

# Femtosecond Time-Resolved Mass Spectrometry and Photoelectron Imaging of Selected Aromatic Molecules

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## Pyrrole & Derivatives

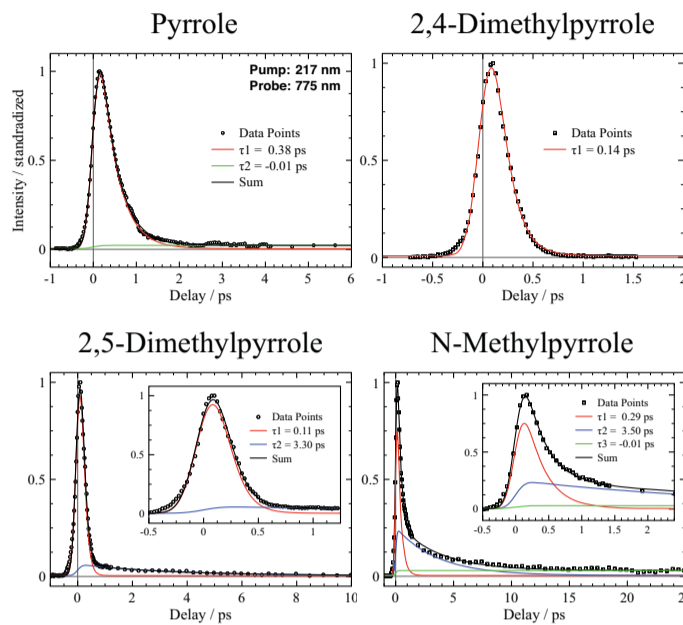
Pyrrole is a heteroatomic molecule that represents a common structural element of many biologically important compounds. It is an ideal model system, e.g. for DNA building blocks and proteins, to study the photochemical dynamics in the gas phase. However, its photochemistry is still not fully understood.

Intense research revealed the existence of ultrafast radiationless deactivation channels to the electronic ground state through direct and indirect conical intersections [1,2,3]. These are investigated by femtosecond spectroscopies.

## Hexafluorobenzene

Fluorinated benzene molecules show a distinctive perfluorine effect, which, because of the shift of the electron density to the outer fluorine atoms, leads to a stabilization of the C-F  $\sigma^*$ -orbitals. With increasing degree of fluorination, these  $\sigma^*$ -orbitals become isoenergetic with the lowest unoccupied molecular orbital (LUMO), which has  $\pi^*$  character in benzene. Quantum chemical calculations predict conical intersections between the electronically excited states, with the possibility of ultrafast wavepacket motions between them [5]. Recent experiments in solution confirmed this conclusion [6], but more precise molecular beam experiments had been missing.

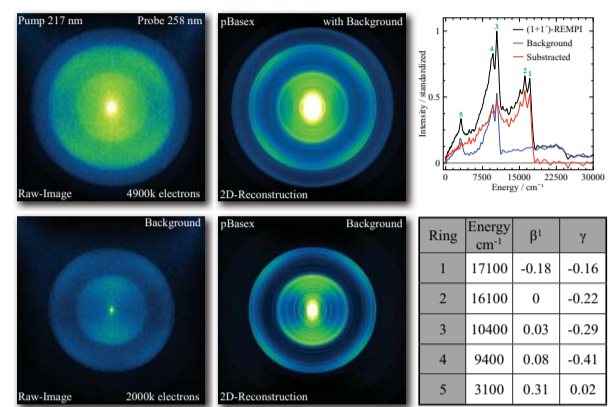
## Transient Mass Spectra of Pyrrole and Derivatives



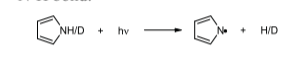
	$\lambda_{\text{pump}}$ nm	IRF ps	$A_1$ standardized	$\tau_1$ ps	$A_2$ standardized	$\tau_2$ ps	$A_3$ standardized	$\tau_3$ ps
<b>Pyrrole</b>	217	0.13	0.99 (1)	0.38 (1)	0.006 (2)	-0.01		
<b>2,4-Dimethylpyrrole</b>	217	0.11	1 (0.05)	0.14 (1)				
<b>2,5-Dimethylpyrrole</b>	217	0.13	0.98 (10)	0.11 (1)	0.02 (0.2)	3.3 (10)		
<b>N-Methylpyrrole</b>	217	0.11	0.83 (4)	0.29 (2)	0.15 (1)	3.5 (5)	0.02 (0.2)	-0.01

## Photoelectron Imaging Results on Pyrrole

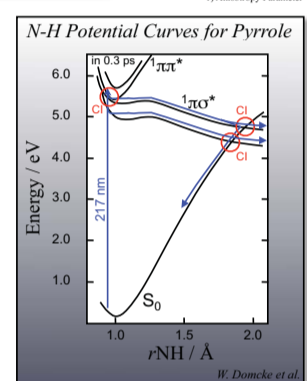
Pump = 217 nm, probe 258 nm, time delay 150 fs



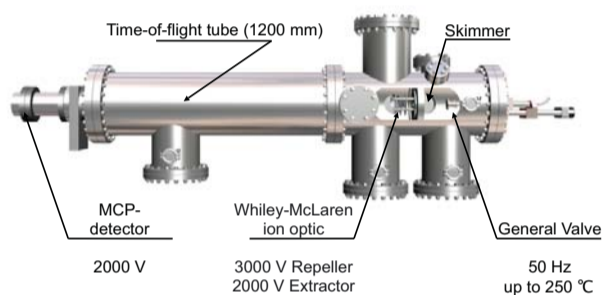
Calculations predict a strong coupling (CI) of the  $\pi\pi^*$ -state to the  $\pi\sigma^*$ -state through an  $a_2$  mode. The repulsive  $\pi\sigma^*$ -state then leads to dissociation of the N-H bond:



The dissociated H atoms have been successfully detected in our group by the method of Photofragment Velocity Map Imaging [2]. The new photoelectron images recorded here show two peaks with a spacing of 5150 cm<sup>-1</sup>, which corresponds to the energy difference between the  $\pi\pi^*$ -state and the  $\pi\sigma^*$ -state of pyrrole!

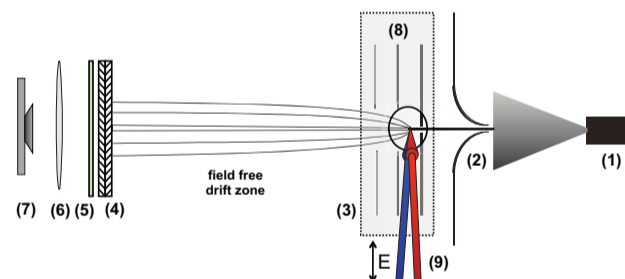


## Transient Time-of-Flight Mass Spectrometry



The molecules expand together with the helium carrier gas through a pulsed nozzle into the first vacuum chamber. The molecular beam is skimmed and interacts with the pump and time delayed probe laser pulses between the repeller and extractor plates of an ion lens. The ionized molecules are accelerated in the direction of the MCP detector and detected after a certain time of flight. A computer controlled oscilloscope records the integrated transient mass spectra.

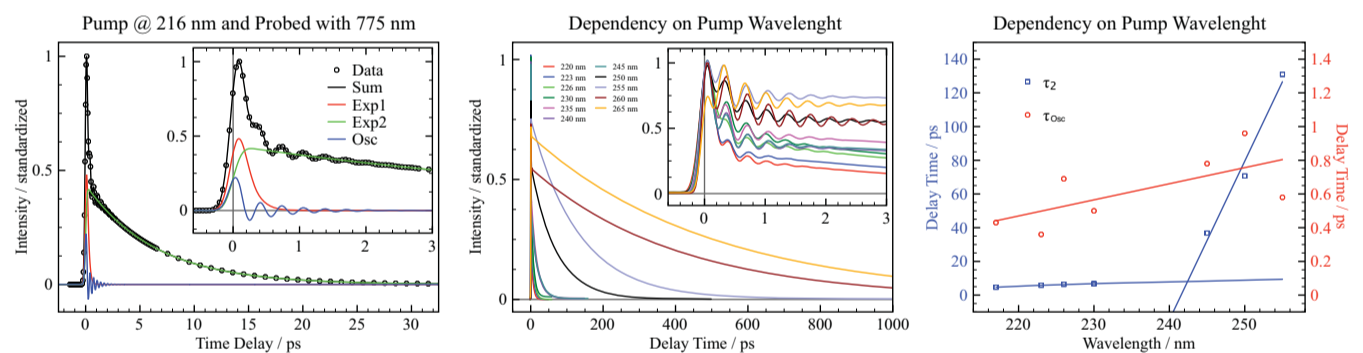
## Time-Dependent Photoelectron Velocity Imaging



The experimental set-up for velocity imaging differs in three details from that for mass spectrometry:

1. The time-of-flight distance is reduced to 350 mm and shielded by mu-metal.
2. Electrons are detected by a space sensitive MCP/phosphorescence detector assembly to provide supplemental information.
3. There is an additional liquid nitrogen cooling unit around the ion optics to reduce the background noise to a minimum when detecting electrons.

## Transient Mass Spectra of Hexafluorobenzene

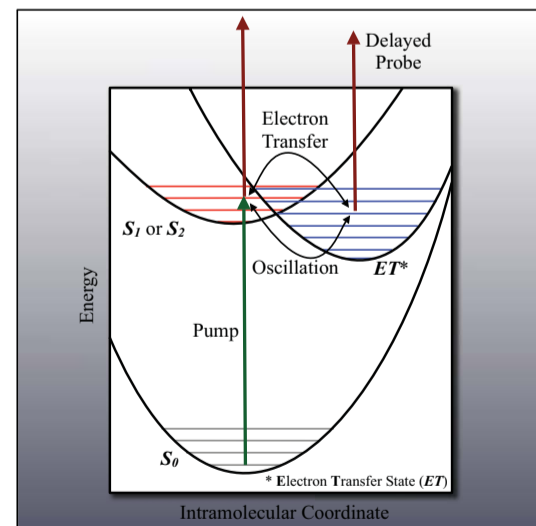


A fit with a sum of two exponential decays and additionally a damped oscillation revealed:

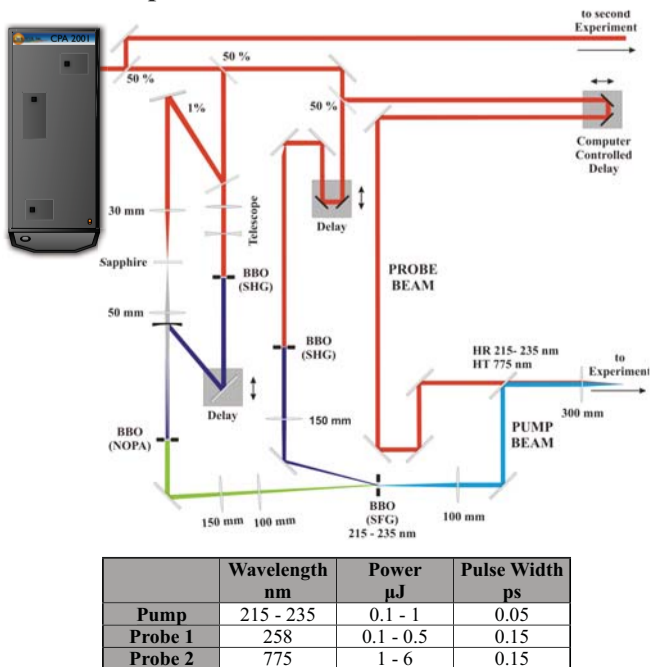
- (1) an ultrafast decay component with  $\tau_1 = 0.16 - 0.38$  ps, that stays for all wavelengths essentially constant,
- (2) a much slower with  $\tau_2 = 4.7 - 131$  ps.  $\tau_2$  decreases drastically with decreasing excitation wavelength until 240 nm. From then on the changes are minor.
- (3) an oscillation with a decay time of  $\tau_{\text{osc}} = 0.36 - 0.96$  ps and a period of  $T = 0.3$  ps.  
 $\Rightarrow v_{\text{osc}} = 104 \text{ cm}^{-1}$

$\lambda$ nm	IRF	$A_1$ standardized	$\tau_1$ ps	$A_2$ standardized	$\tau_2$ ps	$A_{\text{osc}}$ standardized	$\tau_{\text{osc}}$ ps	T ps
217	0.12	0.16	0.16	0.07	4.67	0.77	0.43	0.31
223	0.11	0.36	0.10	0.08	5.84	0.38	0.36	0.33
226	0.11	0.5	0.14	0.17	6.41	0.33	0.69	0.32
230	0.07	0.34	0.37	0.28	6.76	0.38	0.50	0.32
245	0.07	0.46	0.20	0.23	36.8	0.31	0.78	0.34
250	0.09	0.34	0.38	0.34	70.7	0.32	0.96	0.34
255	0.10	0.41	0.13	0.25	131	0.34	0.58	0.35
260	0.06	0.31	0.54	0.40	403	0.29	1.18	0.35
265	0.08	0.17	0.46	0.40	493	0.43	0.69	0.34

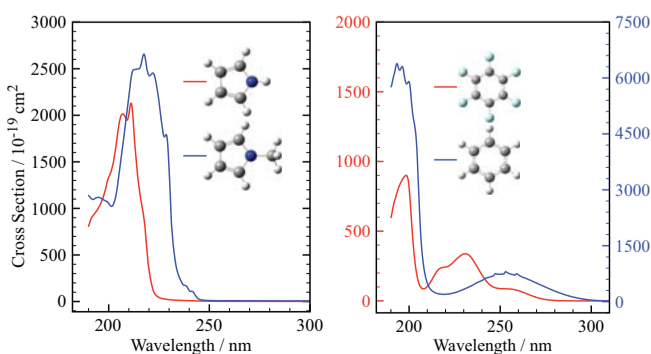
\*IRF in  $\sigma$ , multiply by  $2(2\ln 2)^{0.5} = 2.35$  to get FWHM



## Pump-Probe Laser Beam Generation



## Ultraviolet Spectra of the Investigated Molecules



## References

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- [4] F. Renth, J. Riedel, F. Temps, *Rev. Sci. Instrum.* 2006, **77**, 0033103.
- [5] M. Z. Zgierski, T. Fujiwara, E. C. Lim, *J. Chem. Phys.* 2006, **122**, 144312.
- [6] S. A. Kovalenko, A. L. Dobryakov, V. Farztdinov, *Phys. Rev. Lett.* 2006, **96**, 068301.