Ultrafast Photoinduced Processes in Indole$(NH_3)_n$ and Indole$(H_2O)_n$ Clusters

Max-Born-Institut Berlin-Adlershof

H. Lippert, V. Stert, H.-H. Ritze, C.P. Schulz, I.V. Hertel and W. Radloff

Max-Born-Institut , Max-Born-Str. 2A , D-12489 Berlin-Adlershof , Germany

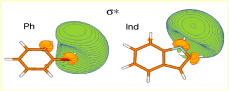
Motivation

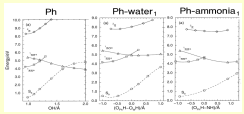
- Elucidation of photoinduced H-transfer reaction in indole$(NH_3)_n$ clusters
- Analysis of photoinduced processes in indole$(H_2O)_n$ clusters
- Comparison of process character in indole$(NH_3)_n$ and indole$(H_2O)_n$ clusters

Indole - chromophore of amino acid tryptophan – as example of aromatic biomolecules with azine(NH) or hydroxy(OH) group

Photochemistry: nonradiative decay of $\pi\pi^*$ state via repulsive $^1\pi\sigma^*$ state

- Theoretical model: W. Domcke, A. Sobolewski, CPL 329, 130 (2000); JPC A 105, 9275 (2001)
- diffuse, repulsive $^1\pi\sigma^*$-state of $^1A'$-symmetry (dark)





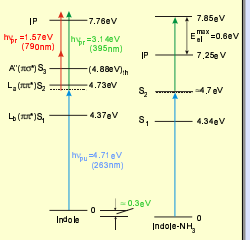
Dissociative H atom transfer in indole$(NH_3)_n$ clusters

$$\mathrm{IndNH}(NH_3)_n \xrightarrow{h\nu} \mathrm{IndNH}(NH_3)_n^*(\pi\pi^*) \xrightarrow{IC} \mathrm{IndNH}(NH_3)_n(\pi\sigma^*)$$

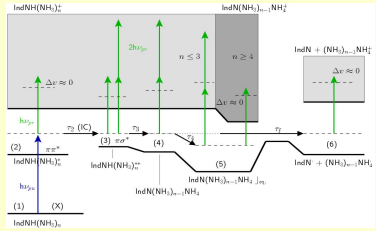
$$\longrightarrow \mathrm{IndN}(NH_4)(NH_3)_{n-1}(\pi\sigma^*) \longrightarrow \mathrm{IndN}+NH_4(NH_3)_{n-1}$$

Photoinduced processes in indole$(H_2O)_n$ clusters

Energy scheme for pump($h\nu_{pu}$) - probe ($h\nu_{pr}$) experiments

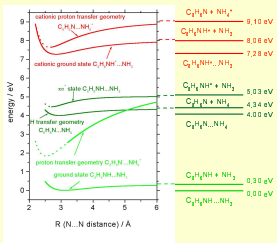


Reaction scheme



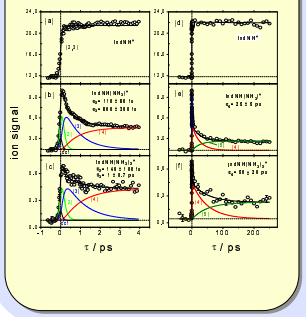
Results: τ_2=50...150fs, τ_3=0.5...1.1ps, τ_4=10...100ps

Ab initio (MRCI) calculations

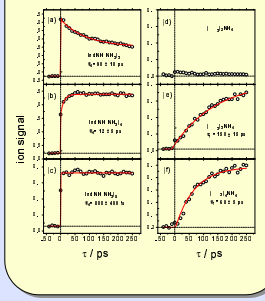


Indole$(NH_3)_n$- experimental results

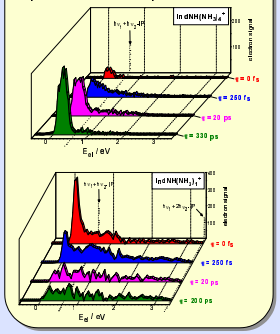
Time-dependent ion signals for λ_{pu} = 263 nm and λ_{pr} = 395 nm (narrow cluster distribution)



Time-dependent ion signals (broad cluster distribution)



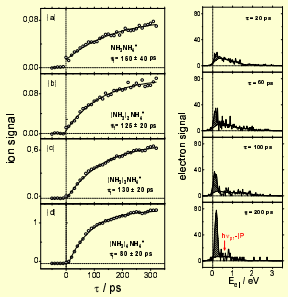
Electron spectra for λ_{pu} = 263 nm and λ_{pr} = 395 nm



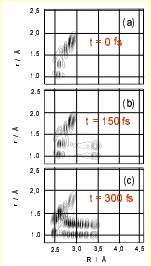
Dissociation products $(NH_3)_{n-1}NH_4$

Time-dependent ion signals at λ_{pu}=263nm and λ_{pr}=790nm

Electron spectra of $(NH_3)_4NH_4^+$ at λ_{pr}=395nm

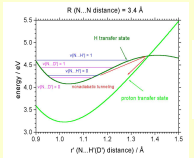


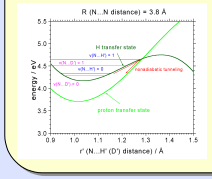
2D quantum dynamics on $\pi\sigma^*$



After H transfer : excitation of N-N vibration and N-H vibration of the ammonium moiety

Mechanism of nonadiabatic tunneling

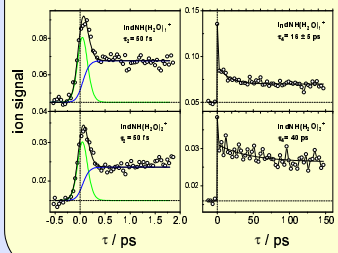




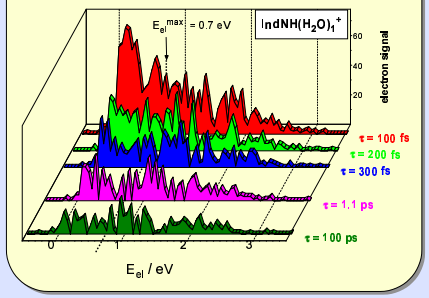
For v(N...H') = 0 or v(N...D')= 0 a nonadiabatic tunneling to the proton transfer configuration is possible (on the picosecond scale). With increasing R the tunneling probability increases. Strong isotope dependence !

Indole$(H_2O)_n$- experimental results (λ_{pu} = 250 nm and λ_{pr} = 400 nm)

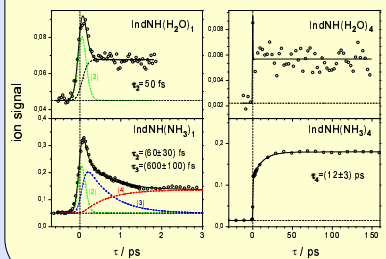
Time-dependent ion signals



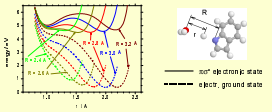
Electron spectra for diff. delay times τ



Comparison of indole$(H_2O)_n$ to indole$(NH_3)_n$

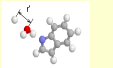


Indole$(H_2O)_1$-theory

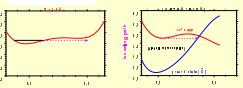


ππ* electronic state
ejectr. ground state

Dynamics on the ps time scale



Tunneling (isotope-dependent) to a H (D) transfer geometry, where H (D) abstraction occurs. Example: R = 2.6 Å, r = 1.0 Å; then variation of r'.



Results

indole$(NH_3)_n$:
dissociative H-transfer reaction
(→ reaction scheme)

indole$(H_2O)_n$:
no (or only partial) H-transfer reaction,
no dissociation products