UP1: H atom (proton) transfer in photoexcited biochromophores and clusters

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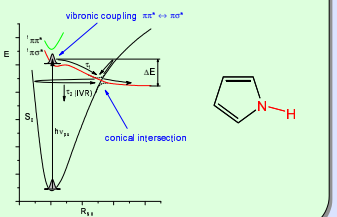
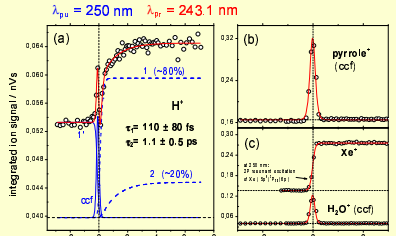
Cooperations:
TP C1 / C2
TP B2 / B7

H atom elimination from photoexcited pyrrole molecules

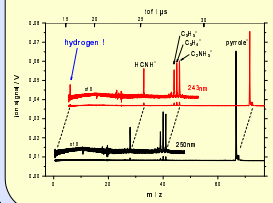
Potential energy scheme



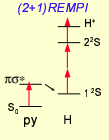
Time-dependent ion signals



H atom detection with fs pulses



at λ = 243.1 nm: *(2+1)REMPI*



within *one pulse*

Results:

- τ_1: *fast direct* dissociation on the πσ* potential surface
- τ_2: *indirect* dissociation after IC to S_0 (associated with IVR)
- agreement with ns experiment (Temps et al., PCCP 5, 315 (2003))

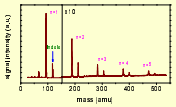
Further studies:

- *time-resolved H atom detection for other systems* excited to a repulsive πσ* state

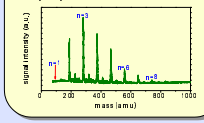
2-Aminopyridine dimer: a model for H-transfer in DNA base pairs

Mass spectra

$(2AP)_n$ cluster spectrum

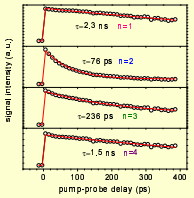


No laser: Cluster ions from disproportionation reaction?

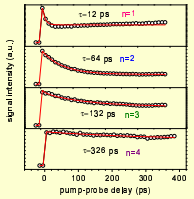


2-Aminopyridine cluster dynamics

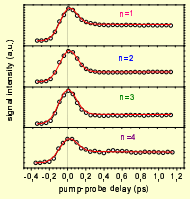
274 nm excitation, 800 nm ionization

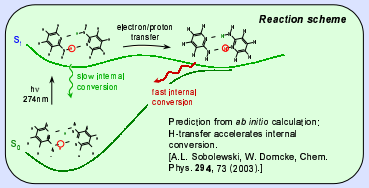


250 nm excitation, 800 nm ionization



Additional ultrafast component at 250 nm excitation:





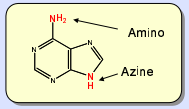
Prediction from *ab initio* calculation; H-transfer accelerates internal conversion. [A.L. Sobolewski, W. Domcke, Chem. Phys. **294**, 73 (2003).]

Results:

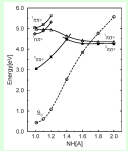
- *2AP-dimer:* 75 ps lifetime, distinct decay probably due to H-transfer.
- *2AP monomer:* ~2 ns lifetime at 274 nm excitation (good agreement with rotational linewidth in literature); Additional τ = 12 ps component at 250 nm excitation.
- *2AP clusters n≥3:* Similar to monomer. Maybe some H-transfer contribution from particular isomers.

Photophysics of DNA bases

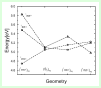
Adenine



Theoretical predictions



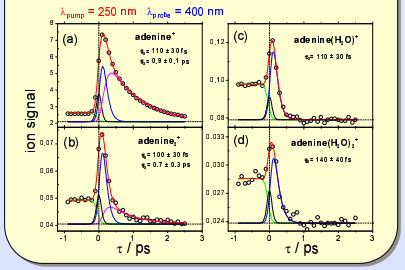
A.L. Sobolewski, W. Domcke, EPJD 20, 369 (2002)



ππ*,nπ*,πσ* - states

- strong *nonadiabatic interactions* expected
- nonradiative decay via *nπ* or πσ* ?*

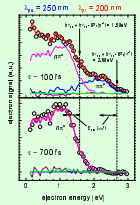
Time-dependent ion signals



Adenine monomer

- τ_1: IC of ππ* to nπ* ?
- τ_2 : IC of nπ* to S_0 ?

TRPES by T. Schultz et al.
S. Ullrich, T. Schultz, M.Z. Zgierski, A. Stolow, J. Am. Chem. Soc. **126**, 2262 (2004).

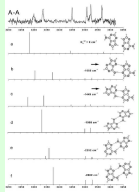


Adenine dimer

- Problem: *different isomers*
- *mixing* of decay mechanisms ?

⇒ *selection required*

IR-UV spectrum by Kleinermanns et al.
PCCP 5, 1158 (2003)

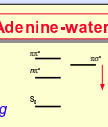


Adenine-water

hypothesis:

πσ* comes into play

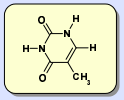
→ possible *lowering*



τ_1:

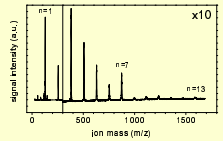
IC of *ππ* to πσ** + *decay* (H diss.)

Thymine



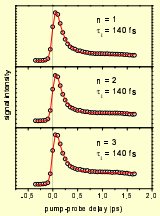
Thymine clusters

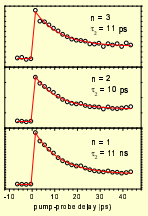
- Heated pulsed valve (260°C) allows good clustering.
- *"magic" clusters* appear with n=6i+1, i=1,2,3.



Thymine cluster dynamics

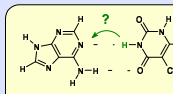
- Complex dynamics: τ_1 = 140fs; τ_2 = 10ps; τ_3 >1ns
- *No cluster specific dynamics*



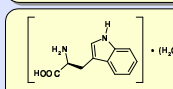


Future work

- dynamics and energetics in biochromophores, *amino acids and DNA bases*
- reactions in dimers and *DNA base pairs*
- microsolvation of chromophores (e.g. *tryptophane water clusters*)
- selective pre-excitation of cluster isomers



Adenine ··· Thymine basepair



Tryptophane $(H_2O)_n$ cluster