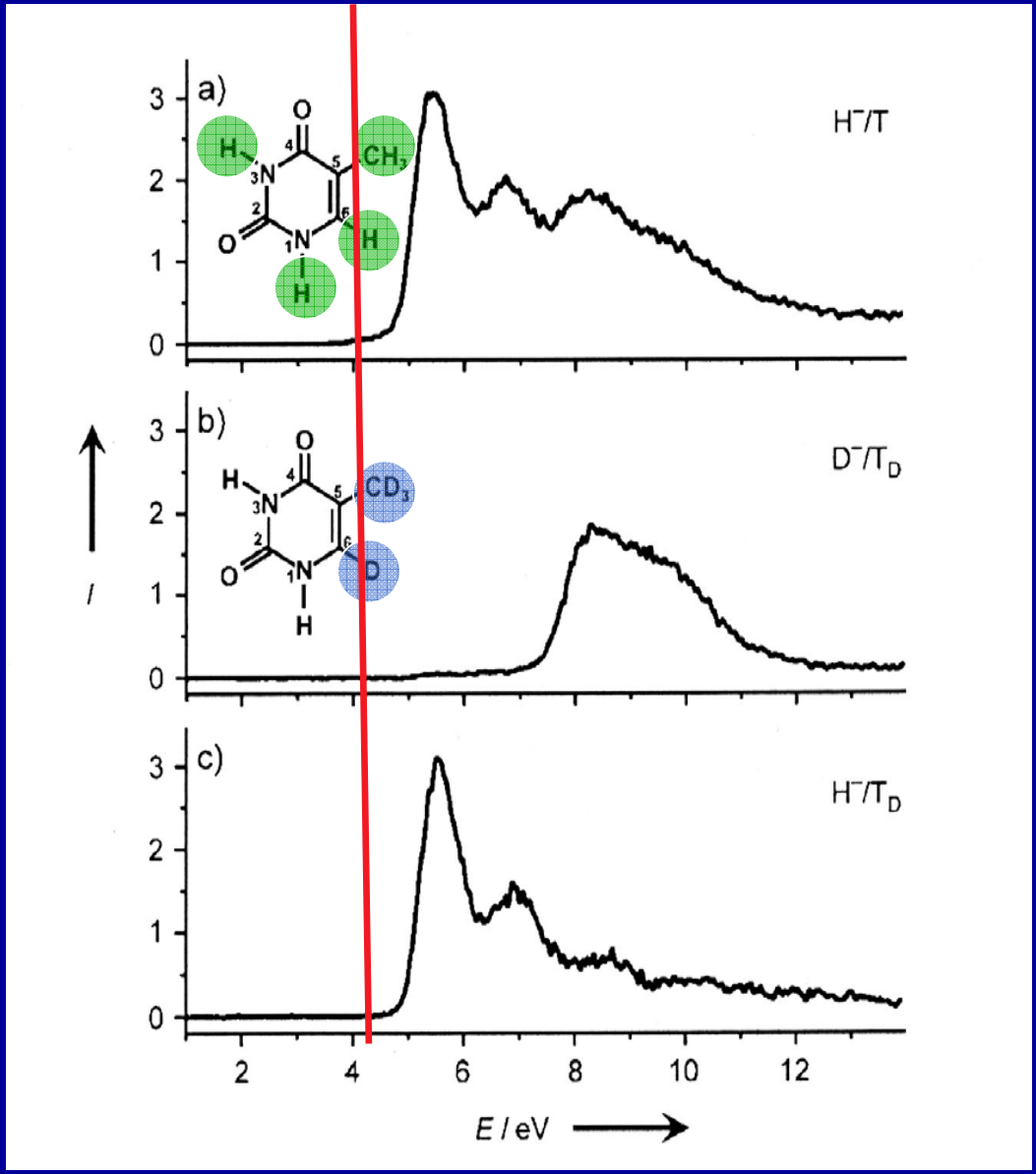
- *strong enhancement of electron capture cross section*

- *chemical reactions induced at very low energy*

Subexcitation energies:

- *No transfer of excess electrons from NBs to the backbone*
- *Sugar unit is very sensitive*
- *Phosphate group is sensitive*
- *Hydrogen bridge is sensitive*

⇒*Molecular mechanism(s) for strand breaks not yet clear*



Bond-selective abstraction

of H^- from thymine

S. Ptasinska, S. Denifl et al.

Angew. Chem. Int. Ed. 44 (2005) 2

(Innsbruck-Berlin)

	D/eV
N1-H	4.4
N3-H	5.8
CH2-H	4,5
C6-H	4.9

EA(H)=0.75 eV

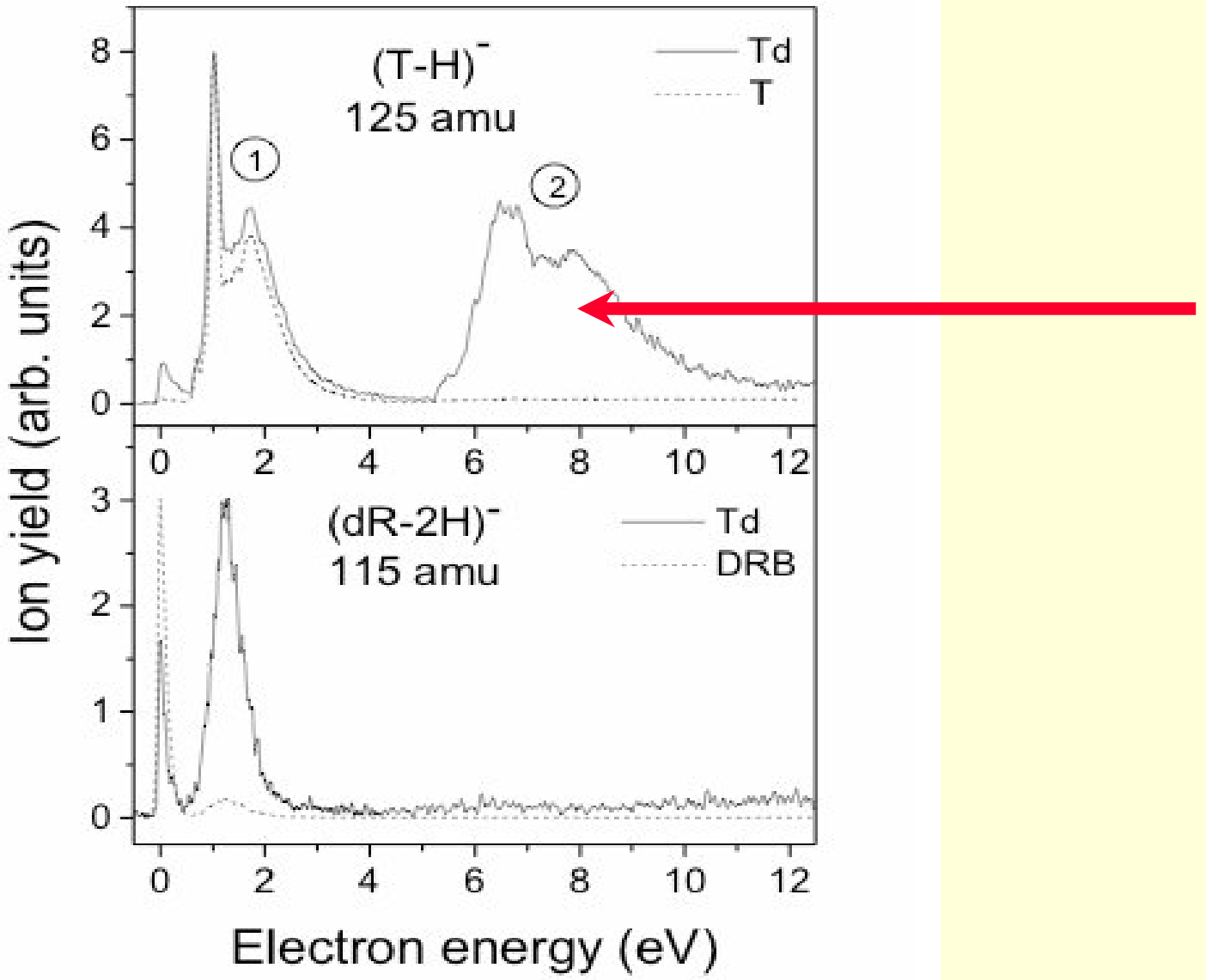
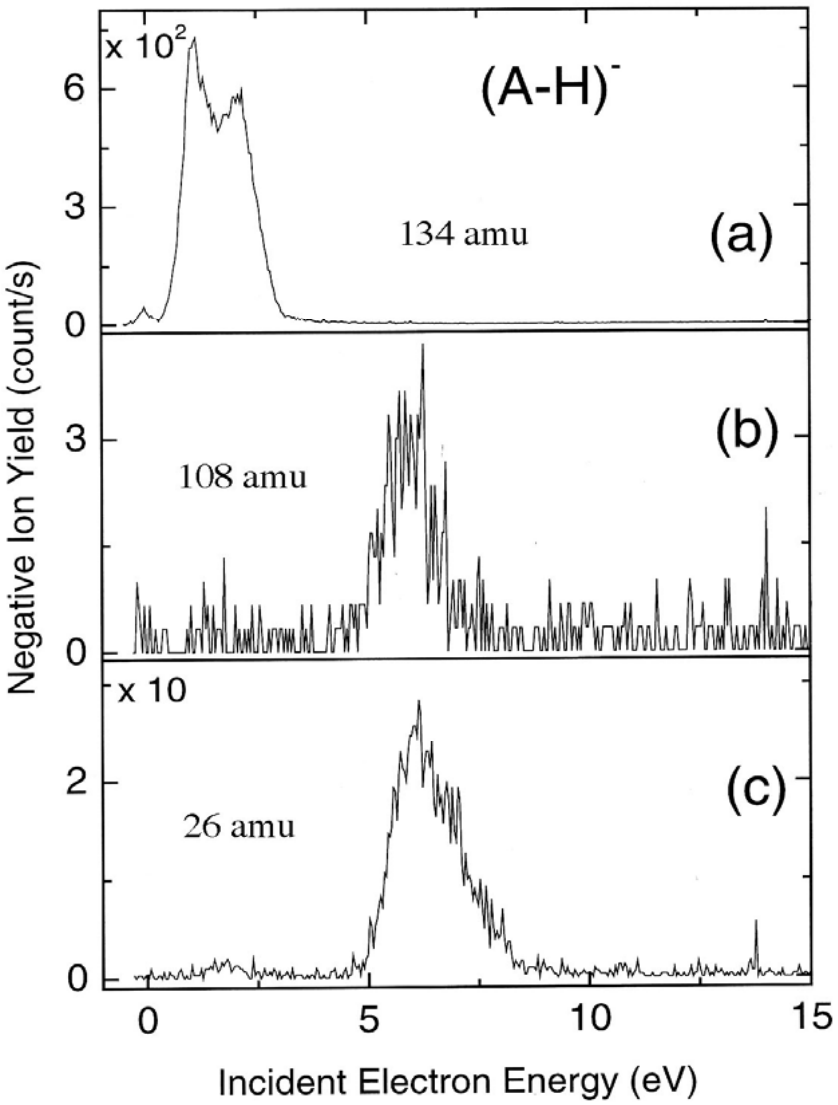


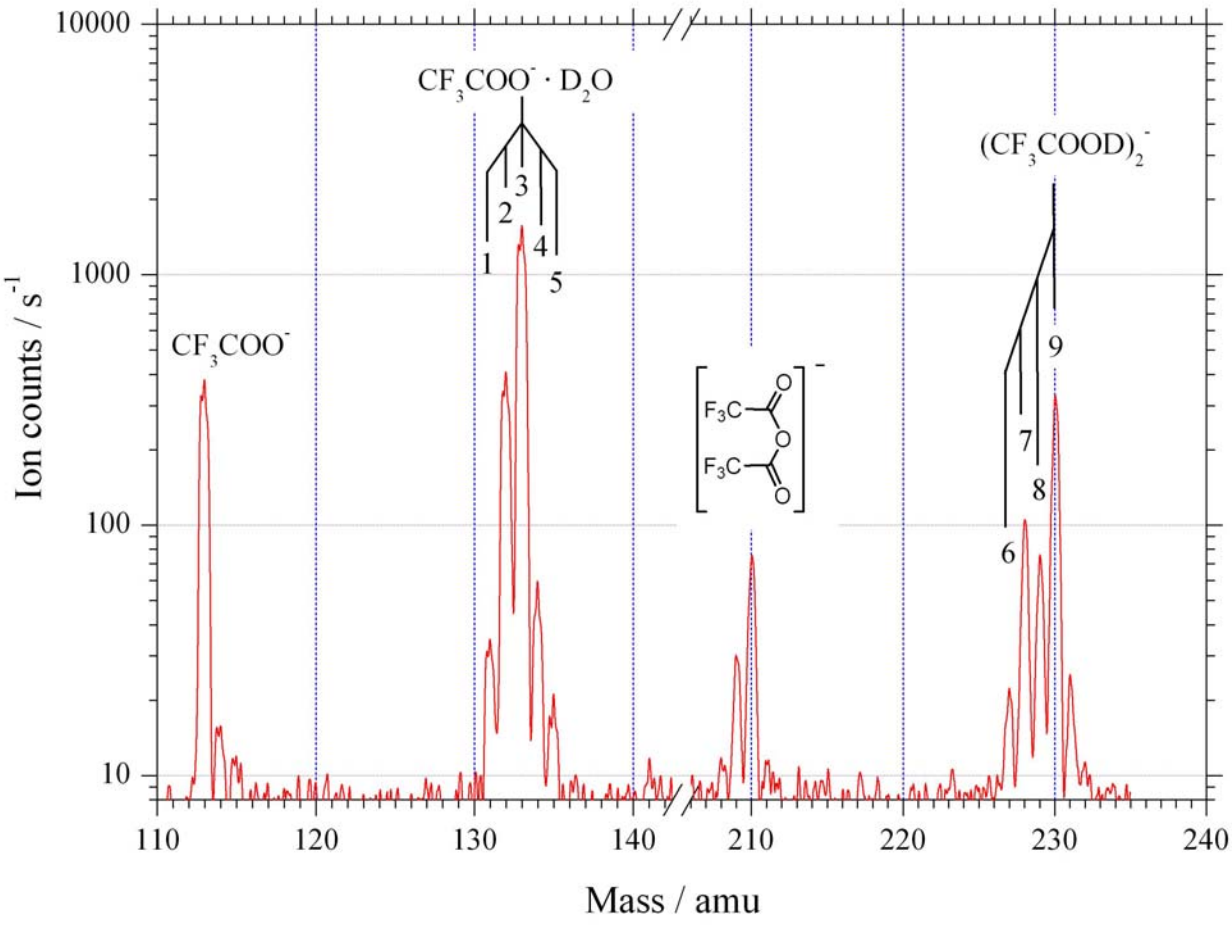
Fig. 3

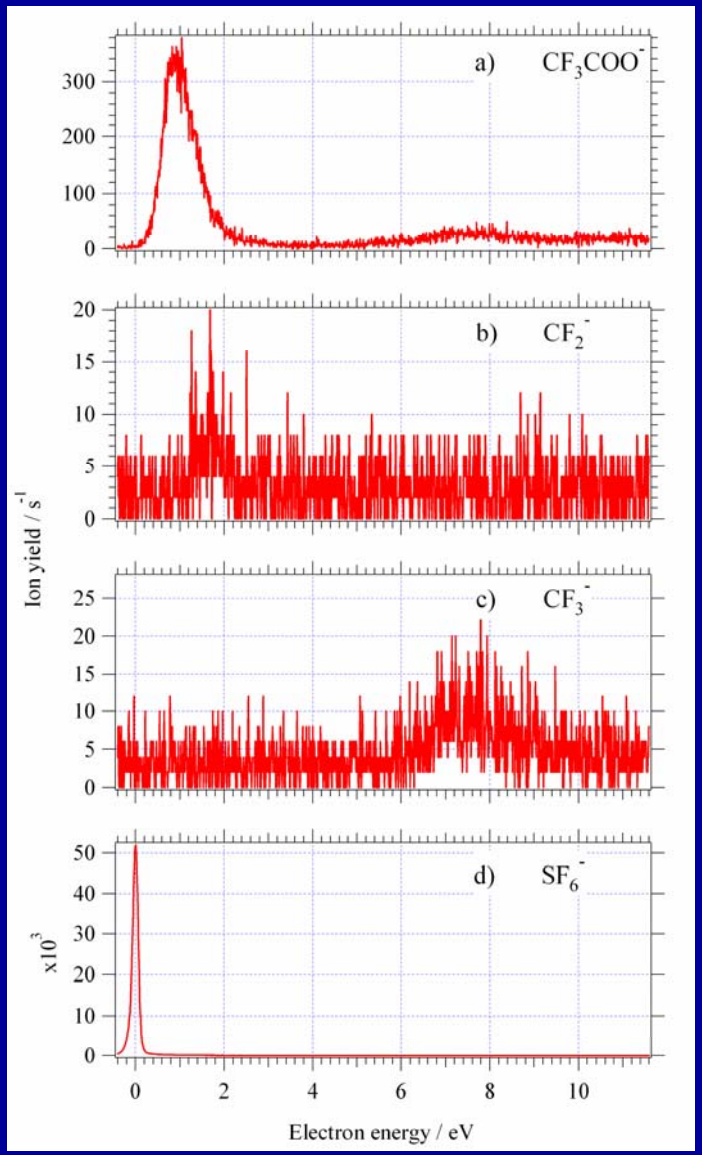
S. Ptasinska, S. Denifl et al., Angew. Chem. Int. Ed. (in print).

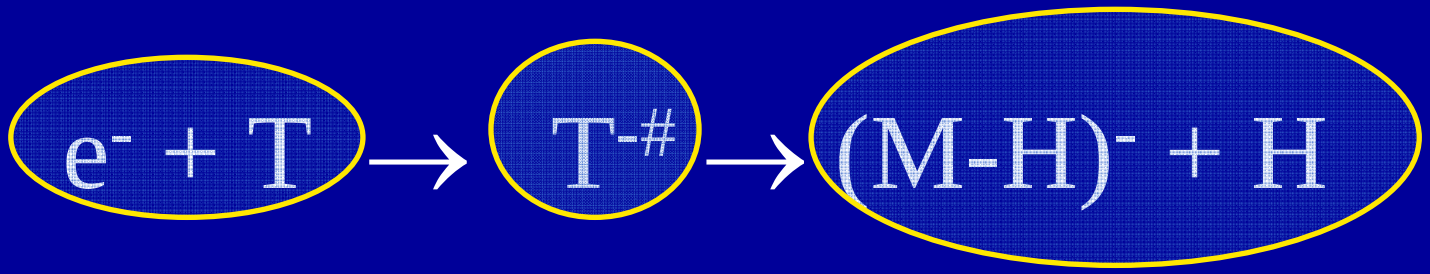


$(A\text{-}CN)^-$

$CN^- / C{=}CH_2^-$


10000
1000
100
10
Ion counts / s-1
CF3COO- · D2O
CF3COO-
(CF3COOD)2-
1
2
3
4
5
6
7
8
9
F3C
O
O
O
F3C
O
O
110
120
130
140
210
220
230
240
Mass / amu


a) CF_3COO^-
b) CF_2^-
c) CF_3^-
d) SF_6^-
Ion yield / s^{-1}
x10^3
Electron energy / eV



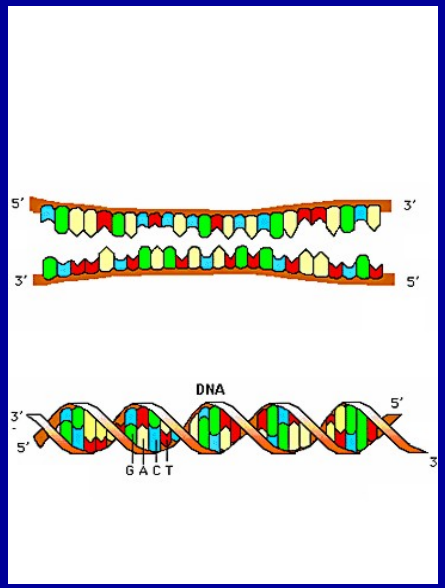
Quantum Chemistry

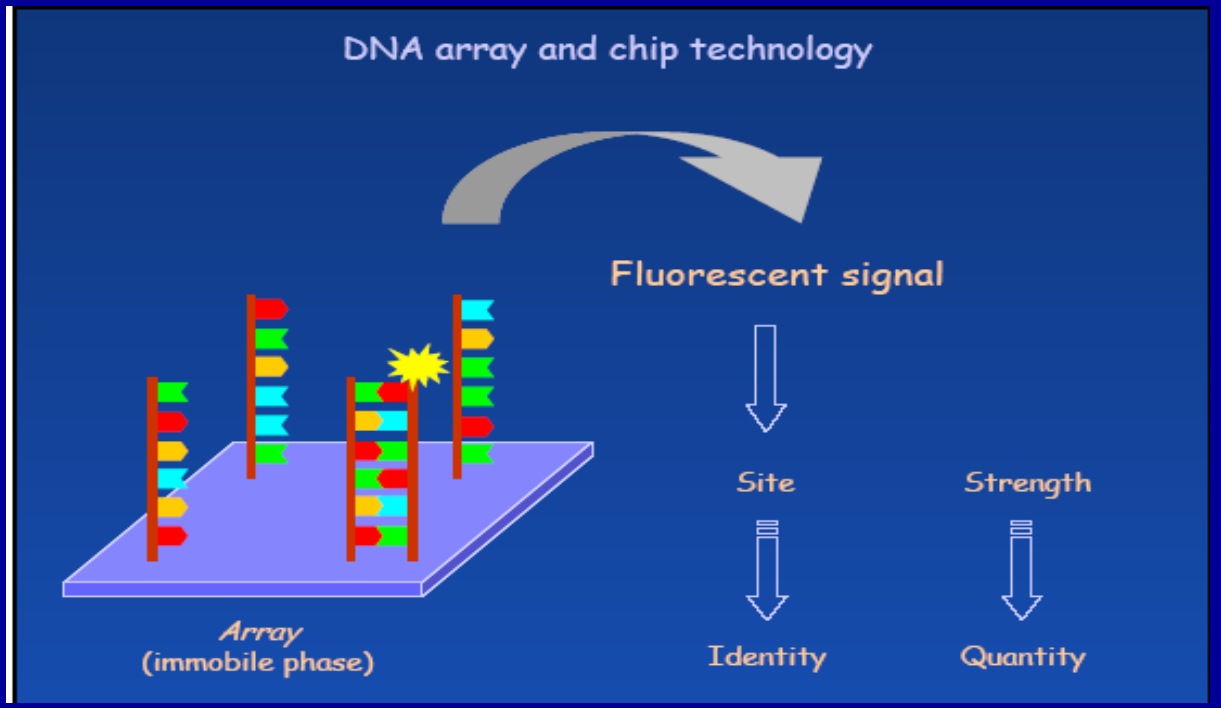
Quantum Chemistry

Scattering Calculation

(F. Gianturco)

Hybridization





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