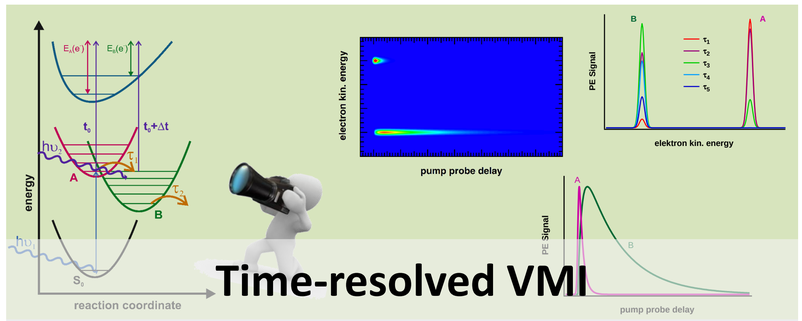
The photophysics of tolane - a time-resolved photoelectron imaging study

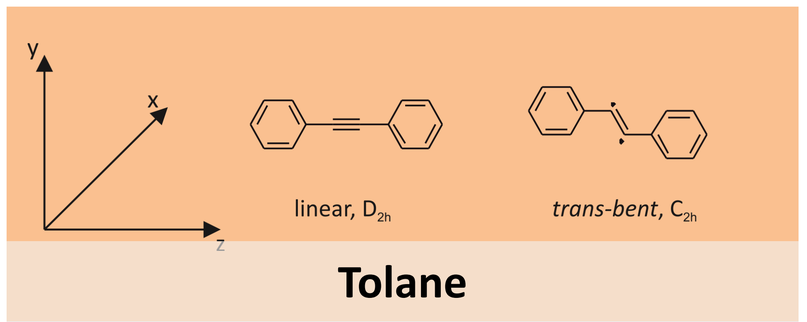
Marco Flock, Lea Bosse and Ingo Fischer
University of Wuerzburg / Germany, Institute of Physical and Theoretical Chemistry

Time-resolved VMI



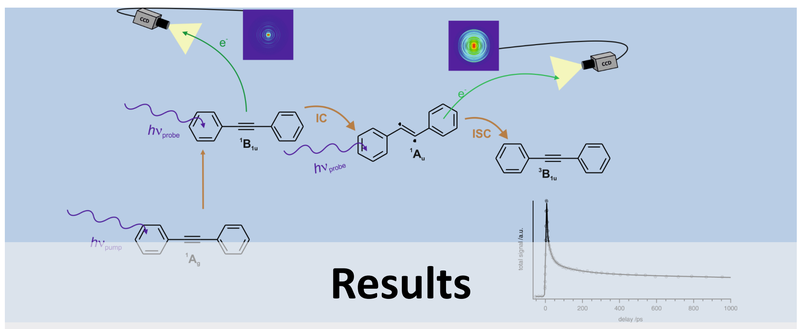
- Supersonic jet expansion
- Resonance-enhanced multiphoton ionization (REMPI)
- Time-resolved photoionization and photoelectron imaging
- Vibrational (20 cm^{-1}) and temporal resolution (4 ps)

Tolane



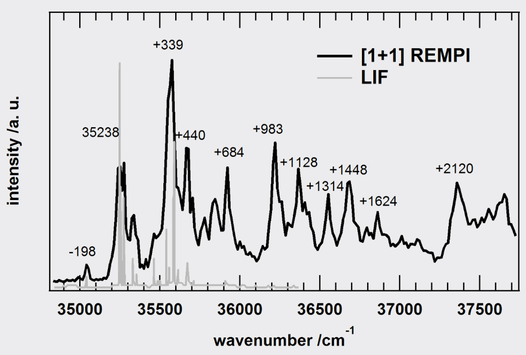
- Two close-lying excited singlet states (A_g and B_{1u})
- Breakdown of fluorescence at vibronic excitation
- Formation of biradicalic *trans-bent* species
- No time-resolved measurements on isolated tolane

Results



- Vibrationally resolved REMPI spectrum
- Dynamics of several vibronic modes
- Two-step sequential relaxation process
- Identification of biradicalic intermediate species

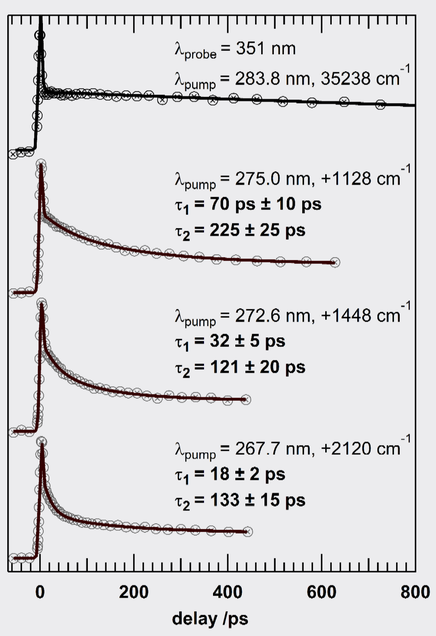
REMPI Spectrum



- Tuneable excitation wavelength, ionization via [1+1] REMPI
- Recording the tolane photoion signal
- Vibrationally resolved absorption spectrum
- Extension of previous LIF spectrum*

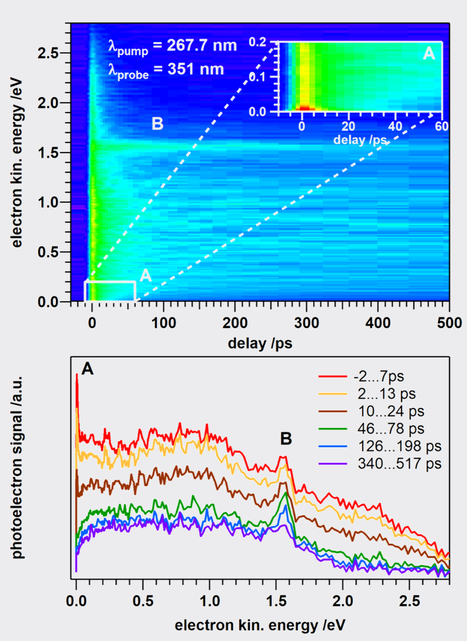
* LIF spectrum was recorded from Okuyama *et al.*, *J. Phys. Chem.*, 1984, **88**, 1711-1716.

Time-resolved Photoionization



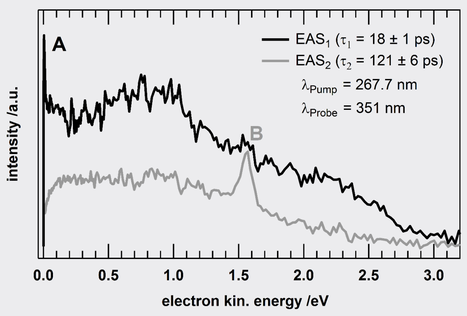
- Fixed excitation wavelength
- Ionization with delayed 351 nm pulses
- Information on lifetime and dynamics
- Dynamics depend strongly on excitation energy
- Long-lived low-energy vibrational modes
- Biexponential decay at higher excitation

Time-resolved VMI



- Fixed excitation (267.7 nm) and ionization (351 nm) wavelength
- Recording the photoelectron energy distribution at different delay times
- Further information on relaxation process
- Peaks show different temporal behavior
- Ionization from different electronic states populated during relaxation

Global Fit



- Sequential relaxation model
- Fit yields time constants and evolution associated spectra (EAS)
- Represent steady-state photoelectron spectra
- Identification of characteristic peaks A and B

Interpretation

- [1+1'] ionization of **linear tolane ($^1B_{1u}$)** → low-energy photoelectrons → **Peak A**
- Multiphoton ionization of ***trans-bent* species (^1A_u)** → **Peak B**
- Ionization via intermediate Rydberg state
- Conservation of vibrational energy E_{vib} (Ryd)
- Anisotropic photoelectron angular distribution (ß = +0.84)

* Many thanks to Dustin Kaiser (Engels group, IPTC) for calculating the IP of the *trans-bent* species!

Relaxation Scheme

- Two-step sequential relaxation process
- Population of biradicalic intermediate state
- Long-lived triplet state

714. WE-Heraeus Seminar

Bad Honnef
February 16-19, 2020

Funding & Support

2GR1K2 DFG UNI WÜ

Affiliation

Marco.Flock@uni-wuerzburg.de
University of Wuerzburg
97074 Wuerzburg / Germany

or follow us on Instagram
akfwuerzburg

Further Information

Just published:
Phys. Chem. Chem. Phys., 2019
DOI: 10.1039/C9CP02222H