The Photophysics of Acenaphthylene

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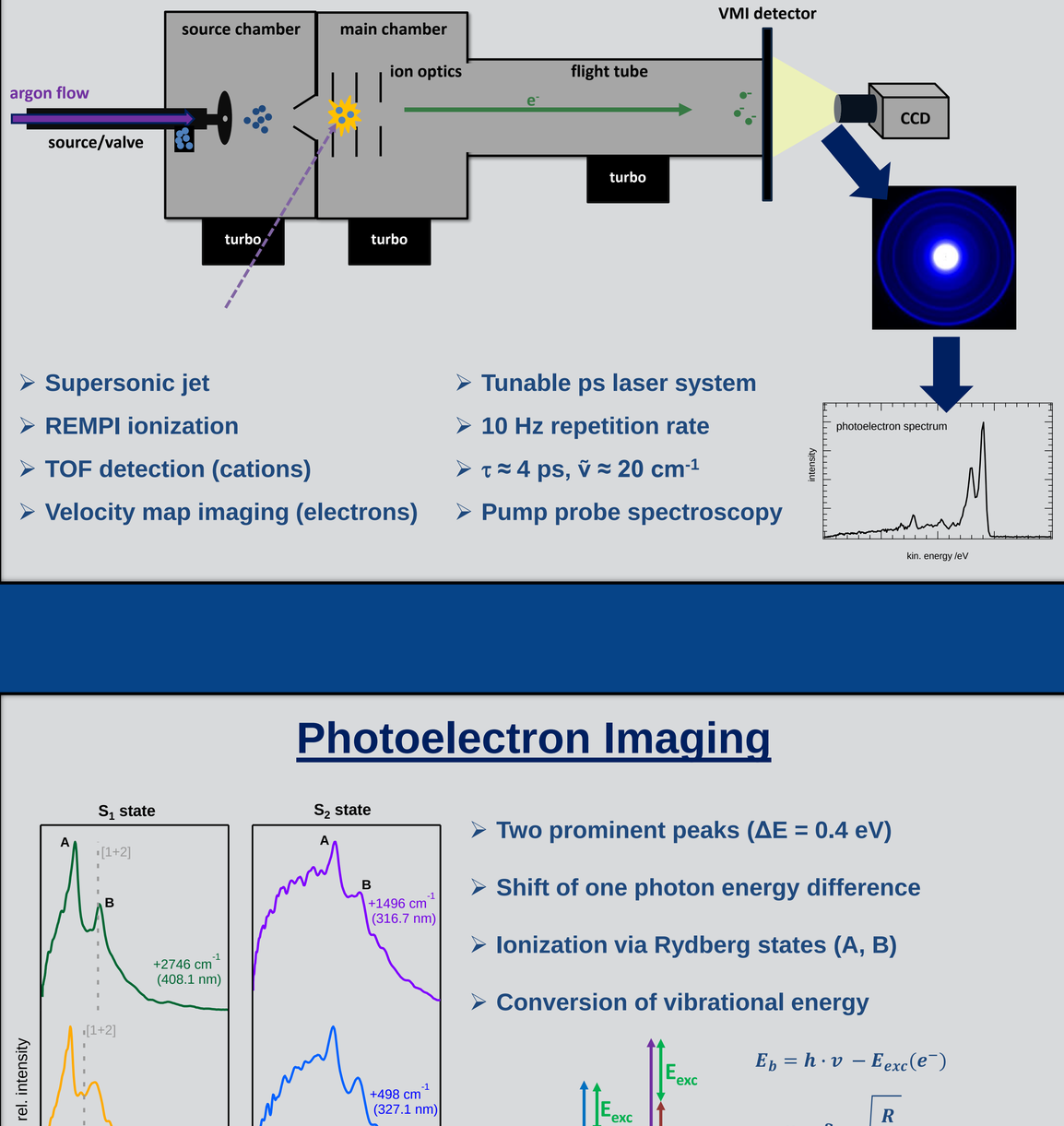
Abstract

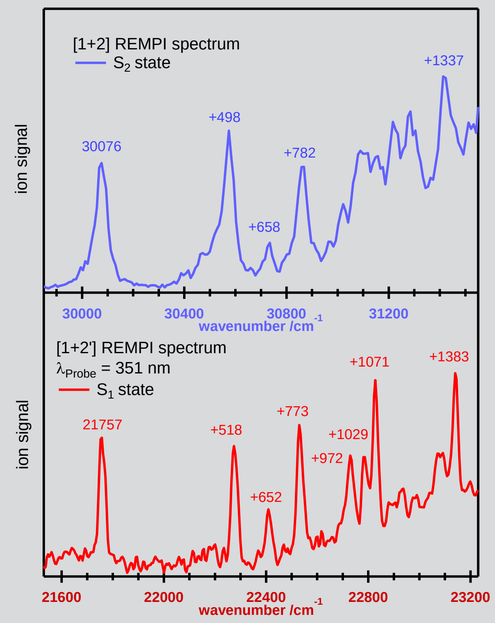
Acenaphthylene is a member of the group of polycyclic aromatic hydrocarbons (PAHs), which are formed in incomplete combustion processes but are also present in interstellar nurseries and play an important role as building blocks for modern organic devices. In ps time-resolved photoelectron imaging experiments we studied the photophysical behavior after excitation of the S_2 state. This short-lived electronic state first undergoes internal conversion (IC) to the S_1 state vibronic manifold, followed by another IC to the electronic ground state (S_0). This last step competes with intersystem crossing (ISC) to the triplet manifold, for which an energetic barrier has to be overcome to be enabled.

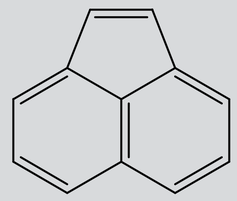
Experimental Setup



- Supersonic jet
- REMPI ionization
- TOF detection (cations)
- Velocity map imaging (electrons)
- Tunable ps laser system
- 10 Hz repetition rate
- $\tau \approx 4$ ps, $\tilde{\nu} \approx 20$ cm^{-1}
- Pump probe spectroscopy

REMPI Experiments



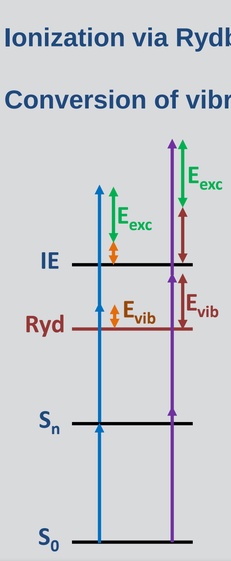


- $C_{12}H_8$
- M = 152 g/mol
- mp = 92°C
- IE = 8.22 eV

- [1+2'] and [1+2] REMPI
- Origins at 21757 (S_1) and 30076 cm^{-1} (S_2)
- Resolution of vibronic bands
- S_2 spectrum is broadened
- Totally symmetric vibrational modes

Photoelectron Imaging

- Two prominent peaks (ΔE = 0.4 eV)
- Shift of one photon energy difference
- Ionization via Rydberg states (A, B)
- Conversion of vibrational energy



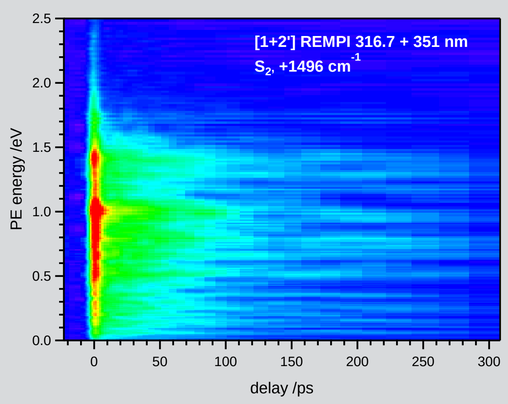
$$E_b = h \cdot \nu - E_{exc}(e^-)$$

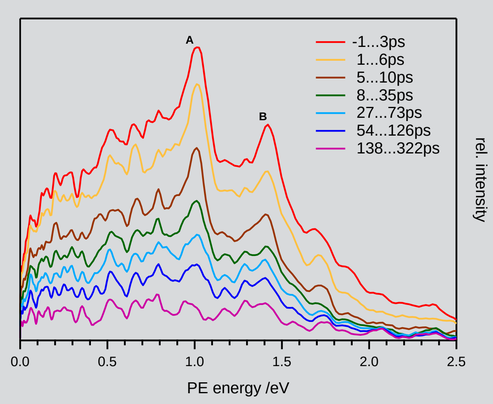
$$n - \delta = \sqrt{\frac{R}{BE}}$$

	A	B
BE (eV)	2.51	2.12
n - δ	2.33	2.53

=> 3s or 3p Rydberg states

Time-resolved PE-Imaging





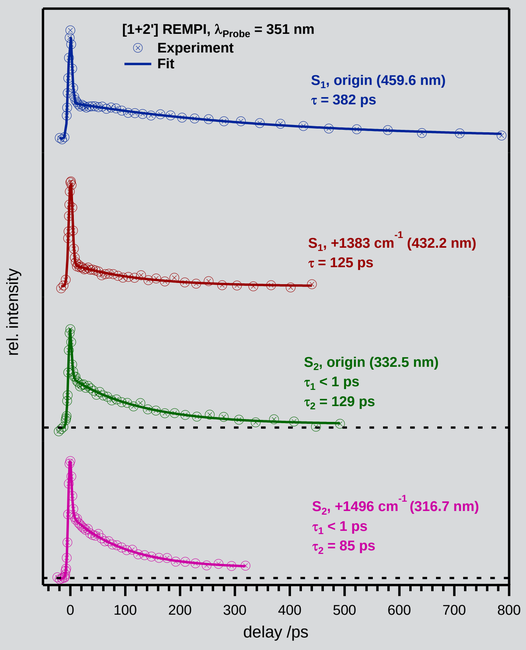
- Pump probe spectroscopy
- Transient photoelectron map
- Ionization via Rydberg states A and B
- Time-dependent behavior

- A and B vanish at long delay times
- Unstructured transient signal remains

→ No ionization from S_1/S_2

→ Population of T-state (→ ISC)

Decay Traces



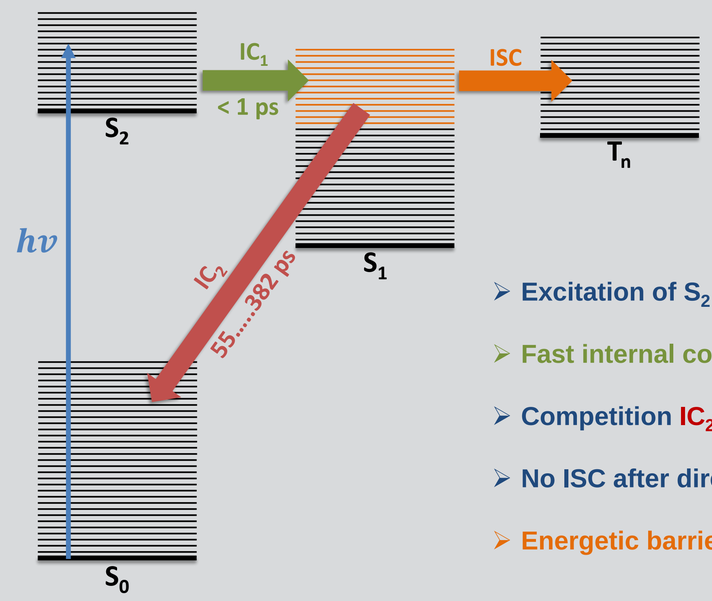
S_1 state

- Mono exponential decay
- Decreasing τ at higher excitation
- Signal drops to zero

S_2 state

- Additional fast time constant (< 1 ps)
- Further decrease of 2nd time constant
- Constant signal offset
- Long-lived component

Relaxation Scheme



- Excitation of S_2 state
- Fast internal conversion $S_1 \leftarrow S_0$ (IC_1)
- Competition IC_2 $S_0 \leftarrow S_1$ vs. ISC $T_n \leftarrow S_1$
- No ISC after direct S_1 excitation
- Energetic barrier has to be overcome

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Bunsentagung

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