

## Motivation

### The Issue of Photostability

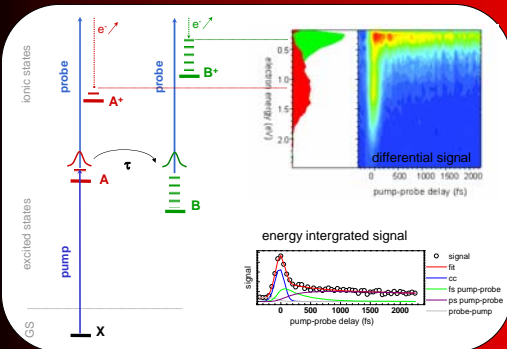
Early life developed under harsh and hostile conditions. There was no significant stratospheric ozone layer thus exposing the building blocks of life to harmful UV radiation.

How did the genetic material survive this early period? The answer must be an inherent **self-protection mechanism**.

The UV photostability of biomolecules relies on **ultrafast deactivation pathways** to compete over photochemical processes that lead to destruction of the molecule.

### How do these deactivation pathways work?

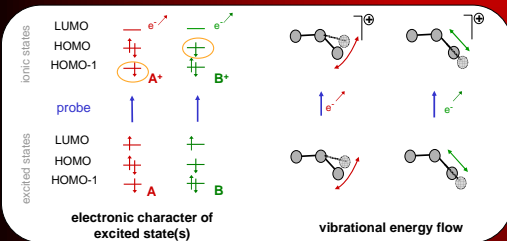
An investigation into the workings of the deactivation pathways can be made with a pump-probe experiment such as time-resolved photoelectron spectroscopy (TRPES). The general scheme involves preparation of an excited state, dynamical evolution and a time-delayed probe through ionization. In TRPES, photoelectron spectra are measured as a function of the pump-probe delay thus providing dynamic and spectroscopic information.



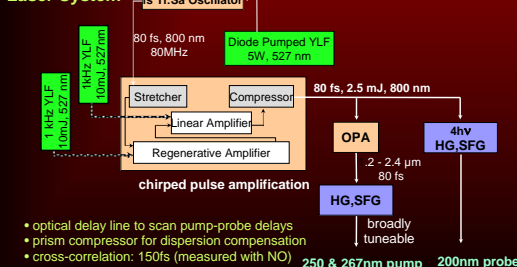
A pump pulse excites a molecule from the ground state to a bright excited state *A* which might be non-adiabatically coupled to an excited state *B*. *A* and *B* have different electronic character and preferentially ionize into ionic states *A*<sup>+</sup> and *B*<sup>+</sup>, respectively. In a TRPES spectrum two photoelectron bands, *a* and *b*, will be observed. The population in state *A* decreases and hence the photoelectron band *a* shows a decay. At the same time the population in state *B* increases and photoelectron band *b* rises. Deactivation pathways might consist of several internal conversion steps and TRPES provides a unique way to directly identify participating electronically excited states.

### Photoelectron Spectroscopy as a Probe Scheme

The theory of Koopman provides an elementary picture for ionization correlations in the case of single photon, single active electron ionization of a given molecular orbital: emission of an independent outer electron occurs without simultaneous reorganization of the core. Similarly for TRPES, the probabilities of partial ionization into specific continuum electronic states can differ drastically with respect to the molecular orbital nature of the excited state. Additionally, vibrational energy flow can be monitored through changes in the structure of the photoelectron bands due to changes in the Franck-Condon overlap ( $\Delta V=0$  propensity rule).

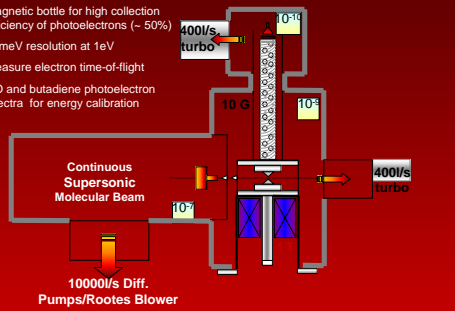


### Laser System



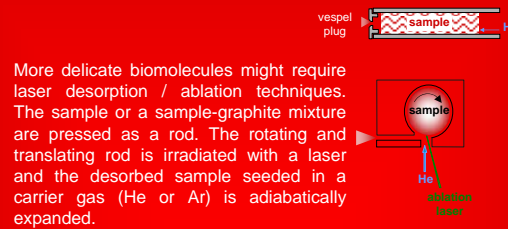
## Magnetic Bottle Spectrometer

- magnetic bottle for high collection efficiency of photoelectrons (~50%)
- 50meV resolution at 1eV
- measure electron time-of-flight
- NO and butadiene photoelectron spectra for energy calibration



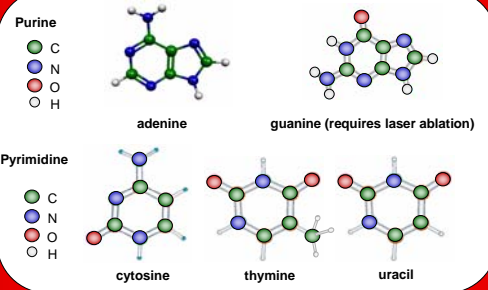
### Biomolecular Beam Sources

Many biomolecules are involatile and decompose upon heating. A high temperature glass nozzle can be used for evaporation of some molecules: The sample is applied to glass wool for increased surface area and any contact with metal surfaces and o-rings is avoided.



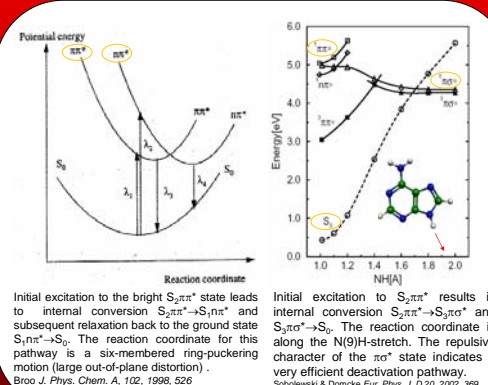
More delicate biomolecules might require laser desorption / ablation techniques. The sample or a sample-graphite mixture are pressed as a rod. The rotating and translating rod is irradiated with a laser and the desorbed sample seeded in a carrier gas (He or Ar) is adiabatically expanded.

### The DNA bases



### Competing Models of Adenine's Relaxation Pathways

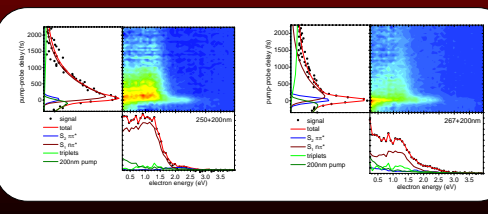
To date, two competing relaxation pathways for adenine have been proposed by ab initio quantum chemical calculations:



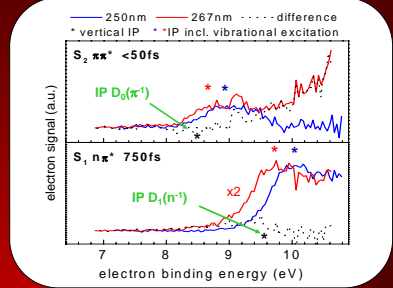
Initial excitation to the bright  $S_{2,\pi^*}$  state leads to internal conversion  $S_{2,\pi^*} \rightarrow S_{1,\pi^*}$  and subsequent relaxation back to the ground state  $S_{1,\pi^*} \rightarrow S_0$ . The reaction coordinate for this pathway is a six-membered ring-puckering motion (large out-of-plane distortion).  
Broo J. Phys. Chem. A, 102, 1998, 526

Initial excitation to  $S_{2,\pi^*}$  results in internal conversion  $S_{2,\pi^*} \rightarrow S_{3,\pi^*}$  and  $S_{3,\pi^*} \rightarrow S_0$ . The reaction coordinate is along the N(9)H-stretch. The repulsive character of the  $\pi^*$  state indicates a very efficient deactivation pathway.  
Sobolewski & Domcke Eur. Phys. J. D. 20, 2002, 369

### TRPES of Adenine at 250 / 267nm pump and 200nm probe



## Comparison of TRPES Spectra of Adenine



### Comparison 250 & 267nm data

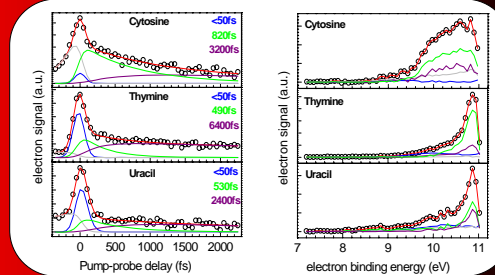
- similar photoelectron bands, shifted by internal vibr. energy
  - $S_2 \pi^*$  signals similar, but large number of slow electrons at 267nm
  - $S_1 \pi^*$  only half the signal at 267nm
- indication that another decay pathway may exist

### Theory predicts $S_2 \pi^* \rightarrow S_3 \pi^*$ internal conversion

- ionization correlation  $S_3 \pi^* \rightarrow D_0 (\pi^{-1})$
- reaction coordinate is NH stretch
- long FC progression expected due to large NH-stretch motion

→ indication for coexistence of  $n\pi^*$  and  $\pi\sigma^*$  decay pathways predicted by theory  
branching ratio is wavelength dependent

### TRPES Spectra of Pyrimidine Bases



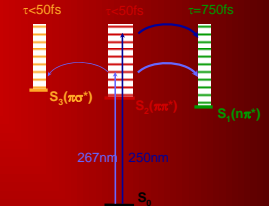
Pyrimidine bases show complex dynamics

- initial excitation to bright  $\pi\pi^*$  state with lifetime <50fs
  - subsequently populated state shows multi-exponential decay: several fs, ps, ns lifetimes
- indication for multiple relaxation pathways

### Conclusions - Photophysics of DNA Bases

#### Adenine

Adenine exhibits dynamics on fs timescale (50fs  $\pi\pi^*$  &  $\pi\sigma^*$ , 750fs  $n\pi^*$ , ns triplet). We propose a *new model* for the relaxation dynamics in Adenine based on the co-existence of a  $\pi\sigma^*$  and a  $n\pi^*$  pathway with a branching ratio that is wavelength dependent.



#### Pyrimidine Bases

We observe several ultrafast decay channels (50fs  $\pi\pi^*$ , several fs, ps & ns) which indicates complex dynamics. A detailed analysis of the photoelectron spectra and identification of the electronically excited states involved in the relaxation process is work in progress.

#### Photostability of DNA bases?

DNA bases show ultrafast relaxation processes to lower electronically excited states and the ground state. decrease in electronic energy ⇔ increased photostability

#### Publications:

- Ullrich, T. Schultz, M.Z. Zgierski, A. Stolow: Electronic relaxation mechanism in DNA and RNA bases studied by time-resolved photoelectron spectroscopy, Phys. Chem. Chem. Phys., invited article for special issue on "Bio-active Molecules in the Gas-phase", 2004, 6, 2796-2801.
- S. Ullrich, T. Schultz, M.Z. Zgierski, A. Stolow: Direct observation of electronic relaxation dynamics in adenine via time-resolved photoelectron spectroscopy, J. Amer. Chem. Soc., Communication 2004, 126, 2262-2263.
- M. Smits, C.A. deLange, S. Ullrich, T. Schultz, M. Schmitt, J.G. Underwood, J.P. Shaffer, D.M. Rayner, A. Stolow: Stable kilohertz-rate molecular beam laser ablation sources, Rev. Sci. Instrum. 2003, 74, 1-6.

#### Acknowledgement:

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