



L7

# Case studies II: Diverse examples in photochemistry

**Mario Barbatti**

A\*Midex Chair Professor  
[mario.barbatti@univ-amu.fr](mailto:mario.barbatti@univ-amu.fr)

Aix Marseille Université, Institut de Chimie Radicalaire



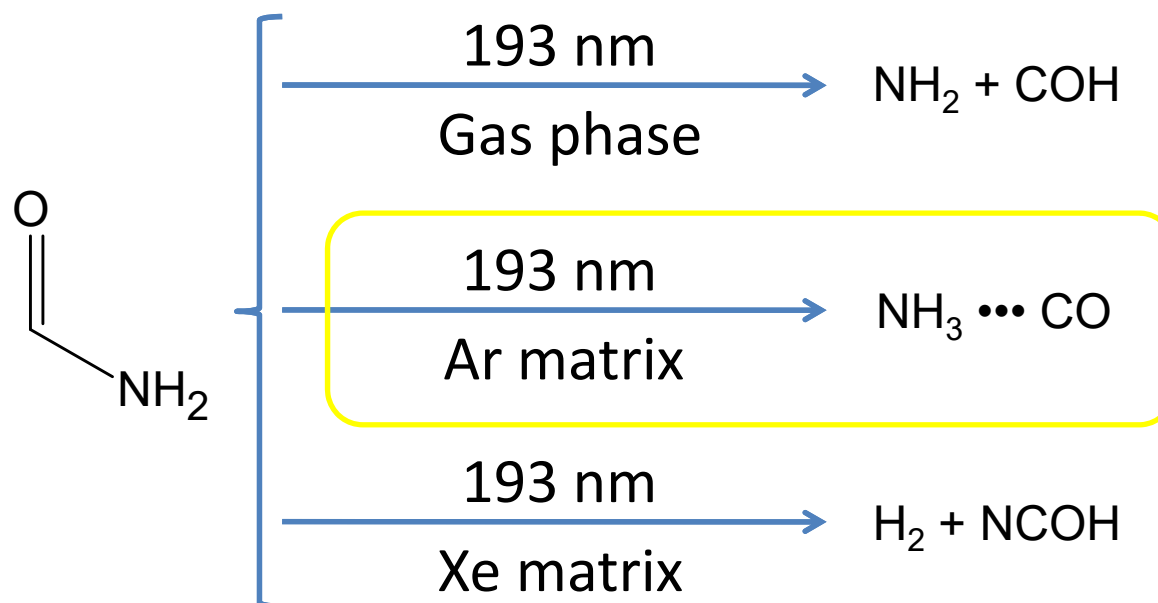
# case study

*When environment matters:  
Formamide dissociation*



# Formamide photolysis

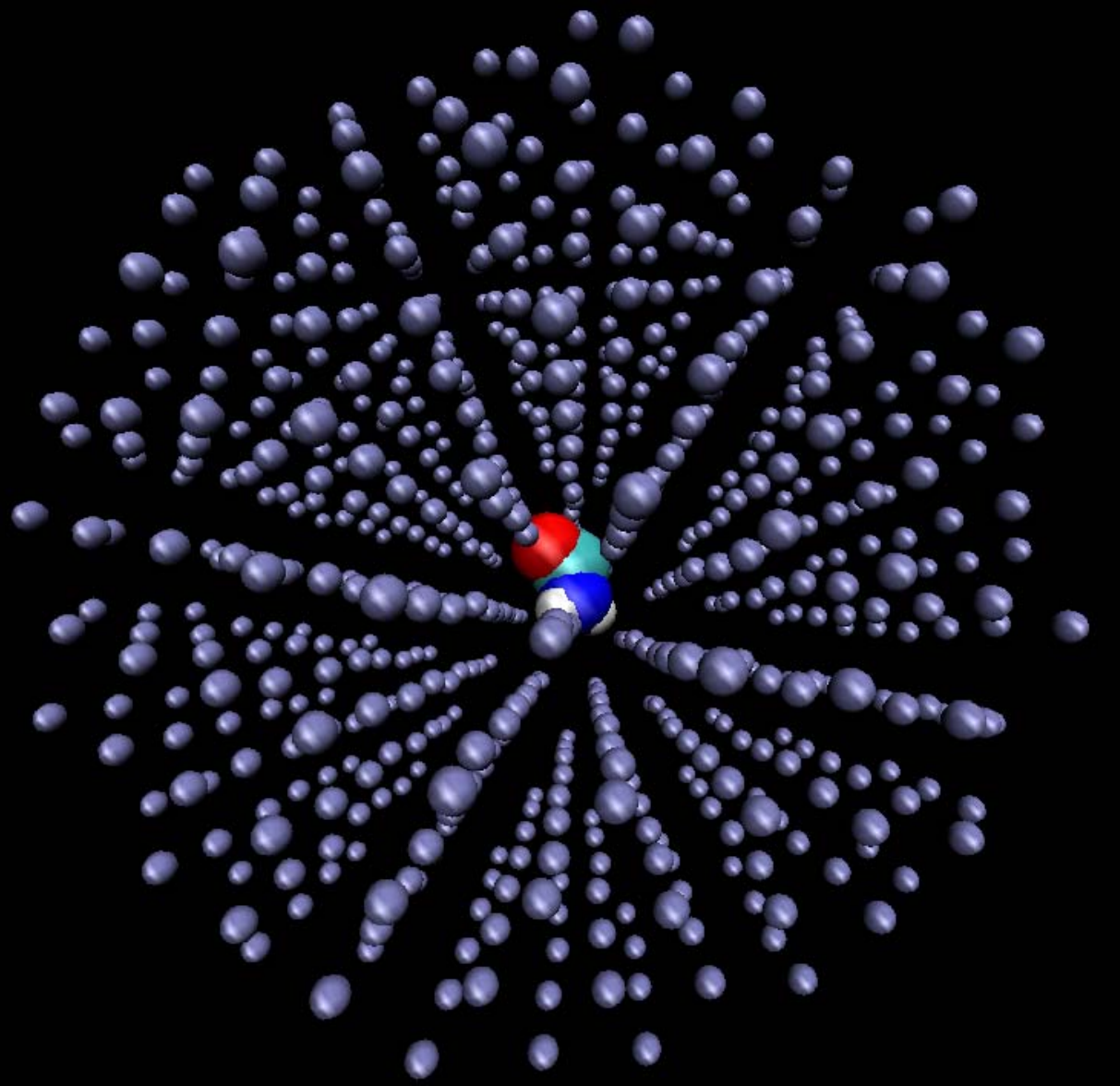
LIGHT AND  
MOLECULES



- Lundell, Krajewska, Rasanen, J Phys Chem A **102**, 6643 (1998)

# *Formamide in Ar matrix*

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QM: formamide

- CASSCF(10,8)/6-31G\*

MM: Ar matrix

- 661 atoms
- 18 K
- OPLSAA force field

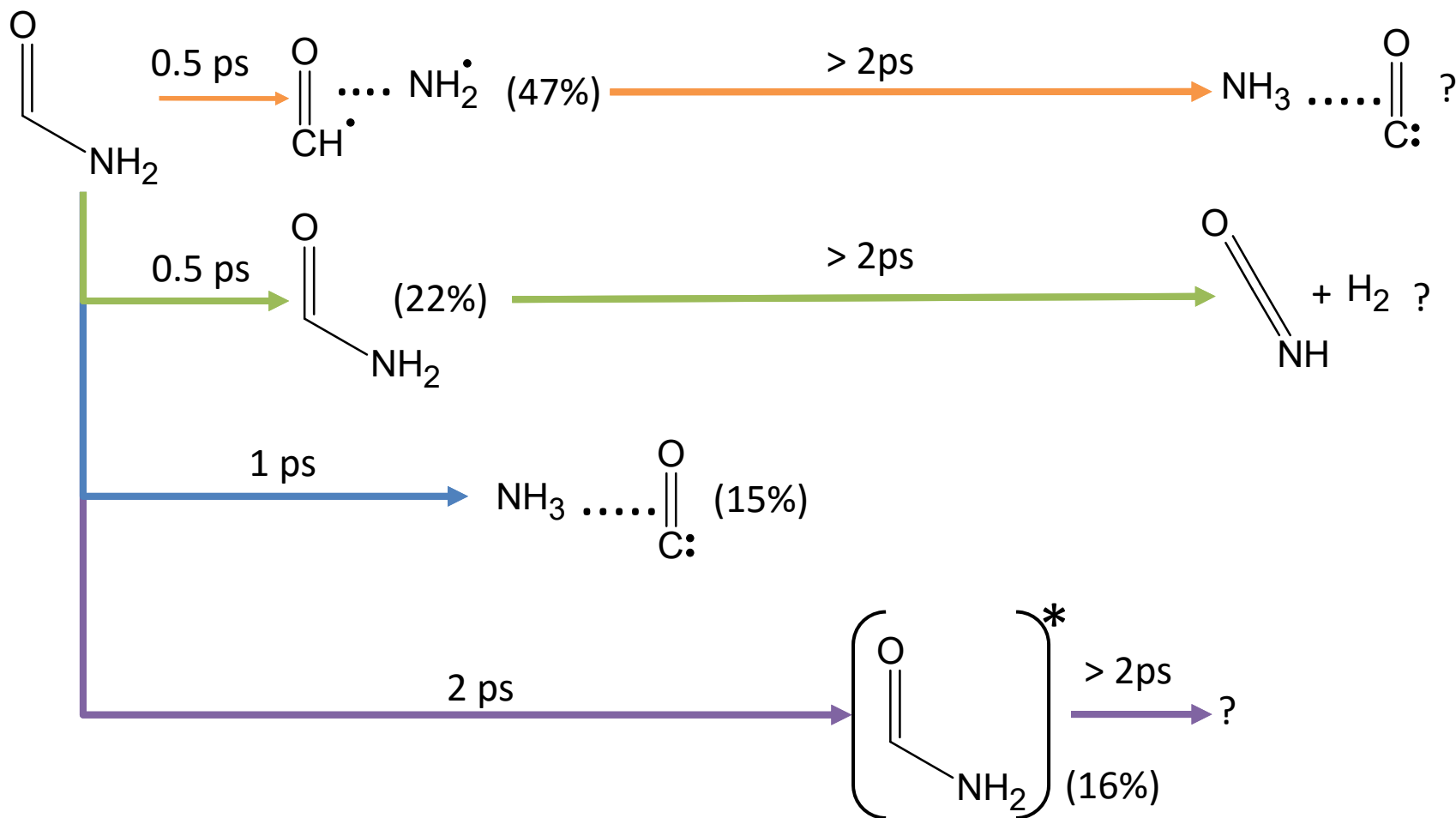
Dynamics

- 100 trajectories
- 2 ps
- 0.5 fs step

- Eckert-Maksic, Vazdar, Ruckenbauer, Barbatti, Muller, Lischka, PCCP **12**, 12719 (2010)

# Formamide in Ar matrix

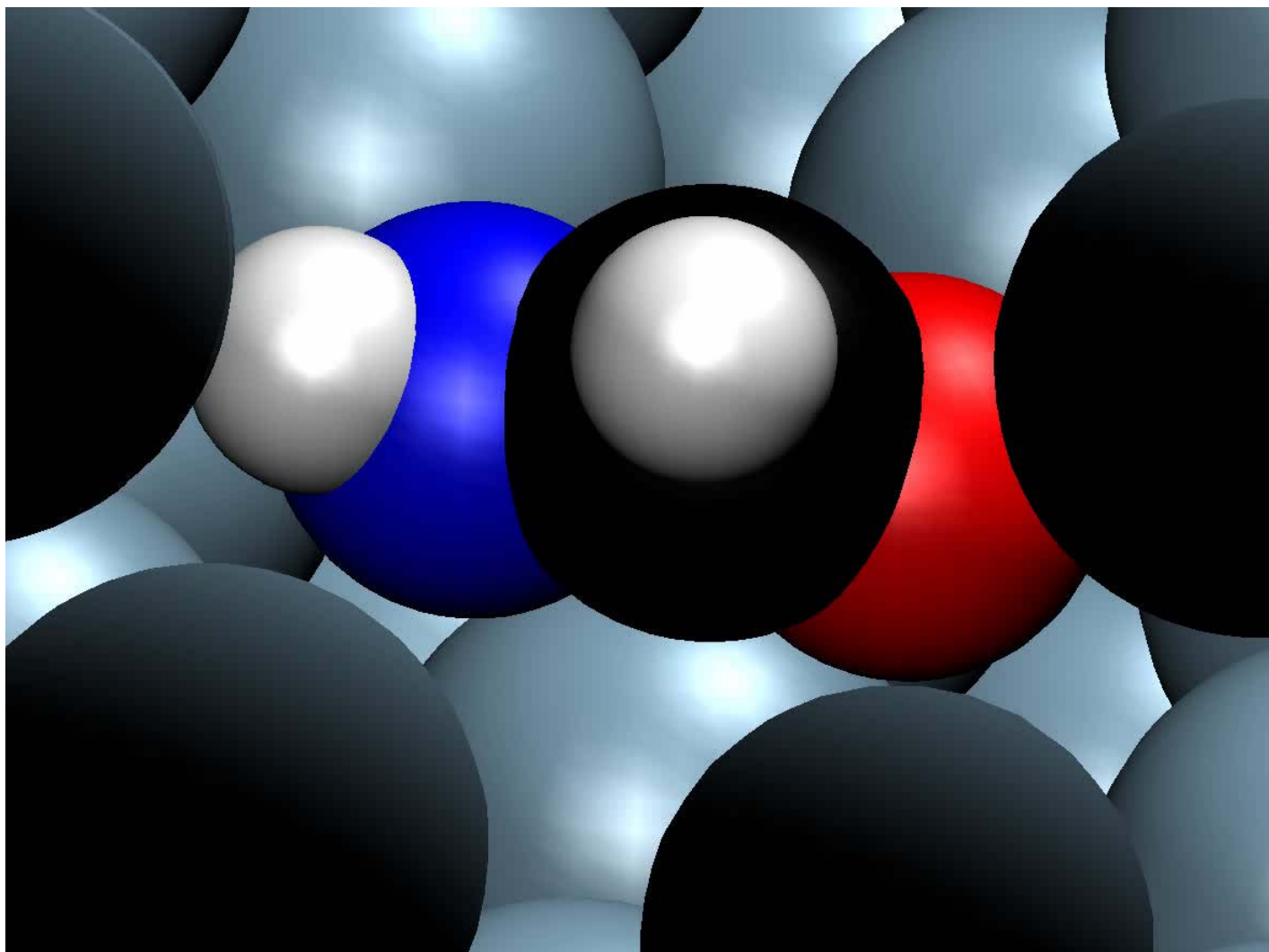
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- Eckert-Maksic, Vazdar, Ruckenbauer, Barbatti, Muller, Lischka, PCCP **12**, 12719 (2010)

# *Formamide in Ar matrix*

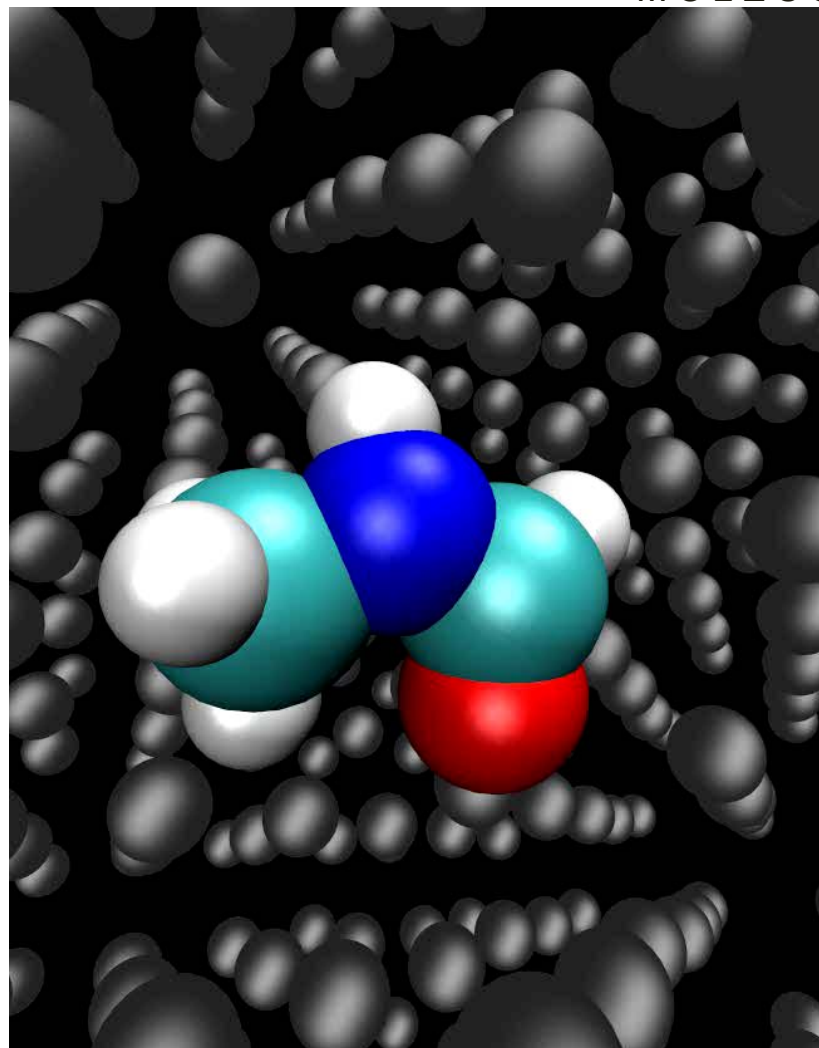
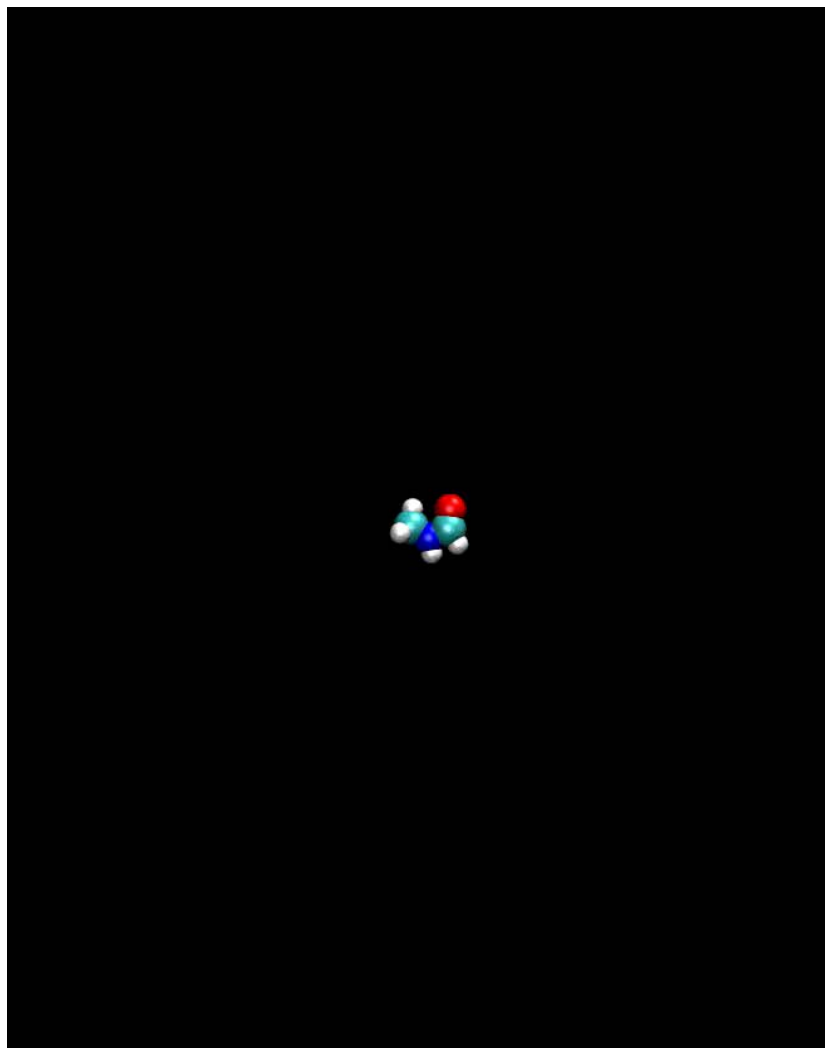
LIGHT AND  
MOLECULES



- Eckert-Maksic, Vazdar, Ruckenbauer, Barbatti, Muller, Lischka, PCCP **12**, 12719 (2010)

# *Me-formamide in the gas phase*

LIGHT AND  
MOLECULES



- Crespo-Otero, Mardyukov, Sanchez-Garcia, Barbatti, Sander, ChemPhysChem **14**, 827 (2013)

# case study

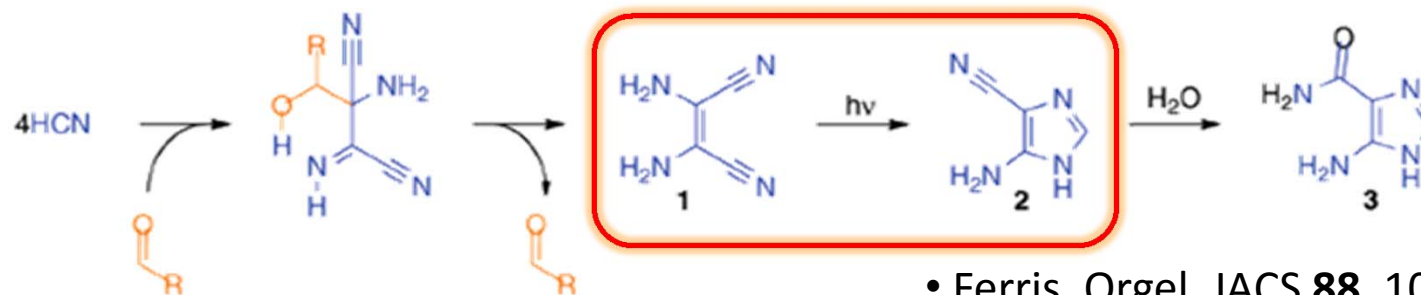


*UV in prebiotic reactions*

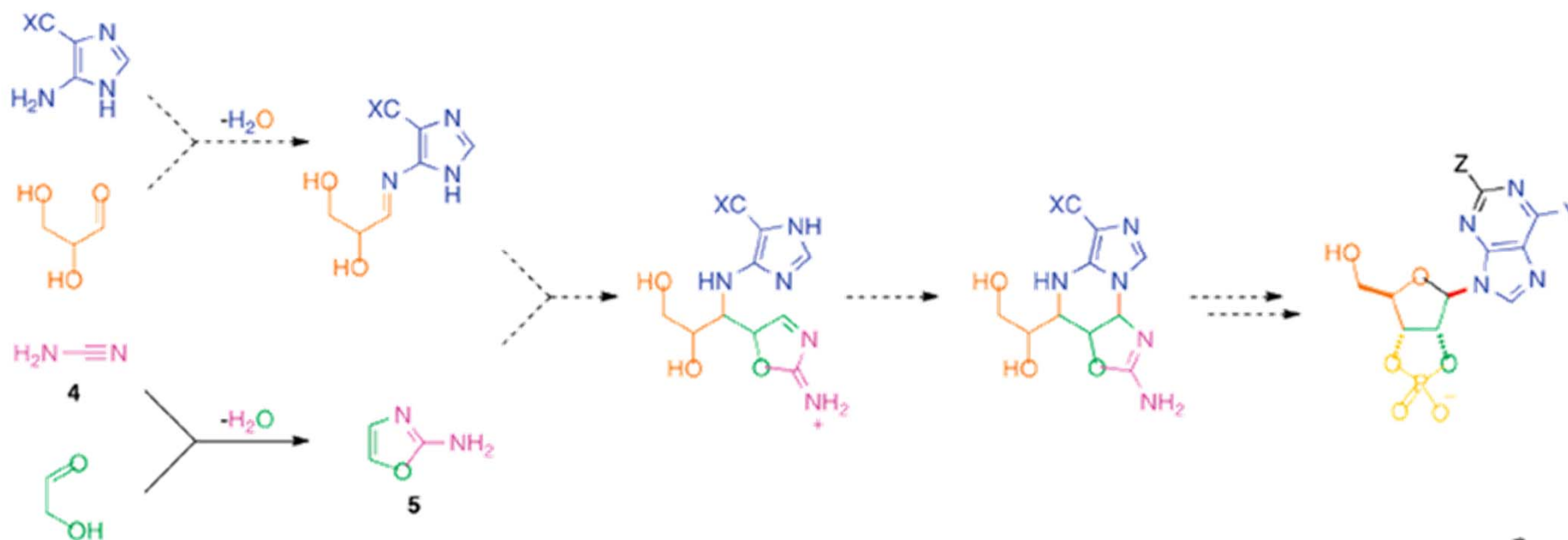


# Prebiotic route for nucleotides

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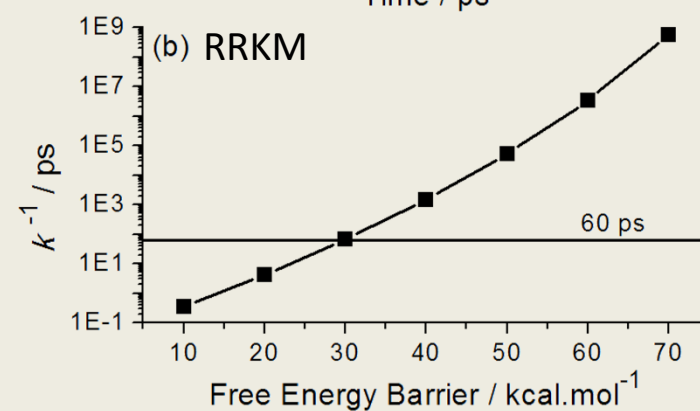
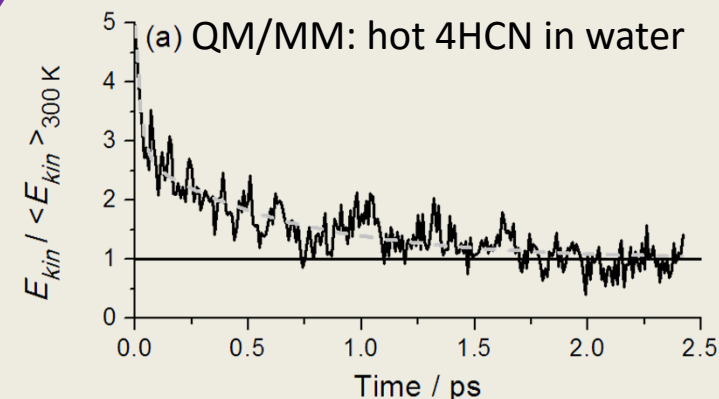
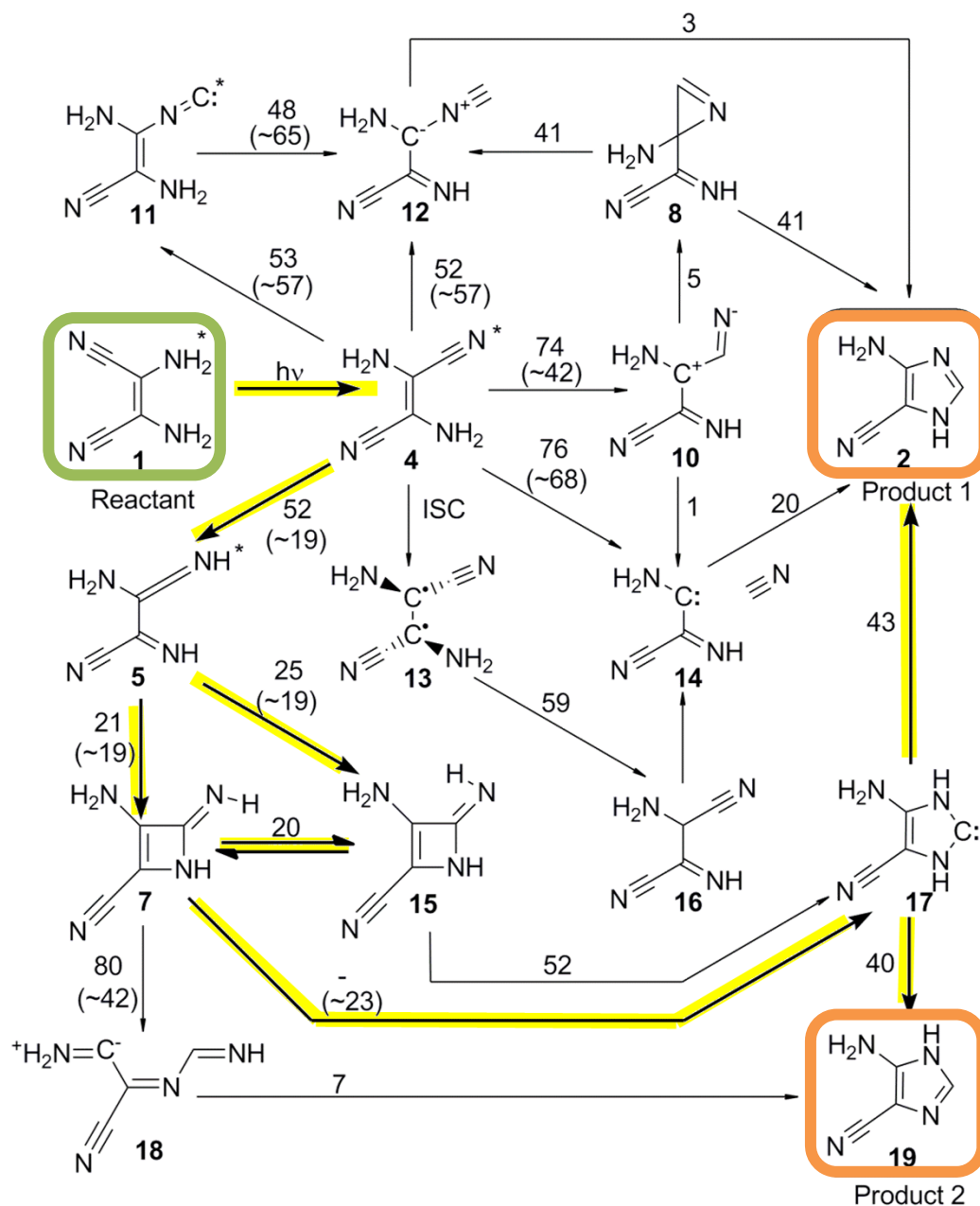
• Ferris, Orgel, JACS **88**, 1074 (1966)



• Powner, Sutherland, Szostak, JACS **132**, 16677 (2010)

# Computational chemistry in action

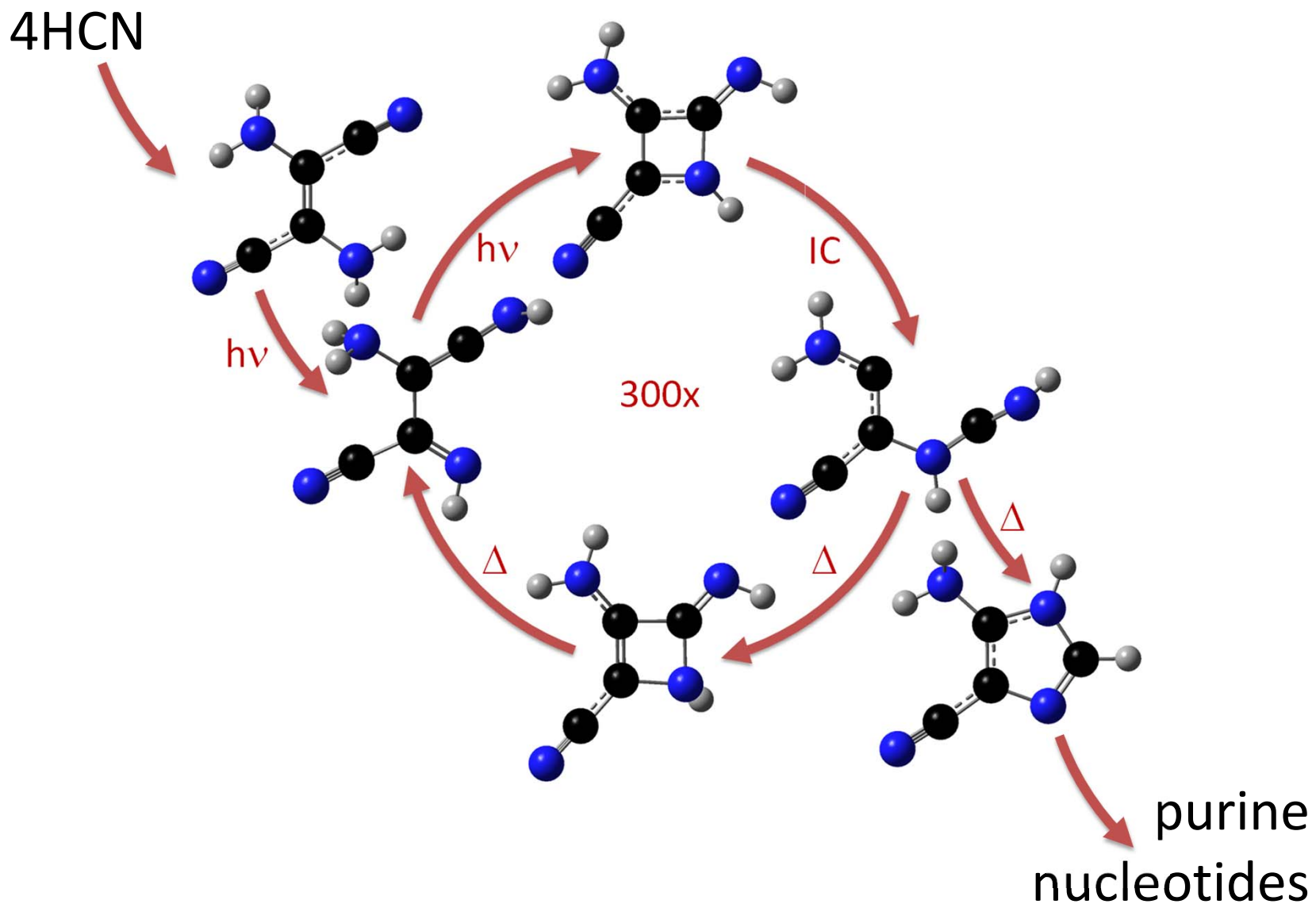
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Dynamics and Chemical Kinetics revealed the only possible route

# Photochem in prebiotic synthesis

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- Boulanger, Anoop, Nachtigallova, Thiel, MB, ACIE **52**, 8000 (2013)

# case study

*Photodynamics of  
Isolated Nucleobases*



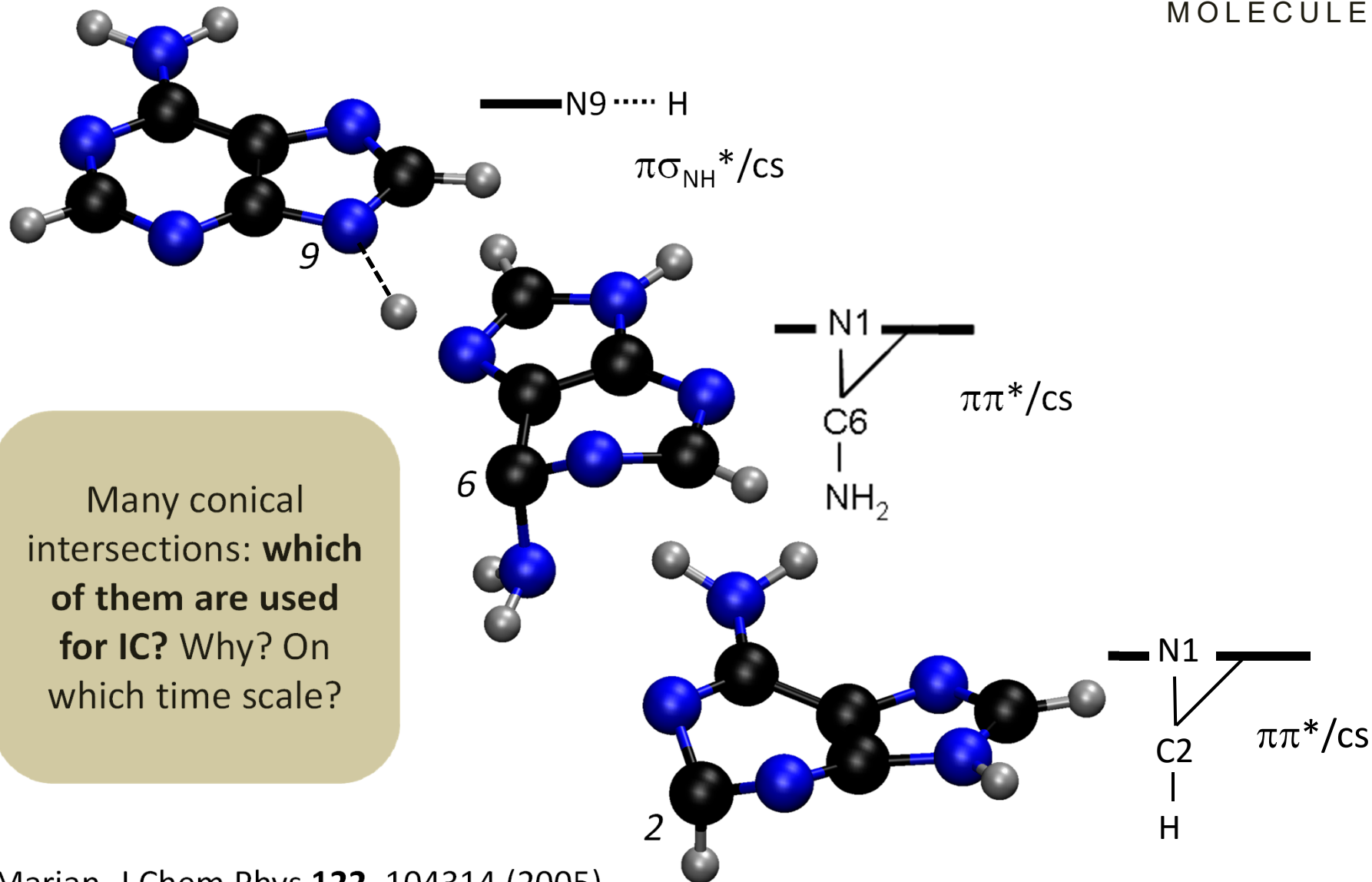
Base	$\Phi_F$	$\tau_1$ (ps)	$\tau_2$ (ps)
Ade	0.0003	1.0	
Gua	0.0003	0.4	
Thy	0.0001	0.5	6.4
Ura	0.0001	0.5	2.4
Cyt	0.0001	0.8	3.2

**Low fluorescence quantum yields and short excited-state lifetimes indicate conversion through conical intersections**

- Ullrich, Schultz, Zgierski, Stolow, PCCP **6**, 2796 (2004)

# Adenine Conical Intersections

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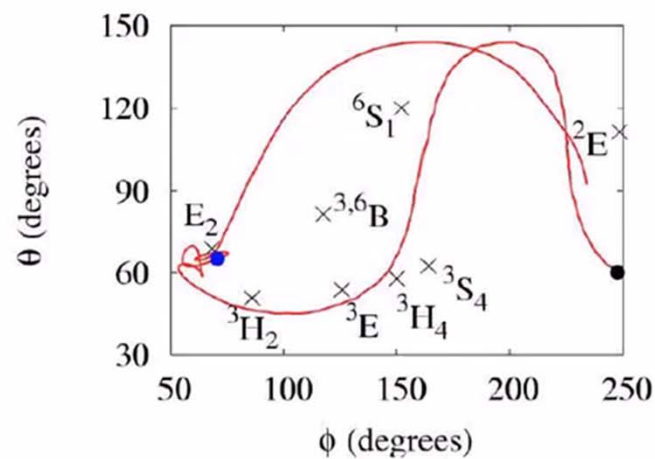
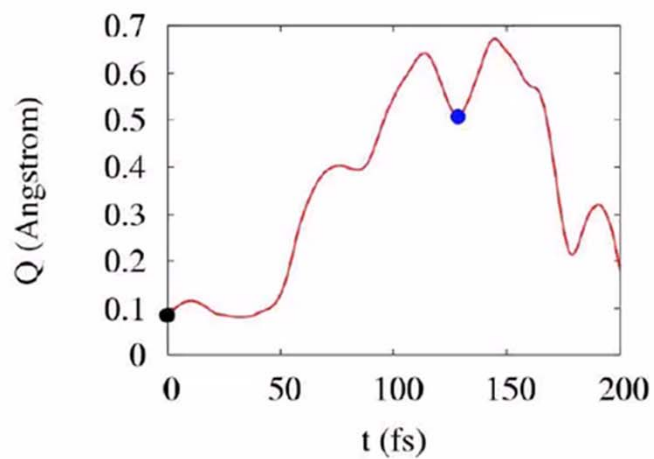
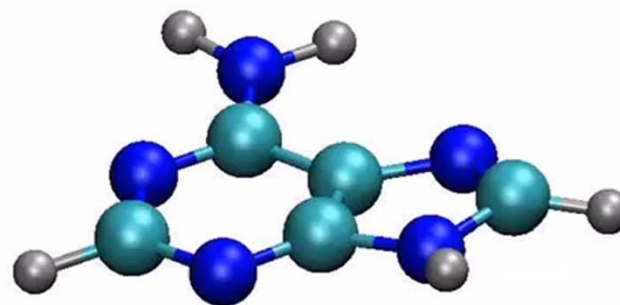
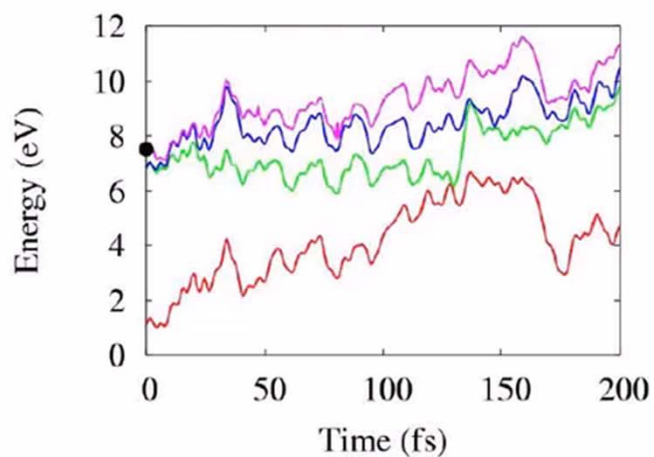
Many conical intersections: **which of them are used for IC? Why? On which time scale?**

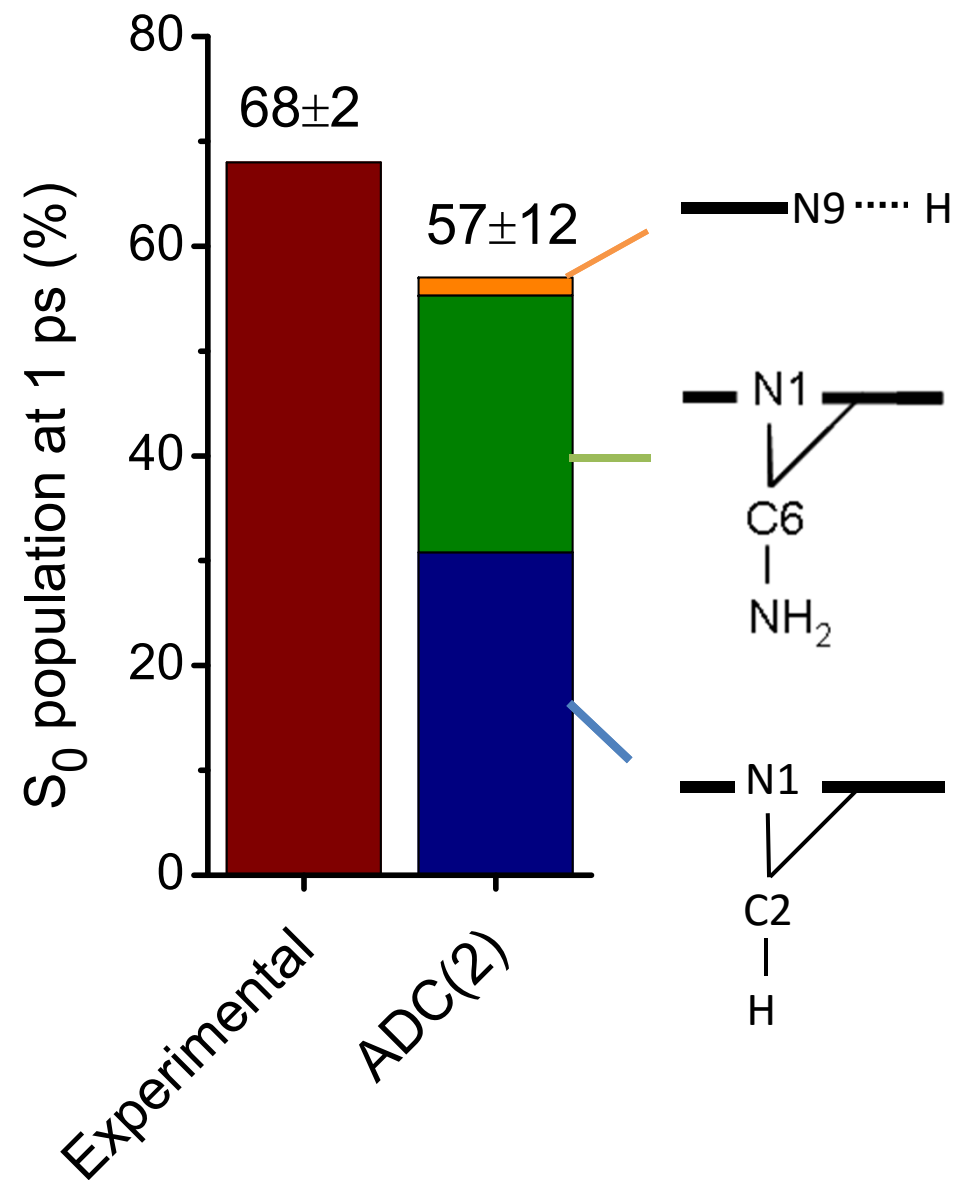
- Marian, J Chem Phys **122**, 104314 (2005)
- Perun, Sobolewski, Domcke, JACS **127**, 6257 (2005)

# Dynamics of Adenine

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 [youtube.com/user/mbarbatti](https://youtube.com/user/mbarbatti)





- Plasser, Crespo-Otero, Pederzoli, Pittner, Lischka, Barbatti, JCTC **10**, 1395 (2014)



# case study

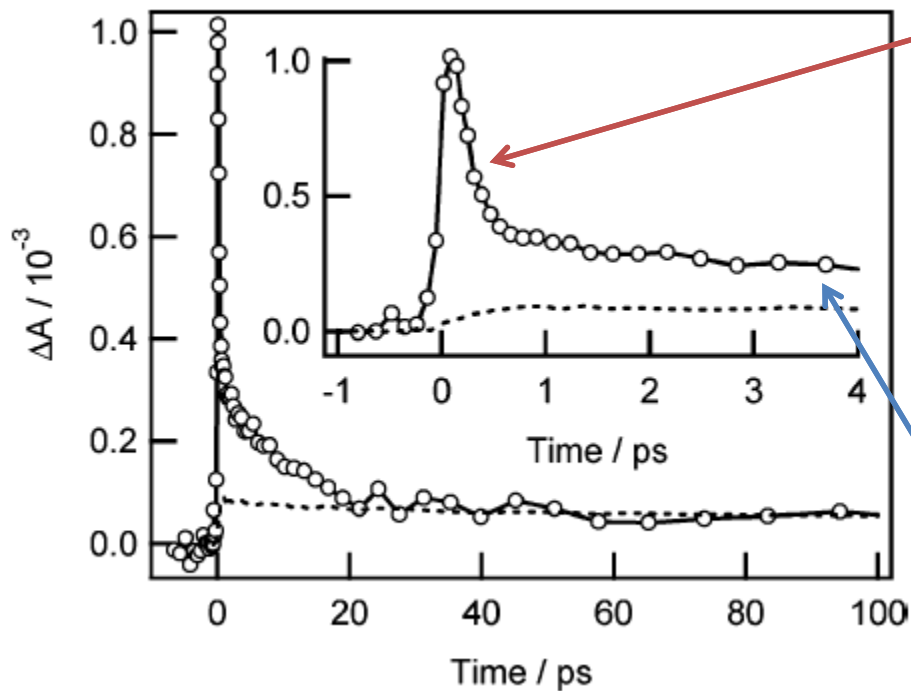


*Tautomers and Solvents*

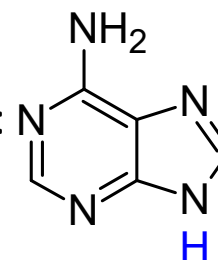
# Transient Spectrum of Ade in Water

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Experimental

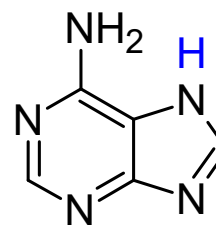


Short time constant (0.18 ps):



9H-adenine

Long time constant (8.8 ps):



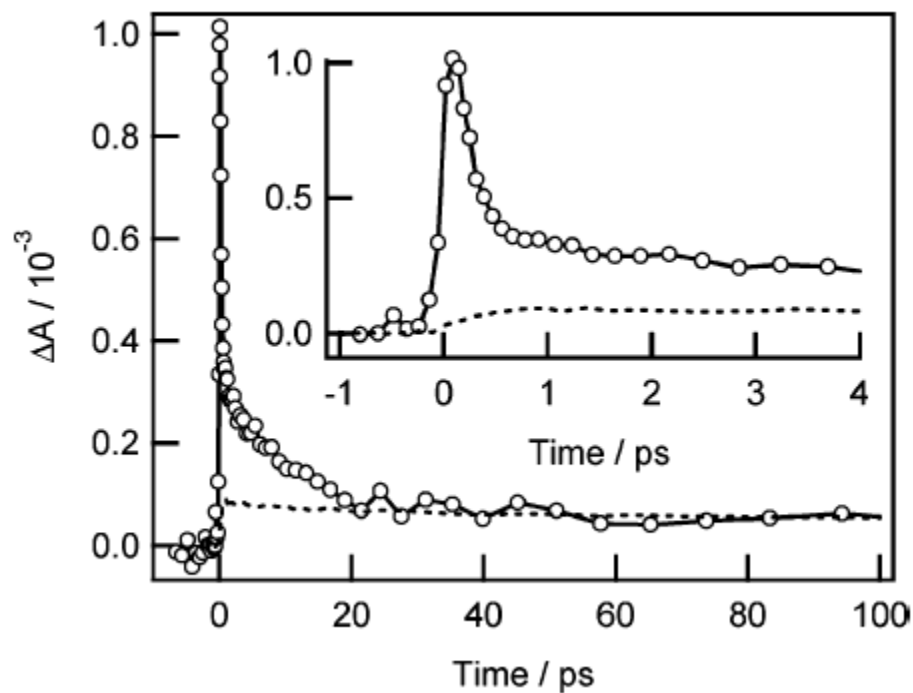
7H-adenine

- Cohen, Hare, Kohler, JACS **125**, 13594 (2003)

# Transient Spectrum of Ade in Water

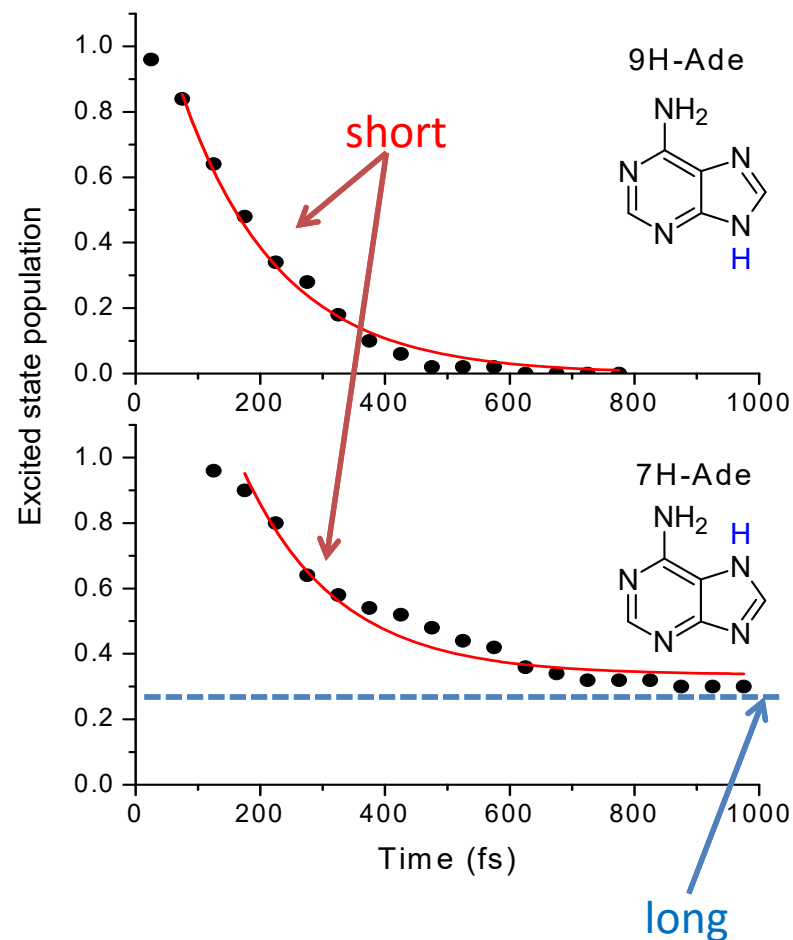
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Experimental



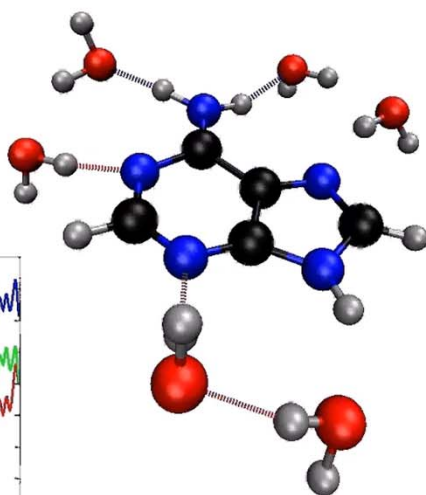
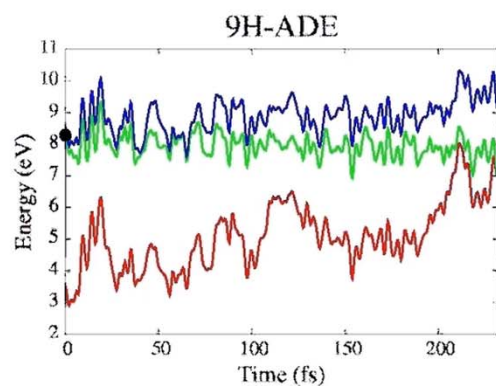
Experimental assignment  
must be reviewed based on  
the computational data

Simulations

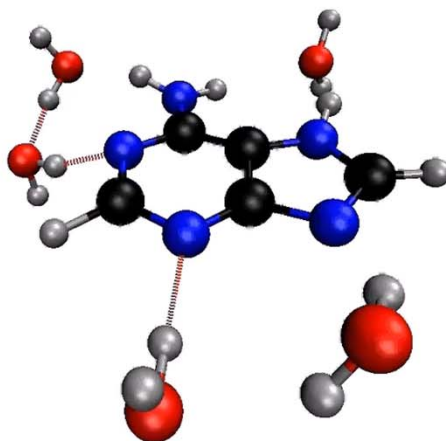
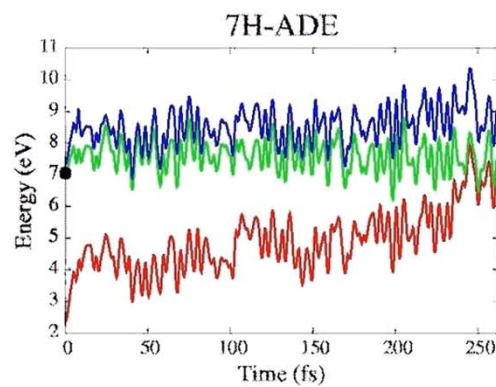


ADC(2)/aug-cc-pVDZ

- Barbatti, JACS **136**, 10246 (2014)



9H-Ade + water:  
C2 puckering  
similar to Gas Phase



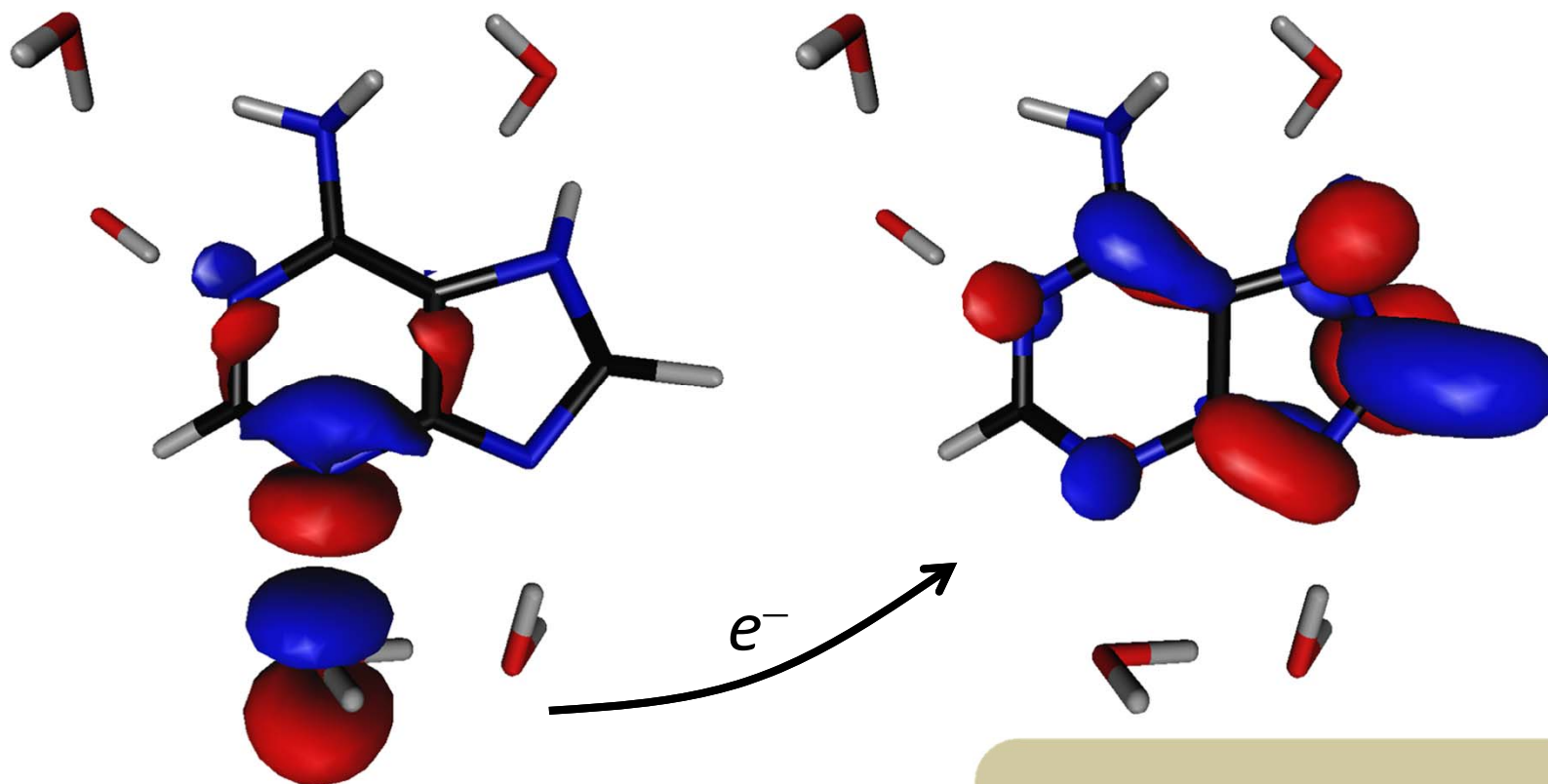
7H-Ade + water:  
Planar  
completely different from GP

ADC(2)/aug-cc-pVDZ

# *S*<sub>1</sub> State at the Conical Intersection

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## Microsolvated 7H-Ade



Water is not only disturbing the system; it plays an **active role** in the deactivation

• Barbatti, JACS **136**, 10246 (2014)

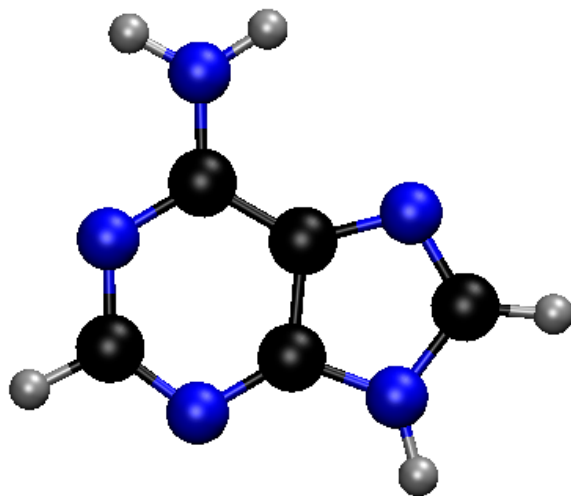
# case study

*Why does 2-Aminopurine Fluoresce  
in Water but not in Vapor?*

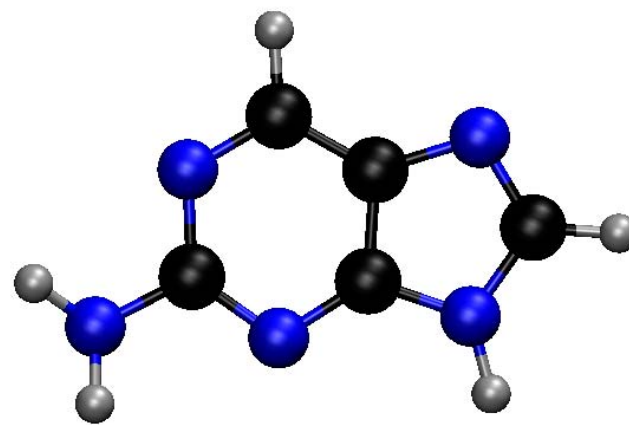


# Adenine x 2-Aminopurine

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Adenine



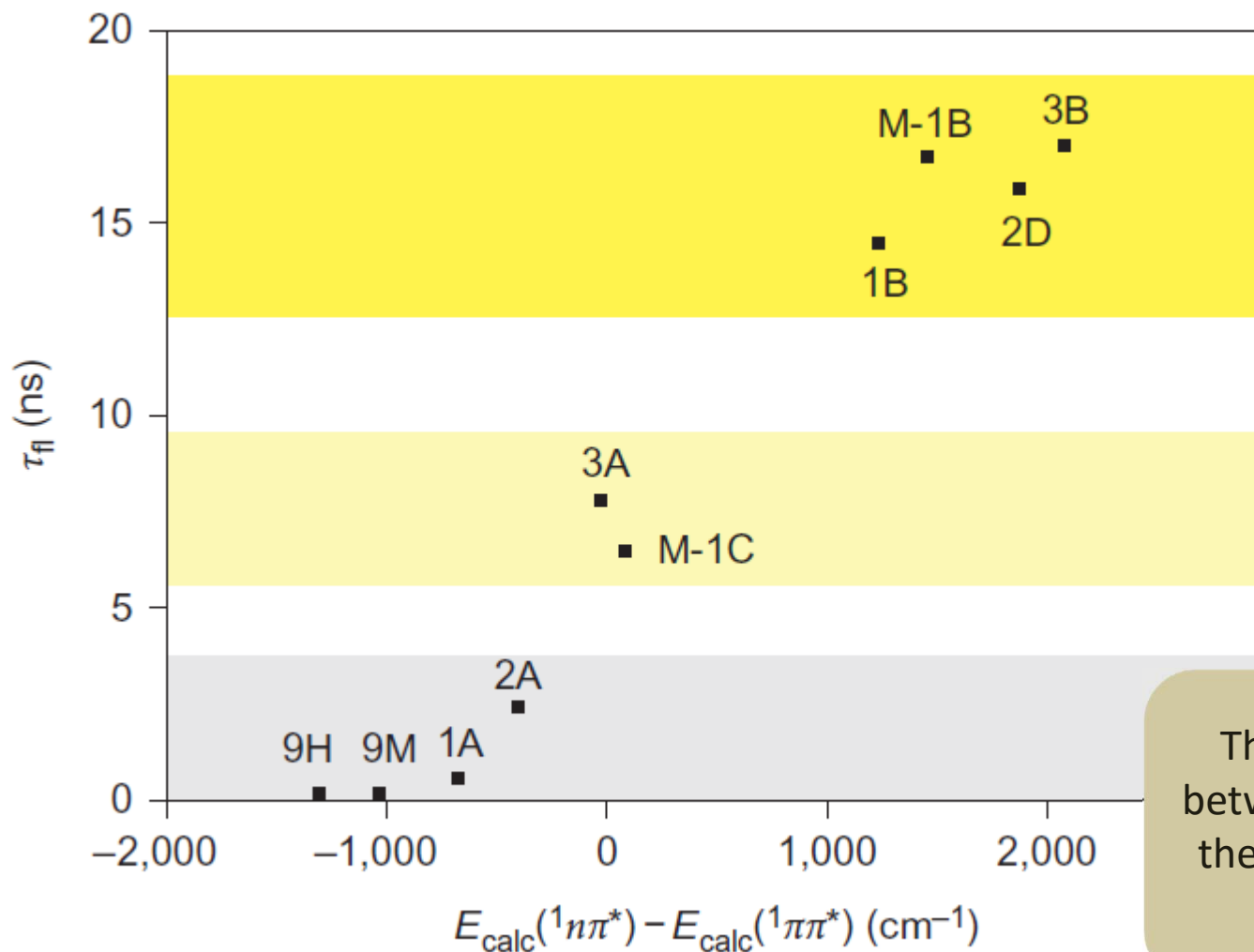
2-Aminopurine

Excited-State Lifetime in ps

	Adenine	2-Aminopurine
Vapor	1	30
Water	0.18	18000

→ ↓

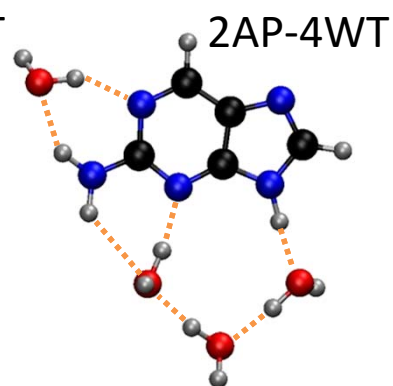
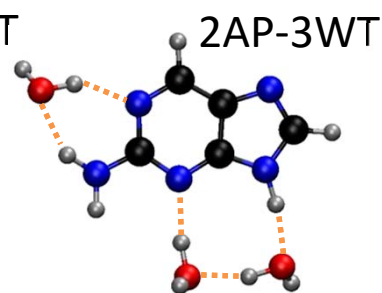
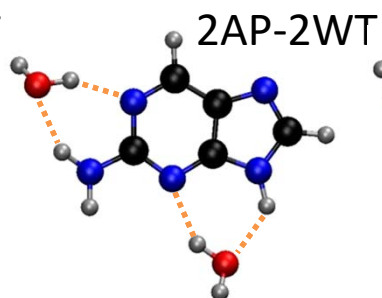
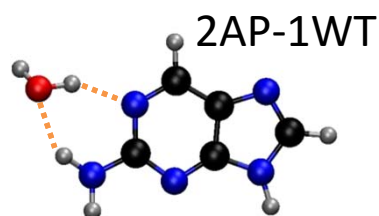
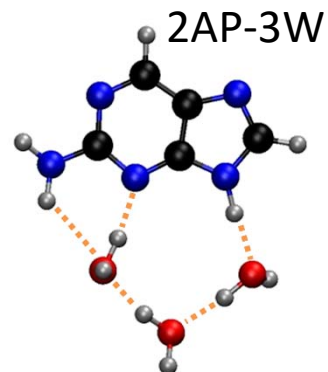
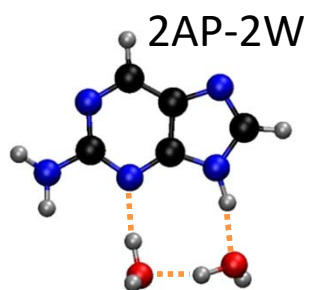
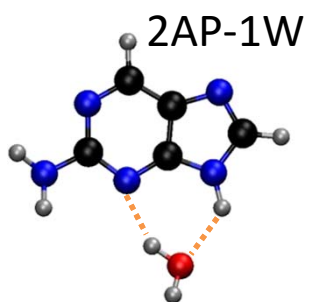
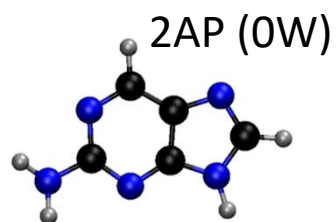
- Canuel, Mons, Piuzzi, Tardivel, Dimicoli, Elhanine, J Chem Phys **122**, 074316 (2005)



There is a correlation between the lifetime and the number/position of water molecules

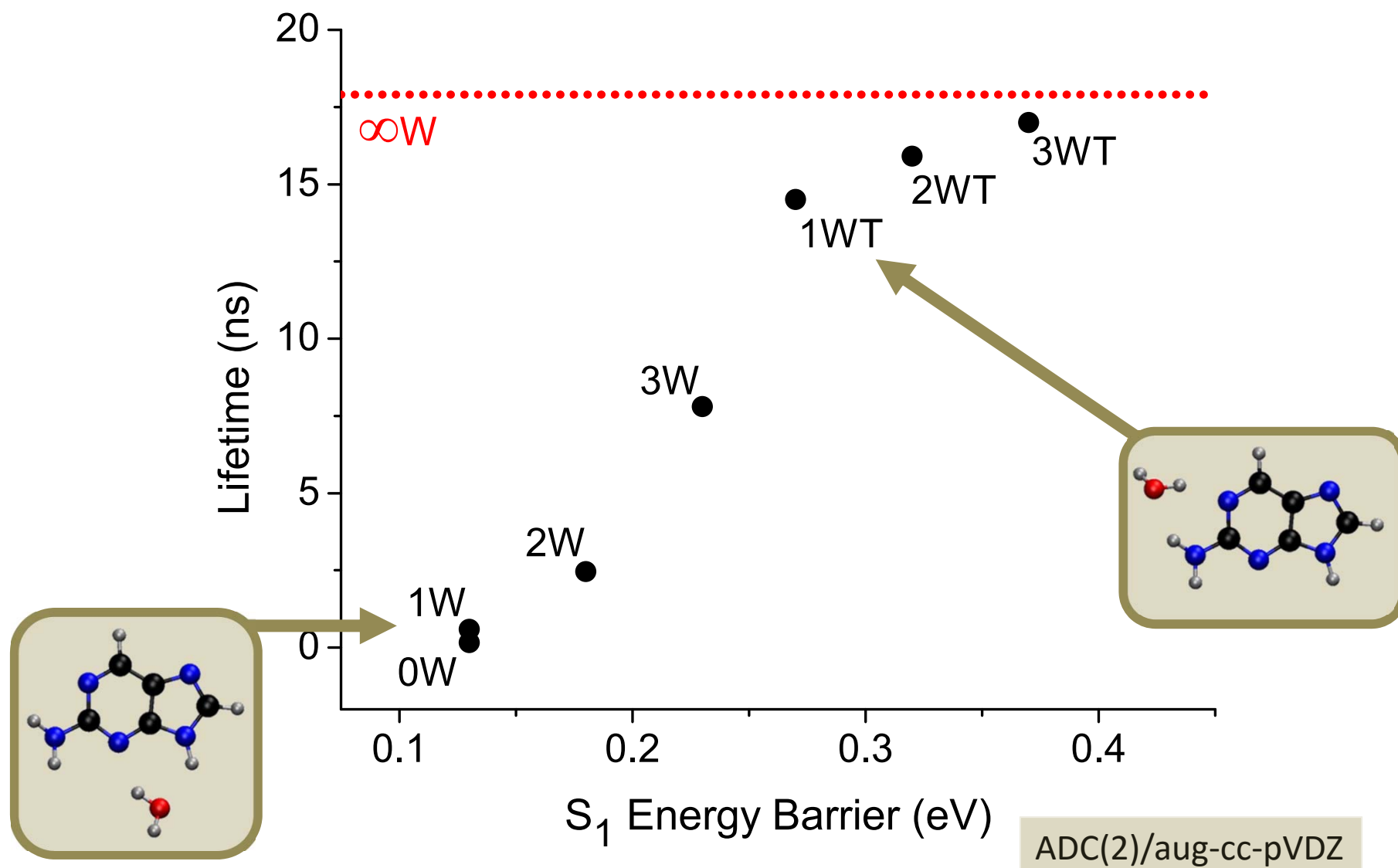
- Lobsiger, Blaser, Sinha, Frey, Leutwyler, Nat Chem **6**, 989 (2014)



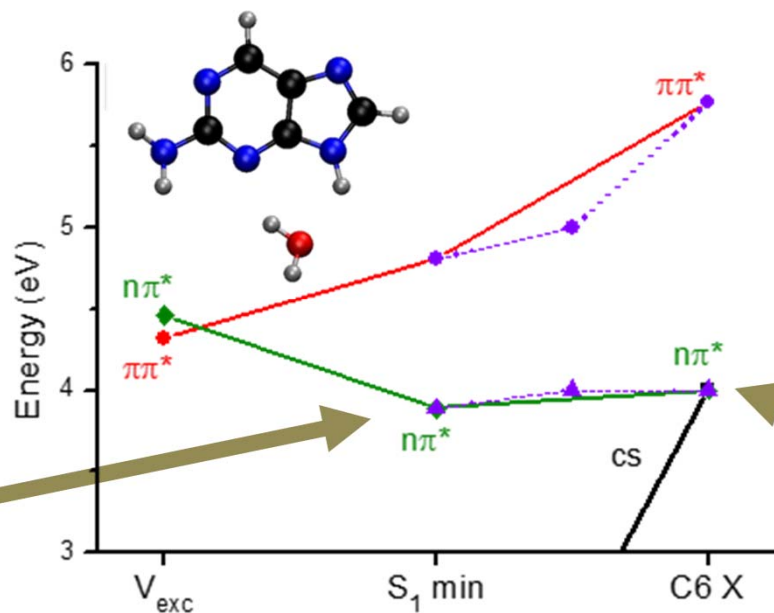
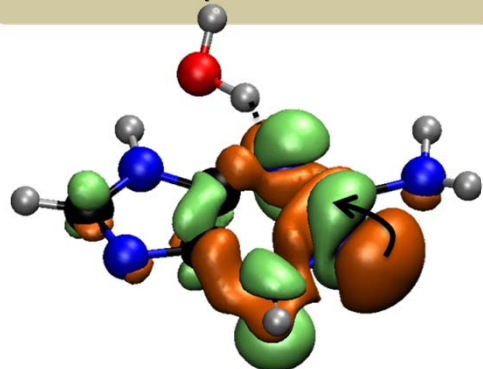


# One Water Makes 2AP Fluorescent

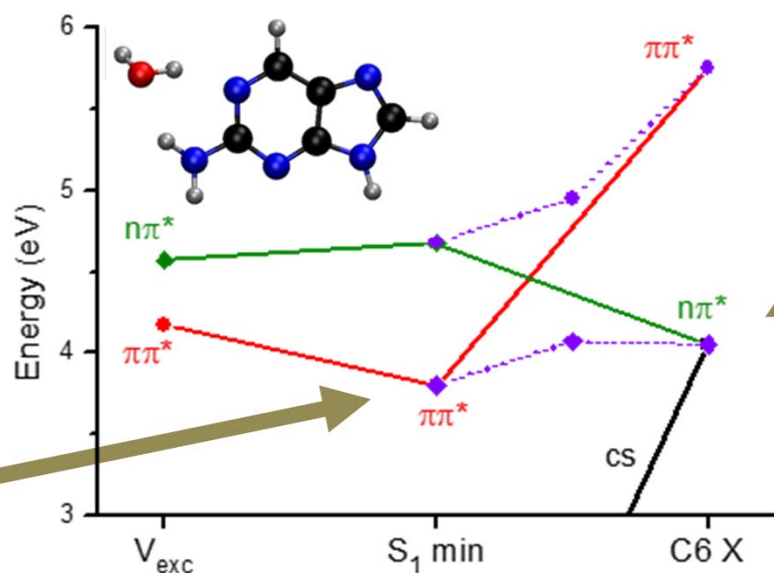
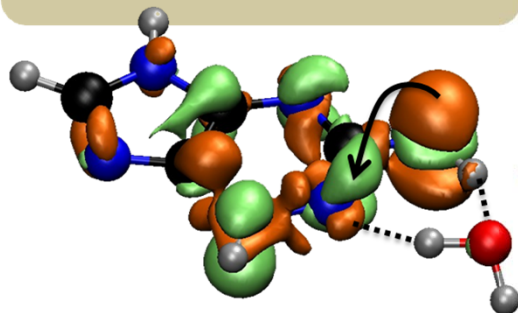
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- Water far from NH<sub>2</sub>:  
adiabatic path to X



- Water near NH<sub>2</sub>:  
nonadiabatic path to X



- Barbatti and Lischka, PCCP **17**, 15452 (2015)

# *Key points*

- A combination of static properties and dynamics allows to get many physical chemical insights.
- Use the imagination to go beyond routine.